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Band edge States, Intrinsic Defects and Dopants in Monolayer HfS₂ and SnS₂ Semiconductors

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Although monolayer HfS₂ and SnS₂ do not have a direct band gap like MoS₂, they are projected to have a much higher carrier mobility than MoS₂. Their band offsets are favorable for their use with WSe₂ in tunnel field effect transistors. Here we study the effective masses, intrinsic defects and substitutional dopants of these dichalcogenides. We find that HfS₂ has surprisingly small effective masses for a compound that might appear ionic. The S vacancy in HfS₂ is found to be a shallow donor while that in SnS₂ is a deep donor. Substitutional dopants at the S site are found to be shallow for donors and acceptors. This contrasts with MoS₂ where donors and acceptors are not always shallow or with black phosphorus where dopants can reconstruct into non-doping configurations. It is pointed out that HfS₂ is a more favorable semiconductor than MoS₂ for semiconductor processing because it has more convenient CVD precursors previously used to make HfO₂.

The open-shell transition metal dichalcogenides (TMDs) such as MoS₂ have been intensively researched as important two-dimensional semiconductors. Their band gap changes from an indirect gap for the bulk to direct gap for the monolayer case [1]. The relatively small dielectric screening in the monolayer case means that complex exciton behavior becomes important even for relative small band gaps [2]. Carriers can be manipulated between the degenerate valley states in valleytronics [3]. TMDs are also interesting as photo- and molecular sensors. On the other hand, for purely electronic devices, we can consider other layered semiconductors which might have a carrier higher mobility.

One proposed electronic device using TMDs is the heterojunction tunnel field effect transistor (TFET). In this case, the continued scaling of transistors for computation creates a need for very low power switches, in particular switches with a steep subthreshold slope below the thermionic limit of 60 mV/decade of a normal field effect transistor [4-7]. We note that TFETs operating in the subthreshold regime are also very sensitive sensor amplifiers [8]. TFETs would normally be built using heterojunctions of two lattice-matched III-V semiconductors with a staggered or broken-gap band alignment. However, the lattice-matching condition is not always met and this leads to interfacial mismatch defects which degrade switching performance. An alternative is to use stacked layer heterojunctions of two TMDs. TMDs offer a wide range of band gaps and band offsets [9-12], and because of the van der Waals inter-layer bonding, no lattice matching condition is needed to avoid dangling bond-type defects. Considering the band offsets of the various 2D semiconductors, a suitable choice is a p-type compound with d² configuration such as WSe₂ paired with an n-type d⁰ compound such as HfS₂ or SnS₂ [9-12]. WSe₂ has a suitable high ionization potential whereas HfS₂ and SnS₂ have suitably deep electron affinities. SnS₂ and HfS₂ have s,p-like band edges and so, like black phosphorus, they have a higher phonon limited mobility of order 1000 cm²/V.s and lower effective masses than MoS₂ [13,14].

The electronic properties of HfS₂ or SnS₂ are much less studied than the standard TMDs such as MoS₂ or WSe₂. It is particularly important to understand the intrinsic defects and anion vacancies because these defects can cause Fermi level pinning at the contacts [15-19], which causes a much

larger contact resistance. This is a principle cause of the under-performance of 2D devices [20,21]. Thus, this paper investigates the band edge states, the intrinsic defects and the substitutional dopants of these chalcogenides.

The calculations are carried out for periodic supercell models of the Hf/Sn disulfides using the CASTEP plane-wave density functional theory (DFT) code [22,23]. Ultra-soft pseudopotentials are used and the Perdew-Burke-Ernzerhof (PBE) form of the generalized gradient approximation (GGA) is used for the electronic exchange-correlation functional for geometry relaxation. The HSE (Heyd-Scuseria-Ernzerhof) [24] hybrid functional is used for the calculation of the band gap and the heats of formation. The HSE parameters α and ω are set to 0.2 as in HSE06 to give band gaps consistent with experimental values. Spin-orbital coupling is not included. The plane wave cut-off energy is taken as 260 eV. All atomic structures are relaxed to a residual force of less than 10^{-5} eV/atom. Van der Waals corrections [25] are included for bulk structures.

