Layer-dependent band engineering of Pd dichalcogenides: a first-principles study

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Abstract

Among the families of transition metal dichalcogenides (TMDs), Pd-based TMDs have been one of the less explored materials. In this study, we investigate the electronic properties of PdX₂ (X = S, Se, or Te) bulk and thin films. The analysis of structural stability shows that the bulk and thin film (1 to 5 layers) structures of PdS₂ exhibit pyrite, while PdT e₂ exhibits 1T. Furthermore, PdSe₂ exhibits pyrite in bulk and thin films down to the bilayer. Most surprisingly, PdSe₂ monolayer transits to 1T phase. For the electronic properties of the stable bulk configurations, pyrite PdS₂ and PdSe₂, and 1TPdT e₂, demonstrate semi-metallic features. For monolayer, on the other hand, the stable pyrite PdS₂ and 1TPdT e₂ monolayers are insulating with band gaps of 1.399 eV and 0.778 eV, respectively, while 1TPdT e₂ monolayer remains to be semi-metallic. The band structures of all the materials demonstrate a decreasing or closing of indirect band gap with increasing thickness. Moreover, the stable monolayer band structures of PdS₂ and PdSe₂ exhibit flat bands and diverging density of states near the Fermi level, indicating the presence of van Hove singularity. Our results show the sensitivity and tunability of the electronic properties of PdX₂ for various potential applications.

1. Introduction

In these recent years, 2D materials have started to attract attention since the discovery of graphene [1] back in 2004. Graphene has been considered as the wonder material because of its novel properties such as being the thinnest and strongest known material in the Universe, its charge carriers demonstrate zero effective mass, large intrinsic mobility, and can travel distances (μm) without scattering at room temperature [2]. However, graphene still has limitations such as, but not limited to, its gapless electronic property and difficulty in mass-producing high quality crystals [3], thus making its research and commercial applications hindered. Due to this restriction, the search for alternative 2D materials has begun. One of the promising candidates is the transition metal dichalcogenides (TMDs), which is defined by a general formula of MX₂ with M corresponding to transition metal, and X corresponding to chalcogen S, Se, or Te. Researches on 2D TMDs are steadily gaining traction because of recent findings for the improvement in crucial technological applications, such as in energy storage [4, 5], gas sensing [6, 7], and valley physics [8–10]. Moreover, it can be straightforwardly synthesized by exfoliating the bulk structures to produce the corresponding 2D structures due to weak interlayer interactions governed by van der Waals forces. The crystal structure of
TMDs commonly exist in trigonal prismatic or octahedral phase and can be stacked into different polymorphs, i.e. 1T, 2H, and 3R [11]. Moreover, recent studies [12–20] have shown that some TMDs can also exhibit orthorhombic structures, specifically pyrite and marcasite structures.

Studies have also demonstrated that the electronic properties of TMDs can easily be engineered and manipulated by tuning its thickness [21–23] or introduction of strain [21, 24–27], in which some of the observed phenomena were increasing and indirect-to-direct transition of band gap from bulk to monolayer, and tuning of van Hove singularity (vHs) [28] near the Fermi level. Because of these unique properties, TMDs are now one of the fascinating prospects in condensed matter research, especially in 2D materials.

Among these TMDs, Pd dichalcogenides are still one of those less explored because of the difficulty to synthesize, compared to the most well-studied TMD systems such as MoX2 and WX2. Moreover, studies show that some members of the PdX2 family also adopt another structural phase, specifically pyrite and marcasite, rather than the common 1T or 2H, making their properties different depending on the geometry [29]. Furthermore, recent studies [30–33] have shown that bulk PdX2 exhibit superconductivity and their critical temperatures could be further tuned through change in pressure.

Up until recently, fabrication techniques have been limited to mechanical exfoliation [12, 34] and molecular beam epitaxy (MBE) [35]. These methods, however, lead to low yield and quality, and were not fit for practical applications. With the development of highly efficient fabrication techniques to synthesize TMDs by employing post-chalcogenization through sulfurization [16] or selenization [19, 36], as well as the discovery of its new 2D pentagonal crystal structure [12, 14], the fascination to explore Pd-based TMDs has been reawakened.

