1. INTRODUCTION

Stimulated by the fascinating properties of graphene,\(^1\) massive effort has been made to discover and synthesize other two-dimensional (2D) materials.\(^1\) As a result, many new 2D materials have been made experimentally available. In general, 2D materials can be classified as elemental and compound 2D materials. Elemental 2D materials can be made from group IV elements, such as graphene,\(^6\) silicene (Si),\(^4\) germanene (Ge),\(^8\)\(^-\)\(^10\) and stanene (Sn).\(^11\)-\(^13\) These 2D materials are metallic and possess a honeycomb lattice and unique linear Dirac cone in their band structure. Besides, elemental 2D materials can also be made from group III and group V elements, such as borophene,\(^14\)-\(^16\) phosphorene,\(^7\)-\(^9\) arsenene,\(^10\) and antimonene.\(^20\)-\(^22\) It is found that borophene is metallic,\(^14\)-\(^16\) whereas phosphorene, arsenene, and antimonene are semiconducting.\(^17\)-\(^22\) Beyond elemental 2D materials, various 2D compound materials have also been synthesized. Perhaps, the most studied family of 2D compound films is transition-metal dichalcogenides (TMDCs),\(^23\)-\(^26\) which is a group of semiconductors with a band gap of around 2.0 eV, according to different calculation methods.\(^29\) Obviously, the electronic properties of PtSe\(_2\) can be tuned by layer engineering. In addition, monolayer PtSe\(_2\) also shows an excellent photocatalysis capacity, significantly better than that of traditional PtSe\(_2\) nanocrystals.\(^22\) Last but not the least, PtSe\(_2\) is highly desirable for novel electronic and optoelectronic,\(^29\)-\(^34\) and catalytic and sensing applications.\(^22,30,35\) Further studies on this novel material can be enlightening.

Structure, Stability, and Kinetics of Vacancy Defects in Monolayer PtSe\(_2\): A First-Principles Study

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ABSTRACT: The recent epitaxial growth of monolayer PtSe\(_2\) has raised hope for its novel applications in valleytronic, spintronic, and energy-harvesting devices. Compared with 2H-phase transition-metal dichalcogenides, the 1T-phase PtSe\(_2\) is much less studied and this is especially true for its defects behaviors and their influence on electronic properties. In this article, we systematically explore the structure, stability, and kinetics of both Pt and Se vacancies in monolayer PtSe\(_2\) using first-principles calculations. By examining the relative energies of these vacancies, we identify the most stable Se/Pt single and double vacancies. In particular, we reveal a new type of Se double vacancy structure with the lowest energy. Energetically, both Se and Pt single vacancies prefer to combine to form double vacancies. All Se and Pt vacancies have remarkable influence on the electronic properties. Moreover, Pt single and double vacancies can introduce strong spin polarization in PtSe\(_2\), which may be promising for spintronic applications. These findings not only enrich the fundamental understanding of 1T-phase PtSe\(_2\) but also provide useful guidance to design PtSe\(_2\) for its optoelectronic and spintronic applications.

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small band gap.39−42 The study of defects in TMDCs was mainly focused on MoS2.35,37,38 It was reported that sulfur single vacancy (SV) was the most populous point defect in monolayer MoS2 obtained by mechanical exfoliation and chemical vapor deposition, and the density of sulfur-SV could reach as high as \((1.2 \pm 0.4) \times 10^{13} \text{ cm}^{-2}\), whereas sulfur double vacancy (DV) and Mo vacancy were also observed, albeit with small concentrations.35,37,38 These defects were shown to greatly influence the structural stability and electronic properties of monolayer MoS2.35−38 Similarly, it is expected that defects should also exist in PtSe2, especially for point vacancies formed during the epitaxial growth, and these intrinsic defects may also affect the structure and electronic properties of monolayer PtSe2. It is noted that different from 2H-phase MoS2, PtSe2 has a stable 1T phase.28,29 We have examined the stability of the 2H phase of PtSe2 and found that it is thermodynamically unstable due to the significant presence of imaginary frequencies in the phonon dispersion.