For the 2D Hf/Sn disulfide system, a convergence test finds that a vacuum layer thickness of 20Å in the z direction is enough to converge the formation energy of S vacancy, and that 5x5 supercells in the x,y direction are enough to allow us neglect the interaction of periodic images. The transition states of intrinsic defects are corrected using the Lany and Zunger scheme [26]. The formation energy of each charge state are given by

$$H_q(E_F, \mu) = [E_q - E_H] + q(E_V + \Delta E_F) + \sum_{\alpha} n_{\alpha} (\mu_{\alpha}^0 + \Delta \mu_{\alpha})$$

where q is the charge on the system, E_q is the energy of charged system with a defect, E_H is the energy of charged defect-free system. E_V is the valence band maximum (VBM) and E_F is the Fermi level with the respect to VBM. n_{α} is the number of atoms of species α , μ_{α} is the relative chemical potential of element α . We note that the first two terms are equal to the difference between the total energy of charged defect system and total energy of the neutral defect-free system.

HfS₂ and SnS₂ each have the 2H structure in which the metal site has an octahedral configuration. The lattice constant of HfS₂ is calculated to be 3.68Å in PBE, which is 1.4% more than experimental value of 3.62Å [27]. The lattice constant of SnS₂ is calculated to be 3.74Å, which is 2.9% more than experimental value of 3.64Å [27].

We then calculate the chemical potential for the S-rich and S-poor limits. In the S-rich limit, chemical potential of S is set to 0 eV. In the S-poor limit for HfS₂, the S chemical potential is set to the Hf-HfS₂ equilibrium, from the heat of formation of HfS₂ (Table 1). This is calculated to be -5.10 eV or 2.55 eV/S atom in HSE, compared to -2.58 eV/S atom experimentally [28]. For SnS₂, the monovalent sulfide SnS exists between SnS₂ and Sn metal [28-32], so the zone of S chemical potential for SnS₂ ranges from 0 to -0.50 eV/ S atom, or 0 to -0.50 eV experimentally [30-32].

The band structures of bulk SnS₂ and HfS₂ have been studied for some time [33-37]. Fig. 1 and 2 show the band structures of monolayer and bulk HfS₂ and SnS₂ calculated with the HSE functional. We see that there is an indirect band gap in both monolayer and bulk forms, which is different to the case of MoS₂ and other d² transition metal dichalcogenides. The band gap is from Γ to M for the monolayer and from Γ to L for the bulk.

Table 2 compares the band gaps of these two materials calculated in PBE and HSE and the experimental band gaps for the bulk form [38]. Generally speaking, HSE06 corrects any under-estimation of the band gap of PBE.

The calculated Bader charges are +0.34 for Hf in HfS₂ and +0.3 for Sn in SnS₂ showing that the bonding is relatively non-polar in these compounds despite the formal ionic charges often used to describe their bonding.

Table 3 shows the calculated effective masses for SnS₂ and HfS₂. The non-polar bonding (only 8% ionic for HfS₂) explains the relatively dispersed band structures and the small effective masses of these compounds. The hole masses of SnS₂ differ slightly from those of Gonzalez [37].

Fig 3 shows the calculated band alignments with respect to the vacuum level [11]. These were calculated using supercells containing a monolayer of sulphide and 20Å of vacuum. This shows that WSe₂ has a type II band alignment with monolayer HfS₂ and SnS₂ in HSE as desired for a vertically stacked heterojunction TFET.

We now consider the geometries and formation energies of the intrinsic defects. Fig.4(a) shows the vacancy configuration. When the S atom is removed, the Hf or Sn and S atoms around the vacancy all move slightly away from vacancy center, compared to the defect-free configuration. Fig. 4(b) shows the formation energy as a function of Fermi energy E_F in the S-poor limit and the charge transition states. Here, the energies are plotted with respect to the charge neutrality level (CNL) [39] to enable both compounds to be plotted in a single diagram. For HfS₂, the -2 state is stable across all of the gap and with no state in the gap. The transition state lies at the bottom of the conduction band, so the vacancy is a shallow donor. For SnS₂, there is a transition level for -2 to +2 in the upper gap at +0.2 eV above the CNL. This vacancy is a deep donor.

