Strain engineering and hydrogen effect for two-dimensional ferroelectricity in monolayer group-IV monochalcogenides MX (M = Sn, Ge; X = Se, Te, S)

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Two-dimensional (2D) ferroelectric compounds are a special class of materials that meet the need for devices miniaturization, which can lead to a wide range of applications. Here, we investigate ferroelectric properties of monolayer group-IV monochalcogenides MX (M = Sn, Ge; X = Se, Te, S) via strain engineering, and their effects with contaminated hydrogen are also discussed. GeSe, GeTe, and GeS do not go through transition up to the compressive strain of -5%, and consequently have good ferroelectric parameters for device applications that can be further improved by applying strain. According to the calculated ferroelectric properties and the band gaps of these materials, we find that their band gap can be adjusted by strain for excellent photovoltaic applications. In addition, we have determined the most stable hydrogen occupancy location in the monolayer SnS and SnTe. It reveals that H prefers to absorb on SnS and SnTe monolayers as molecules rather than atomic H. As a result, hydrogen molecules have little effect on the polarization and electronic structure of monolayer SnTe and SnS.

Keywords: two-dimensional material, strain engineering, ferroelectric photovoltaic materials, hydrogen effect

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1. Introduction

At certain temperatures, ferroelectric materials could spontaneously exhibit electric polarization. Moreover, the application of an electric field can switch the direction of the polarization. Due to the potential applications of this phenomenon in solar cells, sensors, field-effect transistors, and non-volatile memories, it has attracted tremendous research attention in recent years.[1–3] To date, however, maintaining ferroelectricity in thin films at room temperature remains a significant challenge.[4] Some common three-dimensional (3D) ferroelectric materials, for example, $PbTiO_3$ and $BaTiO_3$ often lose their ferroelectricity and thus cannot meet the technological demand of the nanoscale devices.[5] Several attempts have been made at developing two-dimensional (2D) ferroelectric materials to overcome this issue.[6–9] In response to this, several 2D ferroelectric materials such as graphene and transition metal dichalcogenides,[10] van der Waals III_2–VI_3 materials,[7] group III–IV materials[3] such as In_2Se_3,[11–13] BiN monolayer,[14] and SnTe[15] have been proposed. 2D materials are considered advantageously due to the large strain engineering of their electronic, magnetic and ferroelectric properties such as in Ga_2S_2 nanoribbons and B_2H_2 layer.[16,17] However, the spontaneous polarization of some of these ferroelectric 2D materials are relatively low, hence are restricted in their application to certain devices.

Very recently, monolayer group-IV monochalcogenides MX (M = Ge, Sn; X = S, Se), monolayer SbN and monolayer BiP thin films were found to be good robustness ferroelectric materials with room temperature less than transition temperature.[6–8,18–20] The in-plane spontaneous polarization of these monolayers is relatively larger compared to other 2D ferroelectric materials. Moreover, these monolayers have excellent thermoelectric properties as well as massive piezoelectricity.[21–23] GeSe and SnSe monolayers, on the other hand, were discovered to be promising candidates for the sensing of NO_2 and NH_3, respectively.[24,25] The electronic properties of monolayer GeSe were affected by gas molecules impurity on point defects.[26] Especially, hydrogen is easy to be diffused or pumped to the 2D materials interfaces.[27,28] However, a thorough understanding of the interaction, particularly the stable configuration of gas molecules in the MX monolayer is still lacking.

In the current study, the first-principle calculations was used to investigate strain engineering ferroelectric properties of group-IV monolchalcogenides, and modulate the resulting ferroelectric properties and their band gap. We also explore the effect of Hydrogen impurities on SnS and SnTe monolayer and find out their most stable site, formation energy, and the influence on polarization. The current findings suggest a method for making 2D ferroelectric materials from otherwise designing nanoscale electronic devices and ferroelectric materials.

The following is the structure of the paper. Section 2 describes the computational details, method, and crystal structure, and Section 3 discusses the in-plane ferroelectric polarization in these monolayers MX. Section 4 discusses the strain

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engineering of the ferroelectricity, Section 5 discusses the hydrogen effect on monolayer SnS and SnTe, and Section 6 summarizes our findings.