Before the structure and property calculations, we first carefully test the kinetic energy cutoff for plane waves (Figure 1c) and the number of mesh for sampling the reciprocal space (Figure 1d). Good convergence is achieved with the energy cutoff of 400 eV and \((12 \times 12)\) mesh for the primitive cell \([2 \times 2] k\)-mesh for \((6 \times 6)\) supercell). To avoid the interaction of vacancies with their images, we choose a large \((6 \times 6)\) supercell.

2. RESULTS

There are three common phases for monolayer TMDCs, that is, 2H, 1T, and 1T′ (distorted 1T).43−46 Among them, 2H and 1T′ structures and their transition are well studied because MoS2 forms these two phases under different strain and charge doping conditions.47−50 As shown in Figure 1a,b, PtSe2 takes the distinct 1T phase,28,29 in which Pt atoms form a triangle lattice and the Se atoms occupy the centers of the Pt triangles alternately above and below the Pt plane. We have examined the stability of the 2H phase of PtSe2 and found that it is thermodynamically unstable due to the significant presence of imaginary frequencies in the phonon dispersion.

In this article, we systematically explore a variety of vacancies, including Se/Pt-SV and Se/Pt-DV, in 1T monolayer PtSe2, focusing on local atomic structure, stability, diffusion pathway, and energy barrier. To provide guidance for experimental observations, we also present the simulated scanning tunneling microscope (STM) images of these defects by ab initio calculations. We also examine the influence of these defects on the electronic and magnetic properties of PtSe2. These results not only significantly enrich our fundamental understanding of intrinsic defects in 1T-phase PtSe2 but also provide possible viable strategies for the control of vacancy defects in PtSe2 monolayer for novel device applications.

Figure 1. Top (a) and side (b) views of perfect 1T-phase PtSe2 monolayer. The small diamond in (a) shows the primitive cell of PtSe2. Convergence tests for energy cutoff of plane waves (c) and density of k-mesh (d). The band structure (e) from Perdew–Burke–Ernzerhof (PBE) calculations using the \((6 \times 6)\) supercell of PtSe2 shown in (a).
Figure 2. Top (a) and lateral (b) views of Se-SV defect in PtSe₂ monolayer. Top and bottom indicate two asymmetric surfaces of PtSe₂ monolayer with local Se-SV defect. The simulated STM images obtained from top (c) and bottom (d) surfaces at −0.5 V bias. The band structure (e) and DOS (f) of (6 × 6) supercell of PtSe₂ with one Se-SV defect. Gray, blue, and orange balls denote the Pt atoms and upper and lower Se atoms, respectively.

Figure 3. (a) Schematic of the construction of Se-DV by forming the second vacancy from one of the six possible sites (labeled from 1 to 6) with different distances from the first vacancy (labeled as 0). The upper and lower Se atoms are represented by blue and orange, respectively. (b) The energy difference of Se-DVs as a function of the distance between the two Se-SVs. The simulated STM images of various Se-DVs obtained from two sides of the monolayer: (c, d) Se-DV1, (e, f) Se-DV2, (g, h) Se-DV3, (i, j) Se-DV4, (k, l) Se-DV5, and (m, n) Se-DV6.
with dimensions of (22.485 Å × 22.485 Å). After full structure relaxation, the band structure of this supercell is calculated using PBE functional and shown in Figure 1e. It is seen that the PBE calculation gives an indirect band gap of 1.4 eV, which is 0.2 eV larger than that in the previous local density approximation calculation but smaller than that in the previous GW calculation result, which is about 2.10 eV.20 Although the PBE calculation underestimates the value of the band gap, it is able to give a reliable band alignment trend compared with the experimental result.29 Besides, GW calculations are computationally too demanding. Hence, in the present work, all of the electronic properties of defective PtSe2 are studied on the basis of PBE-level calculations.