Fig. 5(a) shows the partial density of states (PDOS) of the neutral defect state. For HfS₂, there is a peak in the PDOS at the conduction band edge with E_F lying at the conduction band edge. For SnS₂, transition state +2/-2 lies in the upper gap, above a defect band, consistent with Fig 4. The tendency to lose two electrons is the same for HfS₂ except that Fig. 4(b) now has two PDOS peaks for the +2/0 and 0/-2 states.

The behavior of the S vacancy in the d^0 compound HfS₂ differs from that of the S vacancy in the d^2 compounds MoS₂ where the neutral vacancy has a donor state in the upper band gap and a filled state at the valence band edge [18,40].

The sulfur interstitial configuration is shown in Fig. 4(c). This is the adatom configuration found in many layered compounds. The S-S bond is calculated to be 1.99Å in HfS₂ and 1.98Å in SnS₂. The S-S bond is longer than the double bond and shorter than S-S single bond in S₈. Fig. 4(d) shows the formation energies and transition state of this defect in HSE06. PBE gives three transition states in the gap +2/+1, +1/0, 0/-2, while HSE shows two defect states, +1/0, 0/-2. The +1/0 state lies in the middle of gap, and the 0/-2 state lies at the conduction band edge. The orbitals for +2/+1 and +1/0 states are also shown in Fig. 4(c). The +2/+1 orbitals consist of degenerate p_x and p_y states of the S adatom. The +1/0 orbitals have the same two degenerate orbitals but more located in underlying S atom. HSE gives a similar result, but only the +1/0 state is found, lying 0.7 eV below the CBM. This behavior is similar to the S interstitial in monolayer MoS₂ [40]. (It should be noted that the S interlayer interstitial in bulk SnS₂ has a slightly different behavior, where it tries to bond to both layers [31,32].)

The Hf interstitial has two configurations in monolayer HfS₂, as seen in Figs. 4(e,g). (The Sn interstitial in SnS₂ has similar behavior.) One configuration has two Hf atoms stacked vertically on top of each other called the ‘onsite’ or ‘split interstitial’. The other configuration places the extra Hf atom outside the layer at the hollow center of three S atoms in the ‘hollow interstitial’. Their formation energies are shown as a function of E_F in Fig 4(d).

For the split interstitial, the adjacent S atoms move away from defect center to allow space for the extra metal atom. The two metal atoms are equivalent for the split interstitial. These atoms form in-plane bonds with the three adjacent S atoms. The system is symmetric in the z direction. There are 4 valence electrons on Hf and Sn, two of which form three bonds with S. The other electron forms a Hf-Hf or Sn-Sn bond. There is one unpaired electron left, which can easily ionise. Hence, the +2 charge system dominates. The two electrons in Hf-Hf or Sn-Sn bond ionize if E_F moves across the

transition energy. Both HfS₂ and SnS₂ have a similar mid-gap +4/+2 transition state. A mid-gap peak is seen at 0.4eV in Fig 4(c,d), where the transition state is located.

The symmetry in the z direction is lost for the ‘hollow interstitial’. Three adjacent S atoms distort outward and out of the plane. There are two unpaired electrons in the extra Hf/Sn atom. Fig. 4(h) shows the transition states. The HfS₂ has a +4/+2 transition near the VBM and SnS₂ has nearly no transition state. Overall, plotting the formation energy of both interstitials across the band gap, the hollow site is the lowest for HfS₂ and the lowest for SnS₂ except very close to the valence band.

The metal vacancy states have also been calculated. Their formation energies for the neutral defects for the S-rich (metal-poor) limit are 4.38 eV and 5.31 eV for HfS₂ and SnS₂, respectively. These formation energies are much higher than for the other defects. Therefore, we conclude that Hf and Sn vacancies are not very important.

We have also calculated the formation energies in PBE. We find that while PBE underestimates band gap and the formation energy, in most cases it gives right location of charge transition state with respect to the CNL. As Hf/SnS₂ is used for the n-type layer of the TFET, so E_F will lie close to the CBM. The S vacancy, interstitial and Hf/Sn interstitial each have a positive formation energy near the CBM, which means that they will not form spontaneously.