2. Computational details, method, and the crystal structure

The Vienna *ab initio* simulation package (VASP) was used for the theoretical simulations based on the density functional theory (DFT).[29,30] The projector augmented wave (PAW) method is used to generate the pseudopotentials.[31,32] The revised Perdew–Burke–Ernzerhof functional (PBE)[33] was imposed in the generalized gradient approximation (GGA) exchange and correlation potential since it can describe reasonable structure and electronic properties of crystals. To ensure self-consistency calculations, cutoff energy of 500 eV for plane-wave basis and Γ-centered k-mesh grids $18\times18\times1$ were used. For total energies during the structural relaxations, the convergence criterion is set to 1 meV. A vacuum layer of 15 Å along the z-direction was allowed to avoid interaction between periodically repeated layers. For ferroelectric polarization calculations, the Berry phase method[34] is used. We used a (2×2) supercell with 16 atoms to simulate the effects of hydrogen, and the Brillouin zone is integrated using $8\times8\times1$ Γ-centered k-point mesh.

A typical structure of the monolayer MX (M = Sn, Ge; X = Se, Te, S) is seen in Fig. 1(a). As an example, we consider SnSe, which has a rectangular unit cell with $a = 4.59$ Å and $b = 4.38$ Å and four atoms per cell. Table S1 in the supporting information contains the lattice parameters for other materials. We use GeSe as an example and set the x-axis as in-plane axes, with the yz-axis parallel to the plane normal. In Fig. 1(a), the dashed orange rectangle represents its non-centrosymmetric unit cell, which contains four atoms and belongs to space group *Pmn*21 with only mirror symmetry. Since the two distinct chemical elements in MX monolayers have appreciable differences in electronegativity and high relative displacement, they are likely to exhibit high spontaneous polarization. To prove the above hypothesis, we require a mechanical strain that can cause in-plane polarization and easily initiate the ferroelectric transition.

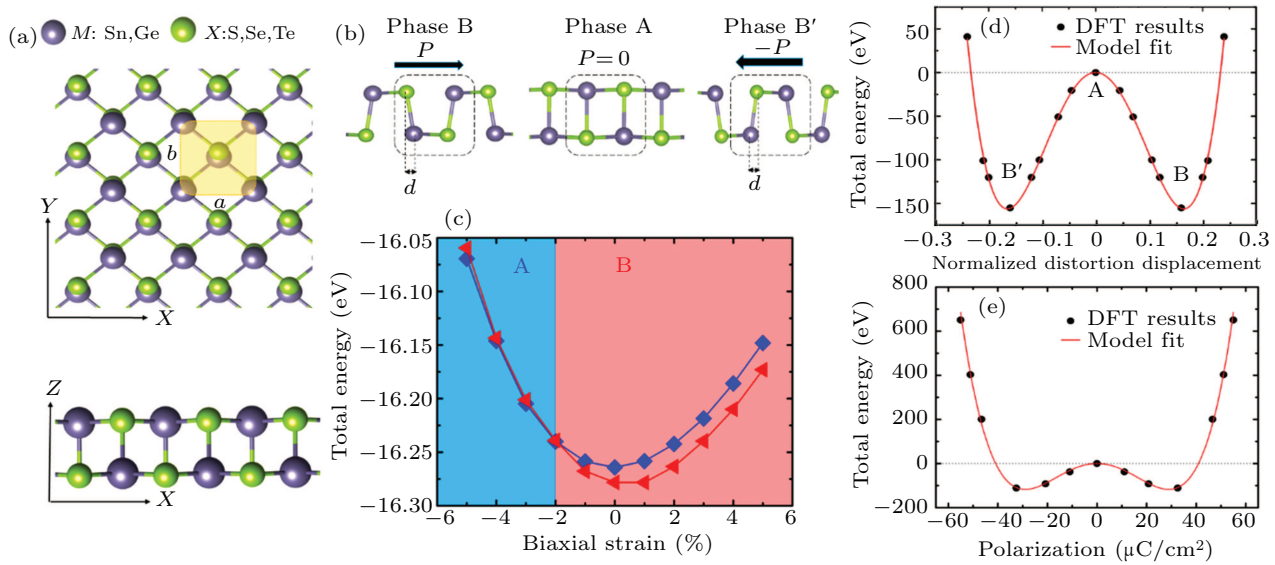

Fig. 1. (a) Top view and side view of monolayer MX structure. The unit cell was dashed by the shaded rectangular region, with a and b being the in-plane lattice constants. (b) Side view of centrosymmetric structure (paraelectric phase A) and two degenerate non-centrosymmetric structures (ferroelectric phase B and B′). (c) Total energy of A and B phases under the biaxial strain of monolayer SnTe, the region where the material represent in-plane polarization is highlighted in light-red. (d) Double-well potential as a function distortion displacement ($\boldsymbol{d}$) of monolayer GeSe. (e) Double-well potential as a function of spontaneous polarization of monolayer GeS.