2.1. Structure, Electronic Property, and STM Image of Se-SV. In general, the chalcogen-SV is the major defect in TMDCs.35,37 Here, we first study the Se-SV, whose optimized structure is shown in Figure 2a,b. The Se-SV is generated by removing a Se atom. Because there are two equivalent surfaces of monolayer PtSe2, these two different surfaces are labeled as top and bottom, as shown in Figure 2b. From the band structure (Figure 2e), it is seen that there are three defective bands emerging in the gap zone compared with the band structure of perfect PtSe2 (Figure 1e). The Se-SV shrinks the band gap of the (6 × 6) supercell of PtSe2 to 0.68 eV, which is nearly half of that of pristine PtSe2. Note that the densities of states (DOS’s) show a similar band gap (Figure 2f). In the defective PtSe2, the valence band maximum (VBM) is still at Γ point, the same as that of the pristine PtSe2, whereas the conduction band minimum (CBM) shifts to K point (Figure 2e).

To facilitate experimentalists to observe Se-SV, we simulate the scanning tunneling microscope (STM) images from both top and bottom sides under −0.5 V bias. Different from dark spots of sulfur-SV in MoS2,33,34 the STM image of Se-SV exhibits some bright spots, which are originated from the strong localized charges caused by the Se-SV defect (see the band structure in Figure 2e). From the top side, the STM image has six spots, which are the six Se atoms around the Se-SV at the top side (see Figure 2c), whereas for the bottom side, the three brightest spots come from the second neighbor Se atoms on the bottom side (labeled as three red circles in Figure 2a). Inside the three brightest spots, there are also three second brightest spots corresponding to the three most neighboring Se atoms on the bottom plane (labeled as blue circles in Figure 2a). It should be noted that STM images reflect the local density of states of the surface under an external bias. As a result, the STM images may change under different external biases. Hence, it is important to choose the bias that includes major defective levels.

2.2. Structure, Stability, and STM Image of Se-DV. For MoS2, a sulfur-DV forms by losing both upper and lower sulfur atoms at the same x−y position.30 Figure 3a shows the possible Se-DVs by losing the second Se atom near the first Se-SV in Γ phase PtSe2 monolayer. The upper and lower Se atoms are represented by blue and orange, respectively. The relative energies of these Se-DVs are plotted in Figure 3b as a function of the distance between the two missing Se atoms. In contrast to the most stable sulfur-DV in MoS2, which forms by losing two nearest S atoms, the Se-DV1, which forms by losing the nearest two Se atoms, possesses the highest relative energy, indicating that it is not energetically favorable. The DV defect with the lowest relative energy is the Se-DV3, which is about 0.8 eV lower than that of Se-DV1. The relative energies for the Se-DV2, 4−6 are in the range of 0.35−0.42 eV higher than those of the Se-DV3. Hence, our calculations clearly show that the Se-DV3 is the most energetically favorable DV defect.

We also simulate the STM images of these Se-DVs. When the atoms of DV are lost from both upper and lower Se layers, the STMs obtained from top and bottom sides (see SV in Figure 2b) are identical, as shown in Figure 3c,d for Se-DV1, Figure 3g,h for Se-DV3, Figure 3ij for Se-DV4, and Figure 3mn for Se-DV6. If the two Se atoms are lost from the same side, the STM images obtained from top and bottom sides are obviously different, as shown in Figure 3ef for Se-DV2 and Figure 3kj for Se-DV5. It is interesting to mention that the STM images of Se-DV1 can be seen as the overlap of the STM-top (Figure 2c) and STM-bottom (Figure 2d) images. Similarly, the STM images of Se-DV4−6 are also made up of the STM images of Se-SV, except for the STM-bottom of Se-DV5 (Figure 3i). It should be noted that the STM images for Se-DV2 and Se-DV4 are more complicated, and thus special attention is needed to identify them.