Fig 5 shows the substitutional doping states at the S site. The Br donor is calculated to be a shallow state, with a transition state near the respective band edge. The As acceptor is deeper, but still reasonably close to the VBM. This is very desirable if these compounds are to be used for a TFET. The fact that neither of the dopant sites reconstructs into a non-doping configuration explains why these sites are basically shallow, unlike the case of dopants in black phosphorus [41].

We summarise the situation of these two compounds for use as a TFET. Their band offsets are as desired. SnS₂ has a low effective mass and is bipolar, with shallow donors and acceptors. Its main disadvantage is that it has only a small range of S chemical potential for which it is stable, which is important for growth by chemical vapor deposition (CVD). Superficially, HfS₂ is more ionic than SnS₂ so might be expected to have higher effective masses. However, in practice, its bonding is *not* very polar, and its effective masses are still low. Its big advantage is that it is the only stable sulfide of Hf, with a large stable range of S chemical potential. It has the great advantage that Hf CVD precursors are highly developed from the use of HfO₂ as a high K oxide in microelectronics, whereas precursors for MoS₂ like Mo(CO)₆ are less volatile and poisonous. The disadvantage of HfS₂ is that the S vacancy is a shallow donor. This will require CVD of HfS₂ to be carried out in S-rich conditions to increase the S vacancy formation energy and decrease its concentration. This might result in the formation of S interstitial adatoms, as already seen by Aretouli et al [42]. Such adatoms may affect the quality of epitaxial growth. This would require careful control of S activity. Thus, HfS₂ is competing with InSe for use in TFETs. InSe has suitable band offsets, bipolar doping ability and suitably behaved intrinsic defects [43], but may be less convenient CVD.

In conclusion, HfS₂ and SnS₂ are indirect band gap semiconductors but otherwise very suitable for electronic devices because of their low effective masses and higher mobility than MoS₂. The high heat of formation makes it convenient for CVD. The main intrinsic defects in Hf/SnS₂ are the S vacancy, S interstitial and Hf/Sn interstitial. The S vacancy forms a gap state in SnS₂ and a shallow donor in HfS₂. The S interstitial is a low formation adatom. Substitutional dopants give reasonably shallow states. Therefore, both HfS₂ and SnS₂ can be considered as building blocks for TFETs.

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Table 1. Heats of formation [28,29].

	eV/mole
MoS ₂	-3.04
HfS ₂	-5.16
SnS ₂	-1.87
SnS	-1.36

Table 2 Calculated Band gaps of HfS₂ and SnS₂ compared to experimental values [13,38,12]. ML = monolayer, CNL = charge neutrality level.

Band gaps (eV)	HfS ₂		SnS ₂	
	ML	bulk	ML	Bulk
PBE	0.98		1.50	
HSE	2.05	1.68	2.40	2.30
SX	2.12	1.95	2.68	2.0
Exp		1.98		2.18
CNL (ML)	1.11		1.55	

Table 3 Effective masses for monolayer. e=electron, h=hole, x and y are along ΓK and ΓM respectively.

	HfS ₂	SnS ₂
m _{ex}	0.25	0.27
m _{ey}	1.85	0.72
m _{hx}	0.48	1.2
m _{hy}	0.49	2.8

