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Asymmetric Band Alignments and Remark Defect Tolerability at The

Interface of High-k Dielectric Sb₂O₃ and 2D Semiconductor MoS₂

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Abstract:

Inorganic molecule crystal Sb_2O_3 has been identified as a promising high-k dielectric for direct integration with the two-dimensional (2D) semiconductor MoS₂. However, a comprehensive understanding of their interface remains elusive, impeding its applications in high-performance 2D electronics. In this study, we elucidate the interfacial interaction, and electronic and defect properties of the Sb₂O₃/monolayer MoS₂ interface using in-depth first-principles calculations. We find that a highperformance quasi-van der Waals interface can be formed between Sb2O3 and monolayer MoS₂, as evidenced by weak interfacial interaction, a dangling-bond-free interface, insignificant electron-hole puddle redistribution, and the preserved semiconducting properties of monolayer MoS₂. Notably, the interface exhibits a remarkable defect tolerance capability during integration, as Sb₂O₃ cluster vacancies (the dominant defect in Sb₂O₃) neither introduce mid-gap states nor significantly affect the interface properties. Besides, our study reveals a strongly asymmetric type-I band alignment at the interface, where the conduction and valence band offsets are predicted to be 1.07 and 0.25 eV at the PBE level, respectively. Our work offers a comprehensive understanding of the quasi-vdW interface between Sb₂O₃ and monolayer MoS₂, which could be useful for the development of inorganic molecular crystals as high-k dielectrics for high-performance 2D electronic devices.

Keywords: two-dimensional semiconductor; high-*k* dielectrics; inorganic molecular crystals; interfacial properties

1. Introduction

Atomically thin two-dimensional (2D) semiconductors have garnered significant interest as channel materials for next-generation nanoelectronics, which offer the potential to mitigate short channel effects and maintain device performance during the scaling-down process ^{1, 2}. Among various 2D materials, molybdenum disulfide (MoS₂) has emerged as a promising candidate for future electronic and optoelectronic applications, owing to its high stability, large-scale growth potential, and appealing electronic properties ³⁻¹³. High-performance 2D electronic devices based on MoS₂ have already been demonstrated, showcasing the advantages of using monolayer MoS₂ as ultra-thin channel layer in field-effect transistors (FETs) ¹⁴⁻¹⁷.

The performance of a 2D MoS₂ electronic device can be further enhanced by employing insulators with large dielectric constant (high-*k*) as gate-dielectrics. Conventional oxides such as HfO₂ and Al₂O₃ have been proposed as high-*k* dielectrics for 2D semiconductors ¹⁸⁻²³. However, achieving high-performance integration of these high-*k* oxides on 2D semiconductors has proven challenging due to dangling-bond-free 2D semiconductor surface, which not only could not provide enough nucleation sites for the direct growth of the high-*k* oxides, but also lead to a high density of interface states ^{24, 25}. To address these challenges, 2D insulators such as *h*-BN have been employed as high-*k* dielectrics. High-performance interface has been achieved due to dangling-bond-free surfaces of both 2D insulators and semiconductors. Consequently, quasi-vdW interface between monolayer MoS₂ and high-*k* oxide SrTiO₃ has been realized by transferring a dangling-bond-free SrTiO₃ (001) ultra-thin film onto MoS₂ ²⁶⁻²⁸. Although these interfaces demonstrate improved device performance, their practical applications in electronic devices might be impeded by their strong dependence on the transfer process.

Recently, inorganic molecule crystals (IMCs) have emerged as novel high-*k* dielectrics for 2D semiconductors. IMCs consist of self-passivated molecule clusters connected *via* weak vdW interaction ²⁹⁻³¹. This unique structural feature of IMCs offers dangle-bond-free surfaces, and more importantly, it enables the deposition of high-quality IMC films on 2D semiconductor MoS₂ surface directly at a temperature below