Mechanical strain is a powerful tool for modifying the structure characteristics of 2D materials.[35] We also looked at the structural characteristic of monolayer MX under biaxial tensile strains up to 5%. We have investigated the strain effect on the total energy of monolayer MX in the distorted *Pmn*21 structure (phase B) and the centrosymmetric *Pnma* structure (phase A) by using a similar structure to bulk MX as shown in Figs. 1(c) and S1, supporting information. We can observe that phase B is stable, and it relaxes spontaneously to phase A. In SnTe, for compressive strains greater than −2%, the non-centrosymmetric B phase becomes more energetically favourable, denoting the transition from phase B into phase A. However, when the material is subjected to slight strain, the ferroelectric phase can still maintain good stability, which means that monolayer SnTe has good robustness. With the application of biaxial strain, similar trend is found in SnTe and SnS, as demonstrated in Fig. S1, supporting information.

3. In-plane ferroelectric polarization in monolayer MX

The vector $\boldsymbol{d}$, i.e., the off-center displacement of the Sn atom, was used to quantify the lattice deformation of the crys-

tals, as shown in Fig. 1(b). The centrosymmetric A phase has $\boldsymbol{d} = 0$ and four equal in-plane Sn–Se bonds, which prevents ferroelectricity formation, but the B phase has a nonzero value of displacement and the two covalent Sn–Se bonds are strengthened, causing the inversion symmetry to be broken. The A phase can revert to the energetically degenerated ground state B′ phase with opposite displacement upon reversal. As a result, the polarizations of the B and B′ phases should be opposing. The lattice parameters are limited to the initial ground state, and the centrosymmetric phase is used as a total energy reference. The pathway through *MX* monolayers centrosymmetric permits us to determine total polarization by using the Berry phase approach from first-principle DFT calculation[34] that includes electronic and ionic contributions. The double-well structure in the total energy as a function of polarization is a unique property of spontaneous polarization in a material. The variation in energy of strained monolayer SnSe with respect to normalized distortion displacement and polarization was also determined, and the results are plotted in Figs. 1(d) and 1(e). Figure S2, supporting information, clearly demonstrates double-well potential characteristics. This raises the possibility of ferroelectric polarization. Spontaneous polarization for GeSe, GeS, SnS, GeTe, SnTe and SnSe monolayer are 36.5, 50.0, 26.5, 33.56, 19.05 and 15.02 μC/cm^2, respectively, equivalence to effective polarization of 35.7, 48.4, 26, 32.8, 19.4 and 18.1 μC/cm^2 in line with recent work.[8,19] Due to a minimal electronic affinity difference between the type of atoms and, more significantly, the smallest displacement between Sn and Se atoms with respect to the paraelectric state, monolayer SnSe has the least spontaneous polarization.

4. Strain engineering of the ferroelectricity monolayer *MX*

External strain can have a significant impact on ferroelectricity.[36] We apply strains using $\epsilon = (a/a_0 - 1)$, where a and a_0 are the strained and unstrained lattice constants along the x- or y-direction to examine the strain modulations of ferroelectricity in monolayer *MX*. Both biaxial ($\epsilon_x = \epsilon_y$) and uniaxial (ϵ_x) tensile strains can increase the displacement of *M* atoms relative to the nearby *X* atoms, thereby increasing the polarization (P_s) values of monolayer *MX*, as illustrated in Fig. 2.