The relative population of various DVs can be estimated from exp(−ΔE/kT) for a given temperature, where ΔE is the relative energy difference, k and T are the Boltzmann constant and absolute temperature, respectively. If we take only the six Se-DVs into account, the ratio of Se-DV3 can be over 99.99% at room temperature and 99.87% at 270 °C (the growth temperature) among these six DVs. Clearly, the Se-DV3 is the most populous DV in PtSe2. Here, we would like to examine its structure and properties in more detail.

The optimized structure of Se-DV3 is shown in Figure 4a. It is seen that the two missing Se atoms are located at different Se layers and along the armchair direction. Figure 4b shows the partial charge density from −0.5 eV to Fermi level. Compared with the STM images, it is seen that the spots match with the Se atoms, which are labeled with different sized circles according to their brightness.

Similar to Se-SV, the VBM of Se-DV3 is at Γ point and the CBM shifts to K point in the band structure (Figure 4c). The band gap is reduced to only 0.17 eV, which is much smaller than that of pristine PtSe2 (1.4 eV). Besides the CBM and VBM, there are four defective levels in the gap zone compared with the pristine band structures (Figure 1e). We also calculate the DOS of Se-DV3 using the tetrahedron method with Bloch corrections, and the band gaps obtained from the DOS and band structure are in good agreement with each other. The significant reduction in the band gap indicates that the Se-DV is able to greatly alter the electronic properties of PtSe2.

2.3. Structure, Magnetic/Electronic Properties and STM of Pt-SV. Besides the chalcogen vacancies, transition-metal vacancies were also observed in previous studies on MoS2.35,37,38 Here, we would like to investigate possible Pt vacancies in PtSe2 monolayer. Figure 5a shows the relaxed structure of Pt-SV, and the blue zones represent the local spin charge density originated from the dangling bonds of Se atoms around the Pt-SV. A large magnetic moment of 6 μB is introduced by a Pt-SV. As the Pt layer is the middle layer of PtSe2, the STM images obtained from the upper and lower surfaces are identical. Figure 5b shows the simulated STM image for Pt-SV, where three spots are clearly brighter than others. It should be noted that the STM image of Pt-SV is similar to that of the Se-SV from the bottom surface (Figure 2d) but the distance between two brightest spots in the STM image of Se-SV from the bottom surface is twice that of Pt-SV. Different from nonmagnetic Se vacancies, Pt-SV shows a strong
spin-polarized band structure and DOS, as shown in Figure 5c,d. The band gap of spin-down (blue) is only 0.27 eV, whereas that of spin-up (red) is about 1.20 eV. Therefore, it is expected that PtSe₂ with a certain density of Pt-SV may have the potential for spintronic applications.

2.4. Structure, Stability, and Property and STM Image of Pt-DVs. Similar to Se-DVs, we construct the Pt-DVs by removing the second Pt atom near the existing Pt-SV (Figure 6a). The variation of the relative energy of Pt-DV with the distance between two Pt vacancies is shown in Figure 6b. It is interesting to see that the most stable Pt-DV is the Pt-DV1 formed by the two nearest Pt vacancies, which is very different from the scenario of Se-DVs.

The simulated STM images of Pt-DVs are shown in Figure 6c−g. The STM image of Pt-DV1 (Figure 6c) has four spots brighter than others, and thus the pattern is similar to that of the Se-DV3 (Figure 3g,h). Hence, during experimental imaging, care should be taken to distinguish Pt-DV1 and Se-DV3. Except for Pt-DV1, other STM images can be easily recognized due to the isolated character of two Pt-SVs, with each having three bright spots. The simple assembly of STM images of Pt-DV2−6 implies that the interaction of two Pt vacancies may be greatly screened.