In this study, we investigated the impact of varying the material thickness to the electronic properties of Pd-based TMDs (PdX2 where X = S, Se, or Te) using first-principles calculations. Here, we primarily focused on the layer dependence of the band structures by varying the thickness from monolayer (1L) up to 5 layers (5L) and bulk under different possible crystal configurations, specifically 1T, 2H, marcasite, and pyrite. With regards to the most stable structures of PdX2, we found that PdS2 bulk and thin films exhibited pyrite phase, while PdTc2 bulk and thin films exhibited 1T phase. Interestingly, PdSe2 exhibited pyrite phase from bulk down to bilayer thin film, while PdSe2 monolayer structure transits from pyrite structure to 1T structure. Moreover, we found that bulk PdSe2 may also exhibit 1T phase since it only has a slightly higher energy than pyrite by 2.0 meV. Finally, we probed the stable monolayer structures of PdX2 and, surprisingly, found that monolayer PdS2 and PdSe2 possess diverging density of states near the Fermi level, indicating the presence of vHs. It was shown in recent studies that vHs near the Fermi level affects specific material properties, such as, antiferromagnetism [37] and ferromagnetism [38, 39], and superconductivity [40–42]. Our results show that PdX2 have distinctive properties that set it apart from others and provide a new ground for material exploration.

2. Methods

First-principles calculations were carried out within the density functional theory framework [43] as implemented in the Vienna \textit{ab initio} simulation package (VASP) [44–47] using projector-augmented wave (PAW) [48, 49] functions under the GGA-PBE [50] pseudopotential with cut-off energy of 400 eV. For the structural relaxation, different van der Waals corrections were tested, and found that SCAN + rVV10 functional [51] replicated the experimental lattice constants. All the crystal structure relaxations were performed until the residual force acting on each atom is less than 0.01 eV Å$^{-1}$, and the self-consistent convergence criterion for electronic structures was set to 10$^{-5}$ eV. For all the self-consistent calculations, meta-GGA SCAN [52, 53] with spin orbital coupling (SOC) was implemented because recent studies [53–55] have shown that there is a significant improvement in SCAN over PBE. The Γ-centered Monkhorst–Pack [56] was used to sample the first Brillouin zone (BZ) using k-point grids of 24 × 24 × 12, and 24 × 24 × 18 for bulk hexagonal and orthorhombic structures, respectively, while 24 × 24 × 1 was used for the most stable thin film structures. To create the finite-layer structures, a vacuum of 15.0 Å was added above the topmost layer to remove the interactions due to periodic boundary conditions. To explore the thermal stability, phonon dispersion was calculated using the Phonopy [57] code. Finally, a 300 × 300 × 1 k-point mesh was used to get an accurate energy contour plot.

3. Results and discussions

In this study, we considered four possible bulk structures, specifically 1T, 2H, pyrite, and marcasite structures, as shown in figure 1. For the rest of the presentation in this manuscript, the results are calculated with SCAN + SOC, unless we state otherwise. The lattice constants of optimized structures and their
Figure 1. Top and side views of the bulk crystal structure of (a) 1T, (b) 2H, (c) pyrite, and (d) marcasite. Correspondingly, the first Brillouin zone of (e) hexagonal (1T and 2H), and (f) orthorhombic (marcasite and pyrite) crystal structure. To better visualize the different layers in top view, a different color scheme was used for the 1st and 2nd layer.

Table 1. Theoretically optimized lattice parameters (Å) using SCAN + rVV10 van der Waal correction. The experimental values are listed in parenthesis for comparison.

| PdX₂  | 1T (Å) | 2H (Å) | Pyrite (Å) | Marcasite (Å) |
|-------|--------|--------|------------|---------------|
| PdS₂  | 3.54   | 3.82   | 5.45 (5.41)| 7.20 (7.45)   |
|       | 4.60   | 9.33   | 5.53 (5.49)| 7.20 (7.45)   |
| PdSe₂ | 3.73   | 3.58   | 5.74 (5.75)| 5.86 (5.87)   |
|       | 4.79   | 10.90  | 7.53 (7.69)| 7.53 (7.69)   |
| PdTe₂ | 4.02 (4.04)| 3.83 | 5.44 (5.13)| 5.44 (5.13)   |
|       | 4.99 (5.13)| 11.60| 6.54       | 6.54          |

Table 2. Calculated total energies using SCAN with SOC for different bulk phases (eV per f.u.).

| PdX₂  | 1T     | 2H     | Pyrite  | Marcasite |
|-------|--------|--------|---------|-----------|
| PdS₂  | −52.828| −51.909| −53.121 | −52.829   |
| PdSe₂ | −73.979| −73.135| −73.981 | −73.804   |
| PdTe₂ | −108.724| −108.164| −108.585| −108.514  |

corresponding experimental values are shown in table 1. With regards to their relative structural stability, the total energy per formula unit (f.u.) of each configuration was used to determine the most stable structure, as shown in table 2.