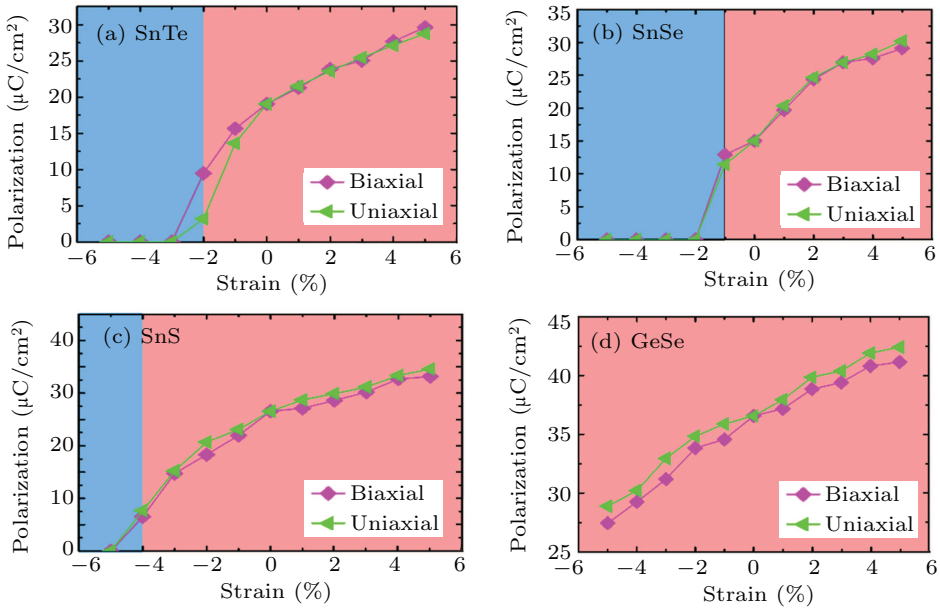

Fig. 2. The evolution of polarization under biaxial and uniaxial strain in (a) SnTe, (b) SnSe, (c) SnS (d) GeSe. The regions of paraelectric and ferroelectric are highlighted by light-blue and light-red, respectively.

As a result, strain engineering may be used to effectively improve the ferroelectricity of monolayer *MX*. Since the behavior of this ferroelectric transition is based on competition between metastable phases, it is worth looking into how polarization behaves near the transition. When tracing the evolution of P_s in these monolayers *MX* materials together with the in-plane strain, the amplitude of P_s discontinuously jumps at some critical points. The strain-tuned phase transition occurs in SnTe. This material is paraelectric at the phase transition point of −2% compressive strain. At the biaxial strain, the in-plane polarization jumps to the transition point value of 3.19% μC/cm^2 for SnTe (Fig. 2(a)). Different situations can be found in 2D SnS and SnSe as illustrated in Figs. 2(b) and 2(c). Biaxial strain (from −5% to 5%) can modulate polarization with a transition point of −1% compressive strain for 2D SnSe, while in 2D SnS transition point occurs up to the compressive strain of value −4%, the value of P_s drops to 6.52 μC/cm^2 and increases above the transition point with an increase of strain. In the case of 2D GeSe, GeTe and GeS under strain display the same order of magni-

tude of polarization with highly changed by a larger strain having $P_s = 36.5$ μC/cm^2, 33.56 μC/cm^2, and 50.0 μC/cm^2, respectively, without strain, they do not go through ferroelectrics to paraelectric transition up to the compressive strain of −5%. (Figs. 2(d) and S3, supporting information).

To gain a better understanding of the ferroelectric properties of *MX* materials, the density of states (DOS) of GeSe without strain, is illustrated in Fig. S4, supporting information. It reveals the semiconductor characteristics with a bandgap of about 1.13 eV, in the line with previous report,[37,38] and is greater than its bulk counterpart, i.e., about 0.68 eV.[39] Figure 3 illustrates the fluctuation in band gaps of monolayer *MX* materials as a function of biaxial strain. Traditional ferroelectric photovoltaic materials are widely recognized for having a significant bandgap and hence a relatively low energy conversion. Interestingly, the band gaps of GeSe, SnSe, GeTe, and SnTe in the current investigation are only slightly smaller than the ideal band gap, and they increase as biaxial strain is applied. The bandgap of GeSe with 3.0% strain, in particular, is 1.32 eV, which is the perfect value for photovoltaic applications. Since ferroelectric polarization and an appropriate band gap are two important features in photovoltaic systems, our strain engineering technique in group IV monochalcogenides also enables excellent 2D ferroelectric materials. We expect that our prediction will spur more research on different types of crystals to develop an efficient atomic-scale for ferroelectric photovoltaic devices.