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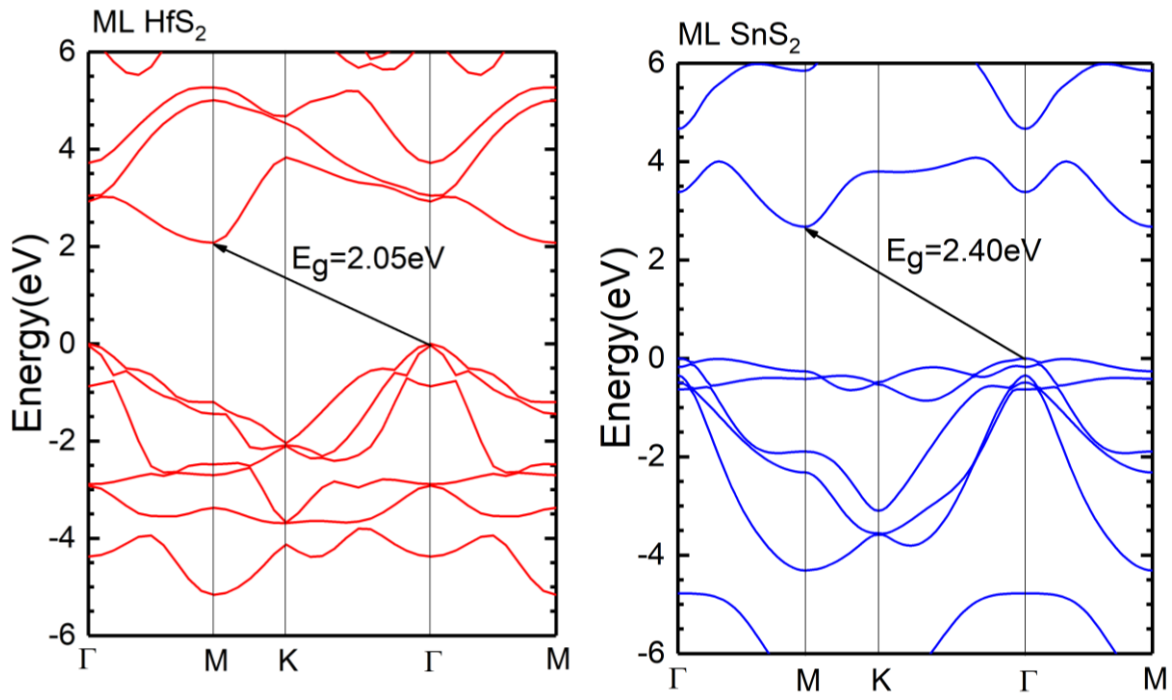


Fig. 1. Band structures for the monolayers.

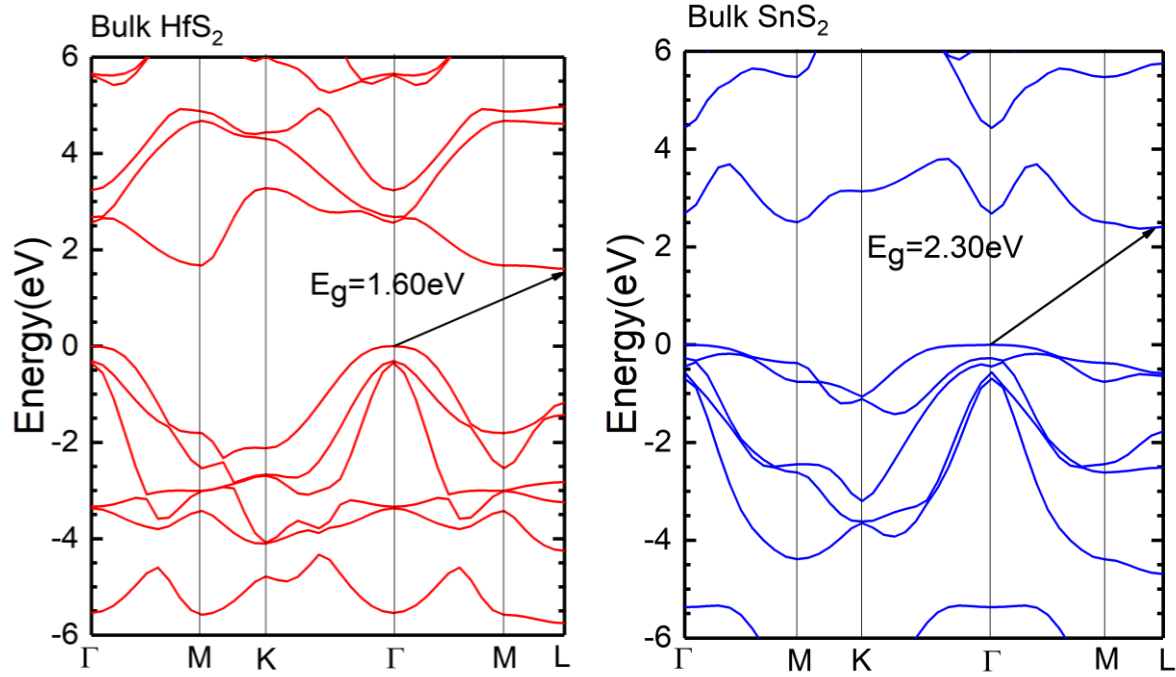


Fig. 2. Band structures for the Bulk.