Starting off with PdS₂, the bulk structure exhibited pyrite phase with the calculated lattice constants of \(a = 5.45 \text{ Å}, b = 5.53 \text{ Å}, \) and \(c = 7.20 \text{ Å}\) in agreement with experimental results of \(a = 5.41 \text{ Å}, b = 5.49 \text{ Å}, \) and \(c = 7.45 \text{ Å}\). Also, we note two metastable phases in PdS₂, namely marcasite and 1T, with only an energy difference of 1.0 meV per f.u.

Moving on to bulk PdSe₂, just like PdS₂, has been experimentally synthesized and demonstrates pyrite structure [17, 19]. This is further verified by our findings in which pyrite PdSe₂ is one of the most energetically stable configuration with the calculated lattice parameters of \(a = 5.74 \text{ Å}, b = 5.86 \text{ Å}, \) and \(c = 7.53 \text{ Å}\) in agreement with experimental lattice constants of \(a = 5.75 \text{ Å}, b = 5.87 \text{ Å}, \) and \(c = 7.69 \text{ Å}\). Interestingly, we also found that the pyrite structure is only more stable than 1T by 2.0 meV, which is close to the limit of DFT accuracy. This implies the probability to synthesize the bulk 1T structure of PdSe₂, as supported by our phonon dispersion calculations in figure S1.

Among the PdX₂ considered in this study, only bulk PdTe₂ demonstrated a stable 1T structure with the calculated lattice parameters of \(a = 4.02 \text{ Å}, b = 4.99 \text{ Å}\) in agreement with experimental results of \(a = 4.04 \text{ Å}, and c = 5.13 \text{ Å}\). The reason behind the preference of PdTe₂ stable bulk structure to 1T originates from the interplay between oxidation state and charge distribution, which are the key factors to understand the stability of these polymorphs [58]. To demonstrate these phenomena, it is useful to note that Pt-based TMDs have a quadrivalent oxidation state due to the inclusion of f-orbitals, thus exhibiting 1T phase [59, 60]. PdX₂, on the other hand, have a lower divalent oxidation state, which can be achieved by formation of \((X₂)²^−\) dimers due to the pairing the chalcogen atoms. This low oxidation state results to stable pyrite- and marcasite-type structures [60]. Kempt et al [60] have shown that the 1T phase of PdS₂ and PdSe₂ results to a higher oxidation state as compared to the pyrite phase which have a lower oxidation state, thus preferring the pyrite structure. Interestingly, they found that the 1T and pyrite phase of PdTe₂...
Figure 2. The bulk band structures for PdS$_2$: (a) 1T, (b) 2H, (c) pyrite, and (d) marcasite. The bulk band structures for PdSe$_2$: (e) 1T, (f) 2H, (g) pyrite, and (h) marcasite. The bulk band structures for PdTe$_2$: (i) 1T, (j) 2H, (k) pyrite, and (l) marcasite. The valence band maximum (VBM) and conduction band minimum (CBM) are shown in magenta and cyan, respectively. All the band structures include SCAN with SOC.

demonstrated no difference in their oxidation states. Since it is highly unlikely to form the Te–Te dimer, the 1T phase of PdTe$_2$ is favored.

For the electronic properties, the calculated band structures of the four bulk structures for each PdX$_2$ material are shown in figure 2. With respect to the band structures of bulk PdS$_2$ (figures 2(a)–(d)), among the four bulk configurations, only 2H is metallic while the rest are semi-metallic. For bulk PdSe$_2$, both pyrite (figure 2(g)) and 1T (figure 2(e)) structures exhibit semi-metallic features, while marcasite (figure 2(h)) and 2H (figure 2(f)) structures exhibit metallic features. Interestingly, the two most stable structures (pyrite and 1T) and two least stable structures (marcasite and 2H) demonstrate similar band properties of being semi-metallic and metallic, respectively. Finally, for PdTe$_2$, 1T (figure 2(i)) is semi-metallic, pyrite (figure 2(k)) is insulating with a band gap of 0.067 eV, while both 2H (figure 2(j)) and marcasite (figure 2(l)) are metallic. Moreover, our band structure for the bulk 1T phase agrees with the results of Noh et al [61] where they experimentally found type II Dirac fermions in the superconductive PdTe$_2$. In addition, there is a significant difference in the band structures of bulk pyrite PdS$_2$ and PdSe$_2$ (figures 2(c) and (g)) with bulk pyrite PdTe$_2$ (figure 2(k)). This phenomenon is due to the difference in the lattice structure as seen in the optimized lattice parameters (table 1). Bulk PdS$_2$ and PdSe$_2$ exhibit an orthorhombic pyrite phase with an elongated c-axis (figure 1(c)) resulting to a square-planar coordination. Moreover, both have a slightly larger b-axis than a-axis (table 1) leading to a nondegenerate Pd d-orbitals [60]. Hence, PdS$_2$ and PdSe$_2$ exhibit similar band characteristics. On the other hand, pyrite PdTe$_2$ exhibits a cubic lattice with a = b = c lattice parameters. This results to a different band structure relative to its PdS$_2$ and PdSe$_2$ counterpart.