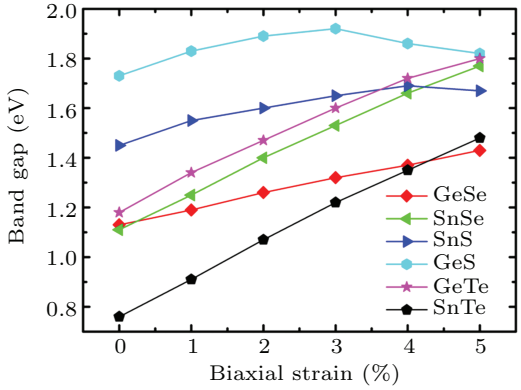

Fig. 3. Band gaps of monolayer *MX* under biaxial strain.

Properties of ferroelectric materials are highly influenced by inevitable defects, such as hydrogen impurity. In the next part, we focus on the theoretical studies of the impact of hydrogen absorption on ferroelectric polarization stability on monolayer *MX*.

5. Hydrogen effect on monolayer SnS and SnTe

We have investigated the effect of hydrogen impurity on the electronic structure of monolayer *MX* using the first-principles calculations. We firstly examine the possible positions of atomic and molecule H in the SnTe and SnS monolayers. Hydrogen molecule is placed with the H–H vertical or parallel to the surface at the beginning. After verifying several other configurations (Figs. S5 and S6, supporting information), the top and side views of the lowest-energy configurations for H_2 absorbed on monolayer SnTe and SnS are shown in Figs. 4(a) and 4(b). Meanwhile, the atomic H are originally placed at the top and right side between Sn–Te(S) bond as indicated in Figs. S7 and S8, supporting information.

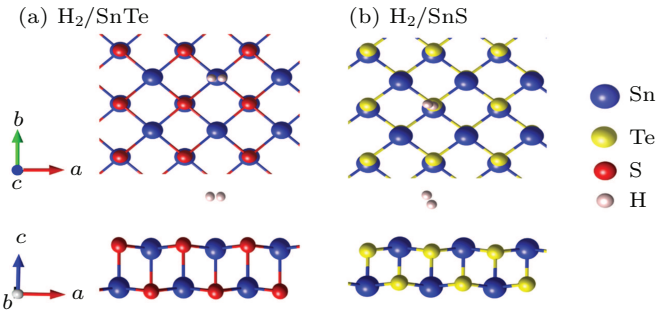

Fig. 4. Top and side views of the relaxed absorbed monolayer with the most favourable configuration for (a) SnTe and (b) SnS.

The formation energy, ΔH_F, calculated to determine the most stable configuration, is defined as $\Delta H_F = E_{2H+MX} - E_{MX} - \mu(H_2)$ where E_{2H+MX}, E_{MX} and $\mu(H_2)$ are the total energies of the two-hydrogen-atom or molecule H_2 adsorbed *MX*, the pristine *MX*, and half the hydrogen molecule, respectively. Interestingly, all the hydrogen atoms are relaxed to hydrogen molecules on these monolayers. The most stable absorption configurations of molecule H_2 absorbed on pristine monolayers are shown in Fig. 4. This is in clear contrast from hydrogen in Fe–Ge–Te systems, where atomic hydrogen can be inserted between the layers under gate voltage.[28] When the SnS and SnTe monolayers are integrated into devices, it is expected that atomic hydrogen could be stabilized by gate voltage as in those Fe–Ge–Te systems. It can be observed that the absorption of the hydrogen molecule introduces a slight distortion to the monolayer of SnTe and SnS, which depend on the binding strength between them. The most stable H molecule adsorption structure is a nearly parallel structure, with the hydrogen molecule pointing toward away or toward the monolayers surface. Based on the most suitable configuration provided above, the following findings for various adsorption systems are achieved.