The energy difference between Pt-DV1 and other Pt-DVs (also two isolated Pt-SVs) can be as large as 1.18−1.22 eV. Therefore, if the migration of Pt vacancy is easy, the Pt-SVs and other Pt-DVs would like to form Pt-DV1. We can also estimate the relative ratio of Pt-DV1 among the five Pt-DVs under the thermodynamic equilibrium condition. According to the Boltzmann distribution law, \( \exp(-\Delta E/kT) \), the ratio of Pt-DV1 among all of the explored Pt-DVs is near 100% both at room temperature and 270 °C (the growth temperature) under thermodynamic equilibrium. Clearly, Pt-DV1 is the most populous of Pt-DVs. Here, we would like to examine its structure and properties in more detail.

Figure 7a,b exhibits the top and side views of the atomic structure of PtSe₂ with a Pt-DV1 after full energy relaxation. Besides, the charge distribution at the region between −0.5 eV and Fermi level is depicted in Figure 6c. Clearly, the charge is localized at Se atoms around the Pt-DV1 and the four atoms that correspond to the four brightest spots in STM images (Figure 6c) are marked by red circles in Figure 7a.

Similar to Pt-SV, strong spin polarization also exists in Pt-DV1. According to the band structure (Figure 7d), the band gap for spin-down (blue) is only 0.21 eV, which is much lower than that of the other spin component (red). This can be verified by the analysis of DOS (Figure 7e). The dispersion of the defective bands in the band structure is very weak, and VBM is located at \( \Gamma \) point, whereas CBM is at \( M \) point. Therefore, the Pt-DV1-contained PtSe₂ is promising for spintronic applications. Besides, several defective levels appear in the band gap zone, which may be used to modulate the optical gap of PtSe₂ for optoelectronics.

2.5. Migration Path and Energy Barrier of Vacancies in PtSe₂. The diffusion/migration capacity of point defects can be dramatically different in different 2D mono-layers. For graphene, the diffusion barrier for carbon-SV is about 0.94−1.70 eV, allowing the diffusion during the radiation, such as STM measurement. However, the transformation energy barriers for different carbon-DVs can be as large as about 6 eV. The migration barrier of SV is very low, which is about 1 order lower than that of graphene. These low migration barriers
enable a fast diffusion of vacancies in silicene and phosphorene even at room temperature, making their imaging challenging.\textsuperscript{54} Compared with these elementary monolayers, the migration barrier of sulfur-SV in MoS\textsubscript{2} can be up to 2.3 eV,\textsuperscript{36,37} making the diffusion and coalescence of sulfur-SV difficult.

For PtSe\textsubscript{2}, we first explore the diffusion of Pt-SV. Figure 8 depicts the single diffusion path and barriers of Pt-SV to its neighboring position. There is an intermediate state in this diffusion process, whose relative energy is about 2.15 eV higher than that of Pt-SV. The whole diffusion barrier is about 2.56 eV. We can estimate the migration frequency of Pt-SV by

\[ D \sim \nu \exp(-\Delta E/kT) \]

where \( \Delta E \) is the diffusion barrier (2.56 eV for Pt-SV), \( \nu \) is the vibration frequency of an atomic bond, which is about 10\textsuperscript{13} per s, and \( k \) and \( T \) are the Boltzmann constant and temperature, respectively. Therefore, the diffusion frequency of Pt-DV is about 10\textsuperscript{-30} Hz at room temperature and 10\textsuperscript{-11} Hz at 270 °C. This means that such a diffusion process of Pt-SV is difficult under these two conditions. Such diffusion can only take place under very high temperature, for example, 3 times per min under 900 K and 100 Hz under 1200 K. It is expected, however,
that PtSe₂ may undergo thermal decomposition under such high temperatures.

Because of the 1T structure of PtSe₂, the diffusion of Se vacancy is more complex than that of Pt vacancy. Figure 9a,c,e describes three possible diffusion paths and related energy barriers of isolated Se vacancy diffusion in PtSe₂. The lowest barrier is 2.17 eV (Figure 9c), which is about 0.39 eV lower than that of Pt-SV diffusion and 0.13 eV lower than that of sulfur vacancy diffusion in MoS₂. However, this diffusion barrier is still too high. For example, at room temperature, the migration frequency is as low as 10⁻²⁴ Hz, indicating that such diffusion is nearly impossible. Even at 270 °C, the diffusion frequency is only 10⁻¹⁷ Hz.