We now move on to the discussion of the thickness dependent properties of thin film PdX$_2$ from 1L up to 5L. As shown in table 3, we considered the two lowest energy structures, 1T and pyrite, for each material. The corresponding calculated band gaps are then shown in tables 4 and S1, while the calculated work functions for the stable PdX$_2$ monolayers are shown in table S2. The work function of a given system represents the minimum amount of energy required to remove an electron from the material surface to the vacuum regime. Moreover, Zeng et al [19] experimentally demonstrated an increasing work function with increasing layer thickness for PdSe$_2$ thin films. We can therefore assume that the other stable PdX$_2$ thin films will follow the same trend. Table 1 shows the bulk lattice constants which were used to construct the layered structures starting from 1L up to 5L. Atomic position relaxations were again carried out while fixing the lattice constants, and the band structures were then calculated. Here, we note that the number of atoms per layer of the pyrite structure corresponds to a 2 × 1 structure of 1T. Thus, we multiplied the total energy per f.u. of 1T thin film structures by two for comparison with the pyrite thin film structures. Upon decreasing the material dimension to monolayer, the most stable phase remained to be pyrite for PdS$_2$, and 1T for PdTe$_2$, while PdSe$_2$ transitioned to 1T phase during the transition from bilayer to monolayer. Owing to the degeneracy of the stable bulk 1T and pyrite PdSe$_2$ structures, the energy difference between the layered structures of 1T and pyrite phase becomes smaller as the thickness reach the bulk limit.
To elucidate further on the stability of PdX₂ film structures, phonon dispersions were calculated to demonstrate the thermal stabilities of the most energetically favorable bulk and monolayer PdX₂ structures, specifically pyrite PdS₂, 1T and pyrite PdSe₂, and PdTe₂, as shown in figure S1. By comparing the stability of bulk structures with its corresponding monolayer structures, we will have an idea regarding the stability of its intermediate thin film structures. As seen in figure S1(a)–(d), (g) and (h), there are no negative frequencies for bulk and monolayer pyrite PdS₂ and PdSe₂, and 1T PdTe₂, thus confirming their stability and is, indeed, already been experimentally realized. Interestingly, we also found no negative frequencies for bulk and monolayer 1T PdSe₂, in figure S1(e) and (f), implying that 1T is a metastable state, as well as the possibility to experimentally synthesize 1T PdSe₂.

For the thickness dependent electronic properties, we will be focusing on the stable thin film structures of PdX₂ (pyrite PdS₂, pyrite PdSe₂, and 1T PdTe₂). For comparison, the band structures of the metastable structures (1T PdS₂ and pyrite PdTe₂) are shown in figures S2 and S3 in the supporting information.

Starting with pyrite PdS₂, the calculated 1L to 5L band structures are shown in figure 3. We observe from figure 3 that 1L to 5L pyrite PdS₂ structures all exhibit insulating phases with an indirect band gap decreasing from 1.399 eV to 0.471 eV (table 4) as the thickness increases, then eventually transitioning to semi-metallic phase in the bulk regime. However, no indirect-to-direct band gap shift was observed as the number of layers decreased to the monolayer regime, in contrast with other well-studied TMDs such as WS₂ and MoS₂ [22, 23, 62]. Nevertheless, we were still able to perceive a shift in the lowest point of conduction band minimum (CBM) from S point to in-between S and Y points to during the transition from 1L to 2L. The highest point in valence band maximum (VBM) remained to be in $\Gamma$ point all throughout the different number of layers with a little swiveling in the VBM during the change from 1L to 2L.