The calculated formation energies, the equilibrium height, and spontaneous polarization of hydrogen in monolayer SnTe and SnS are listed in Table 1. The negative formation energy denotes that the absorption process is exothermic and energetically favored. The equilibrium height is defined as the nearest two atoms center-to-center distance between the hydrogen molecule and Te or S-layer. It is found that the equilibrium heights of the H molecule binding to the monolayer

SnS is 3.38 Å and SnTe is 3.61 Å, which are greater than the total length of the covalent radii of S and Se atom, respectively. The formation energies of SnS and SnTe are −0.008 eV and −0.01 eV, respectively. Molecule H_2 are physisorbed on SnS and SnTe surfaces, based on the relatively low formation energy and high separation height. Based on the negative and appropriate formation energy values, hydrogen molecule should be a little sensitive to monolayer SnTe and SnS. Insight into the H molecule–monolayer interaction is obtained from spontaneous polarization. The polarization for the pure SnS and SnTe monolayers are found to be 26.57 μC/cm^2 and 19.05 μC/cm^2, respectively. With the absorption of molecule H_2, the SnTe and SnS monolayers has no significant changes on the polarization.

Table 1. Calculated formation energies (ΔH_F), equilibrium heights (h), and spontaneous polarization.

Systems	ΔH_F (eV)	h (Å)	P_s (μC/cm^2) with H_2
SnS	– 0.008	3.38	19.03
SnTe	– 0.01	3.61	26.45

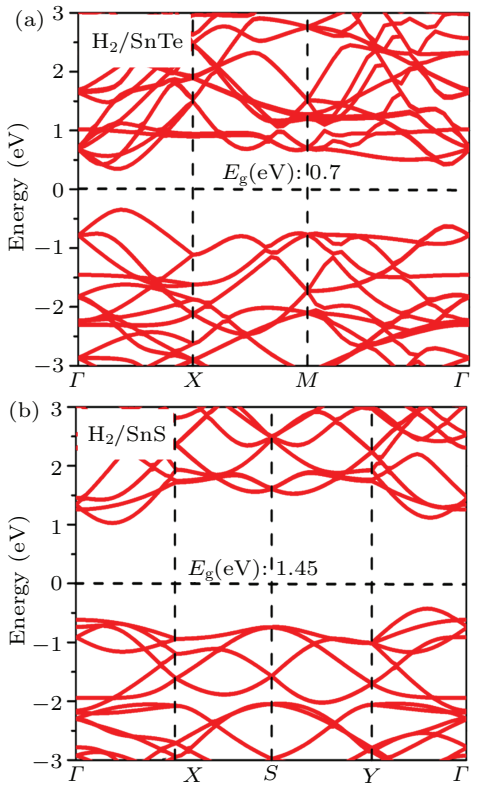

Fig. 5. Band structure of H_2 absorbed on monolayer (a) SnTe and (b) SnS. The E_g represents the band gap.

The band structures of H_2-adsorbed monolayer systems are determined to evaluate the impact of H molecule adsorption on the electronic characteristics of monolayer SnS and SnTe as shown in Figs. 5(a) and 5(b). When H_2 are absorbed in the monolayer SnTe and SnS, the band gap of the absorbed system remains the same, i.e., the both valence and conduction bands of the monolayers remain unaltered comparing with the pristine monolayer SnS. In addition, after H molecules are adsorbed, no impurities states are observed in monolayer SnTe and SnS. As the energy level of 1s in H_2 is about 6 eV below the valence band maximum from our analysis, no impurities states are introduced in the band gap of monolayer SnTe and SnS.

6. Conclusion

In conclusion, based on the first-principles DFT calculation, we proposed a strain engineering approach for generating 2D ferroelectricity in monolayer group-IV monochalcogenides MX (M = Sn, Ge; X = Se, Te, S). The atomic structure and physical characteristics of the materials were investigated. We show that the presence of in-plane ferroelectric polarization in MX monolayers distinguishes them from ferroelectric thin films with out-of-plane polarization, such as perovskite compounds. Moreover, the ferroelectric polarization can increase with an increase of applied tensile strain while compressive strain decreases in all monolayer MX. Our findings also show that the strained GeSe, SnSe, GeTe, and SnTe are promising ferroelectric photovoltaic materials due to their significant ferroelectric polarization and appropriate bandgap.

Furthermore, we study the effect of hydrogen adsorption on monolayer SnS and SnTe. It reveals that hydrogen prefers to physisorbed on SnS and SnTe surfaces as molecules, based on the low formation energy and separation height. It introduces no impurity defects in the band gap of the monolayers, and has little impact to their polarization.

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