In general, when two single vacancies are close to each other, their interaction may affect their individual mobility. In the following, we further explore the migration behavior of two interacting nearest Se vacancies in monolayer PtSe₂. Three possible diffusion paths are shown in Figure 9b,d,f. It is interesting to see that for the first path, the diffusion barrier of Se atom in the presence of the second vacancy nearby is reduced to only 1.30 eV (Figure 9b) from 2.76 eV (Figure 9a). Such an energy barrier reduction is also observed for the third proposed diffusion path, where the barrier is 4.25 eV for isolated Se-SV (Figure 9e) and only 2.19 eV in the presence of the second Se-SV (Figure 9f). In contrast to the first and third possible paths, the diffusion barrier for the second pathway is almost unaffected by the neighboring vacancy. Overall, the diffusion pathway shown in Figure 9b gives the lowest energy barrier for the diffusion, which is about 1 eV lower than others. Therefore, the diffusion of an Se-SV in the presence of another Se-SV can be much faster than that of an isolated Se-SV. For example, the diffusion frequency for the former is 10 Hz at 270 °C, whereas for the latter is only 10⁻¹⁷ Hz. These results indicate the migration frequency is low for both isolated Pt and Se single vacancy at room temperature, but the migration of Se single vacancy can be greatly increased when another neighboring Se single vacancy exists. Moreover, elevating temperature can also efficiently accelerate the migration. Migration behaviors revealed here are important for the vacancy annealing, treatment, and further application of this new 2D material.

3. CONCLUSIONS

We have systematically investigated Se and Pt vacancies in PtSe₂ monolayer using first-principles calculations. We have identified the most stable Se-SV, Se-DV, Pt-SV, and Pt-DV. Because of the 1T-phase configuration, the atomic structure of Se-DV in PtSe₂ is quite different from that of the previously reported sulfur-DV in 2H-phase MoS₂. Both Se-SVs and Pt-SVs prefer to combine together to form DVs. All Se and Pt vacancies have remarkable influence on the electronic properties. Moreover, Pt-SV and Pt-DV can introduce strong spin polarization. Thus, PtSe₂ containing a certain amount of Pt vacancies may be promising for spintronic applications. These findings are potentially useful for engineering the electronic and
magnetic properties of PtSe₂ monolayer for applications in optoelectronic and spintronic devices.

4. METHODS

Ab initio calculations were performed using spin-polarized density functional theory and plane wave pseudopotential technique, as implemented in the Vienna ab initio simulation package. Generalized gradient approximation with the PBE functional was adopted to describe the exchange–correlation interaction. The core electrons were described by the projected augmented wave potentials. During all calculations, the kinetic energy cutoff of 400 eV for the plane wave basis and the convergence criterion of 10⁻⁵ eV for total energy were carefully tested and used.

The primitive cell of PtSe₂ was fully relaxed in terms of lattice constants and atomic positions. Thereafter, a large (6 × 6) supercell of PtSe₂ (22.485 Å × 22.485 Å) with a vacuum space of 25 Å thickness was built to investigate the influence of various local defects. Starting from the perfect PtSe₂ sheet, the initial vacancies were created by removing selected lattice atoms systematically. Then, the atomic positions were fully relaxed with γ point sampling as the supercell is very large. After geometry optimization, accurate total energies were calculated with both the convergence criterion of 10⁻⁵ eV for total energy were carefully tested and used.

To simulate the defect diffusion behavior in PtSe₂, the climbing-image nudged elastic band (cNEB) method was employed to search the diffusion path and energy barrier. During geometry optimizations and cNEB search, the force criterion for structure optimization and cNEB search was set to 0.02 eV Å⁻¹. The STM simulations were obtained using the Tersoff–Hamann approximation, with a constant distance of about 2 Å from the surface.

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Notes
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