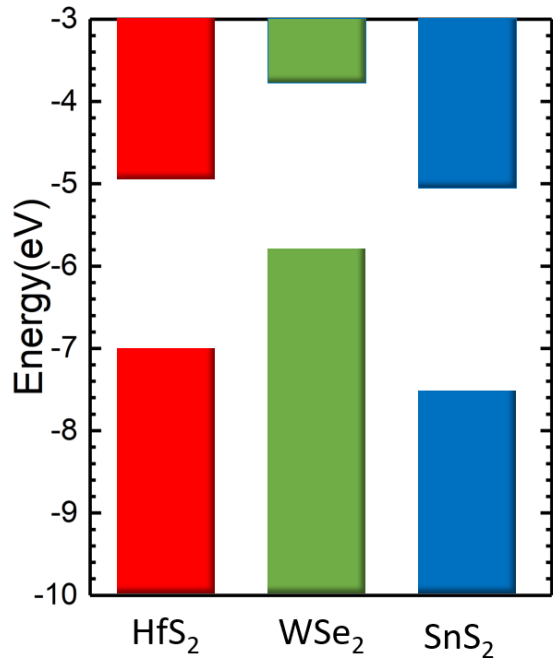


Fig. 3. Calculated band offsets for stacked monolayers of HfS₂, SnS₂ and WSe₂.