Intriguingly, among the layered PdX₂ investigated in this study listed in table 3, PdSe₂ shows a stable structure phase transition from pyrite (5L to 2L) to 1T (1L) structure. This stable structure transition upon changing of thickness is attributed to the balance between strain and chemical energy changes that the system experiences as the number of layers change [63]. To elucidate more on the electronic properties of the PdSe₂ thin film structures, the calculated band structures are shown in figure 4. In figure 4(a), we observe a decreasing indirect band gap in pyrite PdSe₂ from 1.548 eV to 0.569 eV (table S1) as the number

| Table 3. The calculated total energies per formula unit of the thin film structures of PdX₂ using SCAN with SOC. |
|---------------------------------|------|------|------|------|------|
| Structure      | 1L   | 2L   | 3L   | 4L   | 5L   |
| PdS₂, 1T       | $-105.646$ | $-105.709$ | $-105.718$ | $-105.730$ | $-105.726$ |
| PdS₂, pyrite   | $-106.027$ | $-106.197$ | $-106.244$ | $-106.270$ | $-106.276$ |
| PdSe₂, 1T      | $-147.727$ | $-147.835$ | $-147.891$ | $-147.921$ | $-147.939$ |
| PdSe₂, pyrite  | $-147.671$ | $-147.868$ | $-147.921$ | $-147.947$ | $-147.964$ |
| PdTe₂, 1T      | $-216.738$ | $-217.076$ | $-217.216$ | $-217.292$ | $-217.330$ |
| PdTe₂, pyrite  | $-216.218$ | $-216.537$ | $-216.601$ | $-216.782$ | $-216.836$ |

| Table 4. The system band gap (eV) of layered and bulk pyrite and 1T structures of PdX₂ calculated using SCAN with SOC (negative band gap means semimetal). |
|-----------------------------------------------|------|------|------|------|------|
| Material       | 1L   | 2L   | 3L   | 4L   | 5L   | Bulk |
| Pyrite PdS₂    | 1.399 | 0.952 | 0.716 | 0.616 | 0.471 | $-0.137$ |
| 1T PdSe₂       | 0.778 | $-0.244$ | $-0.629$ | $-0.874$ | $-1.035$ | $-1.200$ |
| 1T PdTe₂       | $-0.005$ | $-1.032$ | $-1.060$ | $-1.246$ | $-1.297$ | $-1.369$ |

Figure 3. Band structures calculated using SCAN with SOC for pyrite PdS₂ with varying thickness: 1 to 5 layers. The valence band maximum (VBM) and conduction band minimum (CBM) are shown in magenta and cyan, respectively.
of layers increases from 1L to 5L. Moreover, we are also able to observe a shift in the lowest point of CBM from S point to in-between S and Y points, and highest point of VBM from near Γ region to in-between Γ and X, during the transition from 1L to 2L. For comparison with experimental studies [12, 19, 35], the calculated band gaps (table S1) of the corresponding pyrite thin film structures are relatively in good agreement with experimental findings.

Figure 4(b) shows the calculated band structures of 1T PdSe₂ from 1L to 5L thickness. The 1T PdSe₂ thin film remained to be semi-metallic from bulk to bilayer, and only became insulating in the monolayer regime with a band gap of 0.778 eV (table 4). With regards to the behavior of the band structures with respect to layer thickness, we can discern the shift of the highest point of VBM in Γ point to in-between Γ and M points, as the number of layers decreases from 5L to 2L. It then shifts back to Γ point upon transitioning from 2L to the monolayer, as well as, band gap opening. The lowest point of CBM remains to in-between Γ and M points for all the thicknesses. The drastic changes in the band structures during the transition from bilayer to monolayer pyrite and 1T PdSe₂ clearly depicts the effect of thickness to material characteristics, specifically on structural and electronic properties. We can therefore say that a critical thickness of 2 layers exist for PdSe₂ where the interplay between strain and chemical energy becomes crucial [63].

Next, we found that thin film PdTe₂ interestingly adopted the 1T phase rather than pyrite. Our result agrees with the experimental findings [18, 32, 33] that PdTe₂ crystallizes to 1T phase. Moreover, the electronic property remained to be semi-metallic until the monolayer structure as seen in the band structures in figure 5. However, we still see the system gap (gap between CBM and VBM even if they crossed the Fermi level but did not touch) getting larger as the number of layers decreases. This is further verified by the negative system band gap becoming less and less negative as the number of layers approaches the monolayer regime (see table 4). Furthermore, we still see the shift of the lowest point of CBM from K point to in-between M and Γ points during the transition from bilayer to monolayer.