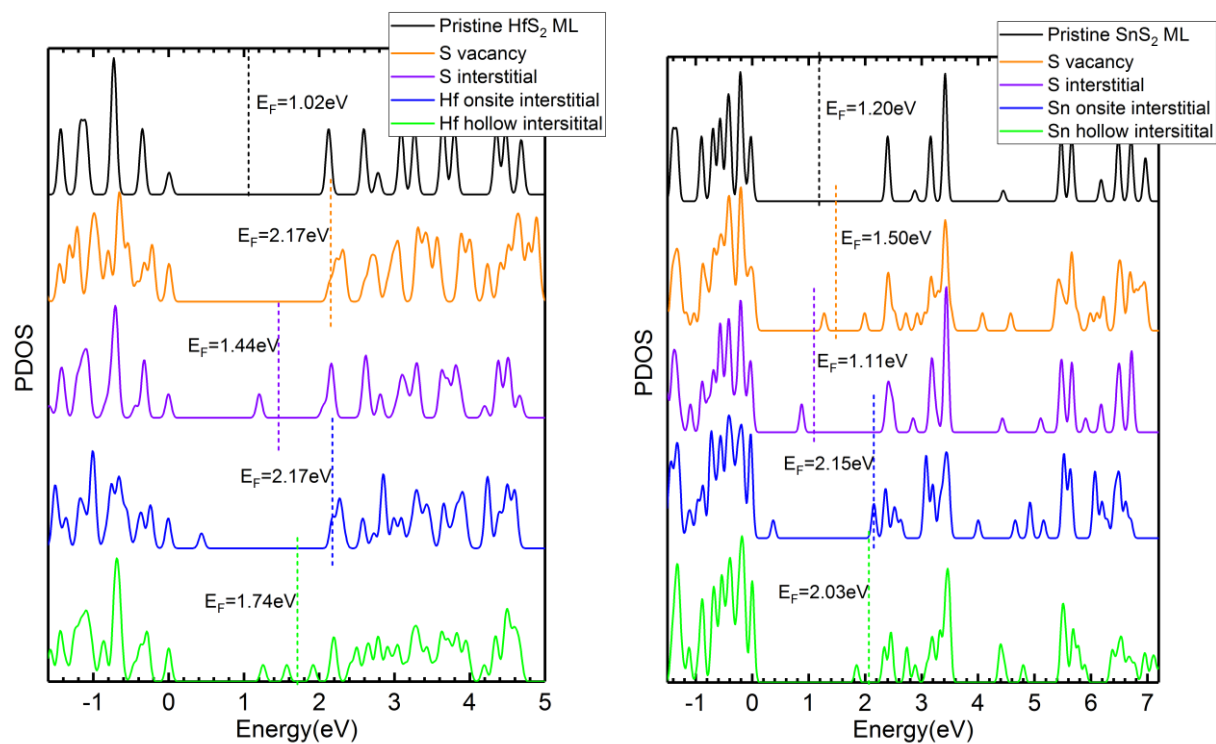


Fig. 4. Partial density of states for the defect-free monolayer, S vacancy, S interstitial, Hf onsite interstitial and hollow site interstitial, all in their neutral states, for HfS₂ and SnS₂.

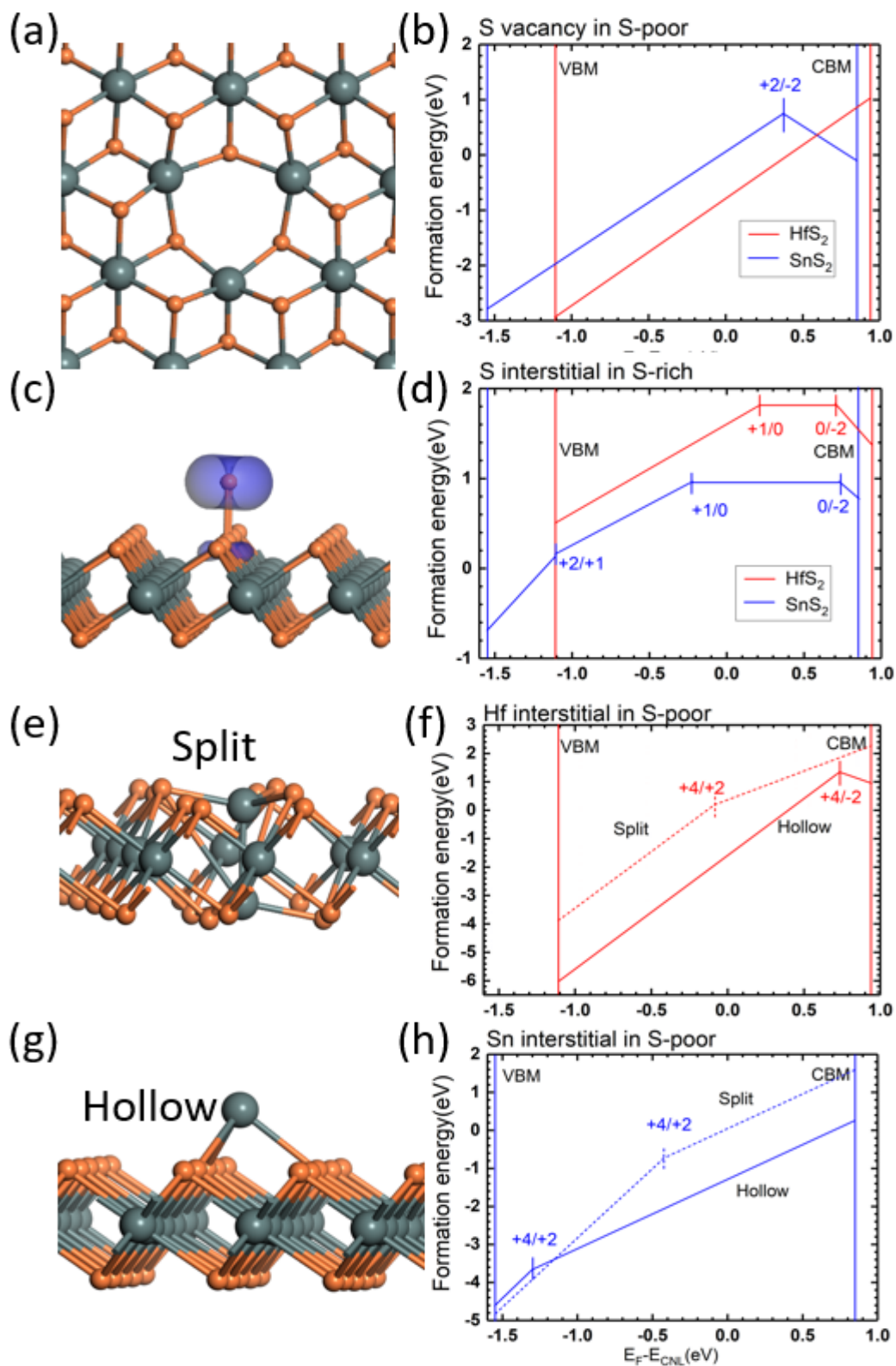


Fig. 5. Geometries and defect formation energies vs Fermi energies for S vacancy, S adatom interstitial, Hf split interstitial and Hf 'hollow interstitial' for HfS₂ and SnS₂. (f,g) compares the formation energies for each metal interstitial defect for HfS₂ or SnS₂ alone.

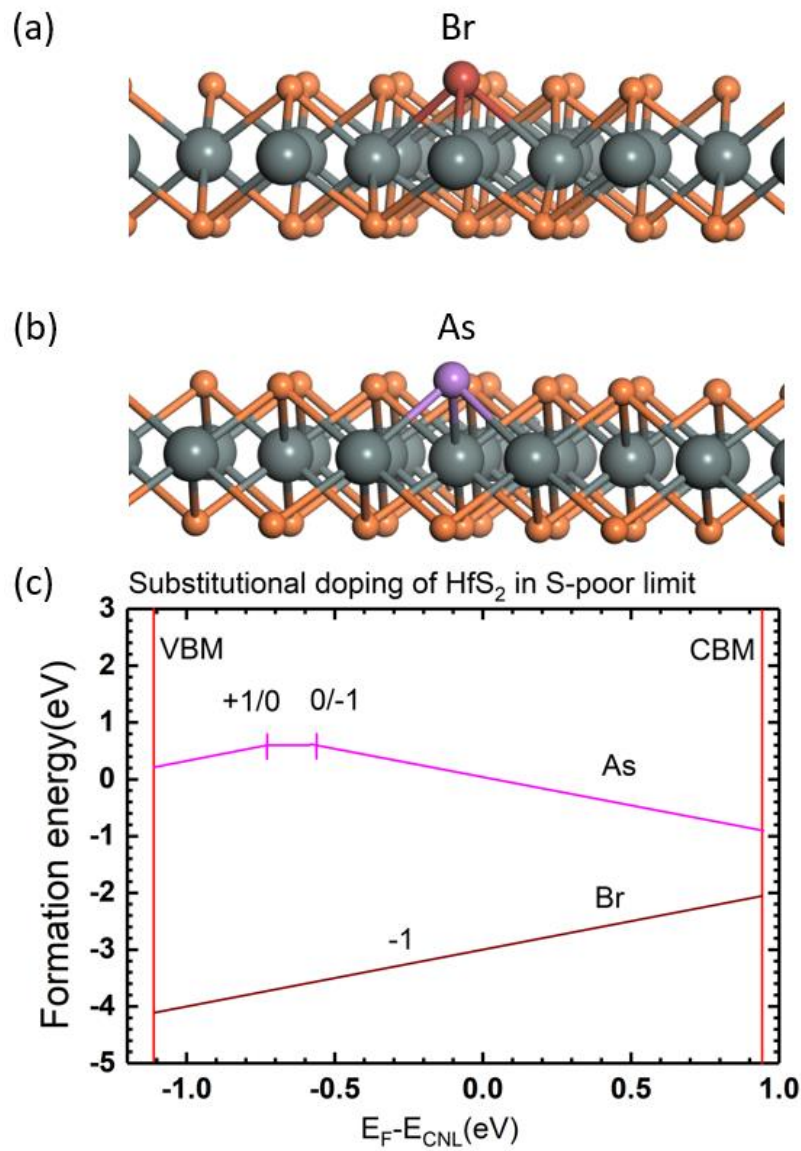


Fig. 6. (a,b) Geometries of substitutional Br and As dopants at the S site, and (c) formation energy vs. Fermi energy.