All the Pd-based TMDs investigated in this study exhibited an increasing system band gap while the number of layers decrease from bulk down to monolayer structures. In comparison to other TMDs such as MX₂ (M = Mo and W; X = S, Se, or Te) demonstrating direct bandgaps at the monolayer regime, no shift
Figure 6. Band structures with DOS calculated using SCAN with SOC for monolayer (a) pyrite PdS₂, (b) pyrite PdSe₂, (c) 1T PdSe₂, and (d) 1T PdTe₂, and their corresponding (e)–(h) contour plots under DFT.

from indirect-to-direct band gap in PdX₂ as the number layers decrease from bulk to monolayer structures was observed. This behavior deviation is due to the dissimilarity in the crystal structure of these materials, specifically since the stable MX₂ structure is 2H, while PdX₂ has pyrite and 1T structures. The difference in crystal symmetries significantly affects the behavior of the electronic properties. In spite of the variance in the crystal symmetries, an inverse relationship between the band gap and the number of layers are still being featured in PdX₂ because of key phenomena such the interlayer interaction through van der Waals interaction [64], and quantum confinement effect [65] which still plays a major role in the electronic properties of a material.

We further explore the electronic properties of the stable monolayer structures by studying the band structures with density of states (DOS), as shown in figures 6(a)–(d). Fascinatingly, flat band dispersion near the Fermi level of PdS₂ (figure 6(a)) and PdSe₂ (figure 6(b)) monolayers in pyrite structures, and PdSe₂ (figure 6(c)) monolayer in 1T structure were observed. This is also commonly seen in the band structures of 2L to 5L of pyrite PdS₂ and PdSe₂. The bands with the flat features in 1T PdTe₂ (figure 6(d)), however, is positioned relatively below the Fermi level. Nevertheless, the location of the flat band can be manipulated through strain [21] to tune the vHs for monolayer 1T PdTe₂. Focusing on PdS₂ and PdSe₂, the flat peaks bands observed are within the VBM. The presence of a flat dispersion curve or a saddle point implies that almost the same energy levels are being occupied by the allowed states of the charge carriers. A high or diverging DOS commonly emerges as a result, a common characteristic feature of vHs [42, 66], as highlighted by the green arrows in figures 6(a)–(d). To further confirm the presence of vHs in these structures, we plotted the band energy contours, as shown in figures 6(e)–(h), where we immediately see the saddle points, which are the indicators for the presence of vHs near the Fermi level in the monolayer structures. The saddles points are found specifically along Γ−X for pyrite PdS₂ (figure 6(e)), along Γ−Y for pyrite PdSe₂ (figure 6(f)), and along Γ−K for 1T PdSe₂ (figure 6(g)) (highlighted by the green dashed circles). These findings suggest the possible superconductivity of these materials, in support of previous experimental studies [30–33, 61, 67] that found PdX₂ to demonstrate superconductive properties.

4. Conclusion

In conclusion, we demonstrated that electronic properties of 2D TMDs could be manipulated and engineered through changing the thickness. Using first-principles calculations, the layer dependence of the electronic properties of PdX₂ TMDs were examined. Here, we found that PdS₂ exhibited pyrite phase, while PdTe₂ exhibited 1T phase. Interestingly, PdSe₂ exhibited pyrite phase from bulk until the bilayer structure, while its corresponding monolayer structure transitioned to 1T phase. Moreover, bulk 1T PdSe₂ phase may exist because of the comparable total energy with pyrite. All stable PdX₂ bulk demonstrate semi-metallic features. The monolayer structures for pyrite PdS₂ and 1T PdSe₂ are insulating with band gaps of 1.399 and 0.778 eV, respectively, while 1T PdTe₂ monolayer remained to be semi-metallic. With regards to the material electronic properties, a decreasing or closing of indirect band gap with increasing thickness was observed, as well as shifting in the peaks of the CBM and VBM. Moreover, the monolayer pyrite PdS₂, and monolayer pyrite and 1T PdSe₂ band structures exhibit flat bands and diverging density of states near the Fermi level, indicating the presence of van Hove singularity. With these results, the electronic properties of PdX₂ are indeed highly sensitive and tunable for various potential applications and new grounds of material exploration.
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