500 K. Among various IMCs, Sb₂O₃ has been identified as a promising high-*k* dielectrics for monolayer MoS₂. This is due to its high dielectric constant (~11.3) and relatively large band gap (~3.9 eV)²⁹. It is noted that IMC Sb₂O₃ has been deposited on MoS₂ layers and the resulting devices show promising photodetection performance.³² More recently, IMC Sb₂O₃ has also been used as a buffer for direct growth of HfO₂ on monolayer MoS₂, and the resulting devices show much-improved performance³³. Despite these notable advances, the understanding of electronic properties at the interface between Sb₂O₃ and MoS₂ has not yet been conclusively determined, and the impact of intrinsic defects in Sb₂O₃ on the interface properties remains unclear. In this study, we perform in-depth first-principles calculations to investigate the interface between IMC Sb₂O₃ and monolayer MoS₂, providing a comprehensive understanding of this emerging quasi-vdW interface.

2. Method

All first-principles calculations were performed using the density-functional theory (DFT) based Vienna Ab initio Simulation Package (VASP.5.4.4.18) ³⁴⁻³⁶. The Perdew-Burke-Ernzerhof (PBE) functional in generalized gradient approximation (GGA) and the projector augmented wave (PAW) pseudopotentials were employed to describe the exchange-correlation effect and the interaction between electrons and ions, respectively ³⁷⁻³⁹. A cutoff energy of 500 eV was adopted for the plane wave expansion. $18 \times 18 \times 1$, $9 \times 9 \times 9$, $1 \times 1 \times 1$, and $2 \times 2 \times 1 \Gamma$ -centered *k*-point meshes were employed to sample the first Brillouin zones of monolayer MoS₂ and Sb₂O₃, respectively. A vacuum layer of 15 Å thickness was inserted along the out-of-plane of all the slab structures to minimize the interaction between the periodical slabs. The DFT-D3 method was adopted for the treatment of vdW interaction ⁴⁰, and dipole correction has been applied. To investigate defect properties of Sb₂O₃, cluster vacancies in the Sb₂O₃ supercell. The convergence

threshold for total energies and the Hellmann–Feynman forces on each atom were set to 1.0×10^{-6} eV and 0.01 eV/Å, respectively. With these settings, the calculated lattice constants of bulk Sb₂O₃ and monolayer MoS₂ are a=b=c=11.06 Å and a=b=3.18 Å, and the corresponding PBE band gaps are 2.97 eV and 1.67 eV, respectively, which agrees with previous studies ^{6, 18, 41-43}. In addition, we calculated the dielectric constant of bulk Sb₂O₃, which is 9.04, consistent with the experimental results ²⁹.

The adsorption energy (E_{ad}) is calculated by using below equation:

$$E_{\rm ad} = E_{\rm MoS_2 + Sb_2O_3} - (E_{\rm MoS_2} + E_{\rm Sb_2O_3}), \tag{1}$$

where $E_{MoS_2+Sb_2O_3}$, E_{MoS_2} and $E_{Sb_2O_3}$ are the total energies of the corresponding MoS₂/Sb₂O₃ hybrid structure, isolated MoS₂ monolayer and isolated Sb₂O₃ (111) surface, respectively. Similarly, the charge redistribution $\Delta \rho$ for monolayer MoS₂ on the Sb₂O₃ (111) surface is defined as:

$$\Delta \rho = \rho_{\rm MoS_2 + Sb_2O_3} - \rho_{\rm MoS_2} - \rho_{\rm Sb_2O_3}, \tag{2}$$

where $\rho_{MoS_2+Sb_2O_3}$ is the charge density of the MoS₂/Sb₂O₃ interface structure, and ρ_{MoS_2} and $\rho_{Sb_2O_3}$ are the charge density of the isolated monolayer MoS₂ and the Sb₂O₃ (111) surface, respectively. The defect formation energy $E_f(D)$ for a defect D is evaluated as follows:

$$E_f(D) = E_{tot}(D) - E_{tot}(Bulk) + E_{fr},$$
(3)

where $E_{tot}(Bulk)$ and $E_{tot}(D)$ are the total energies of the supercell without and with the defects, E_{fr} stands for the energy of Sb atom, Sb₂O₃ cluster, and half the energy of an O₂ molecular, respectively, corresponding to the three types of vacancies (O vacancy, Sb vacancy and Sb₂O₃ cluster vacancy) in Sb₂O₃.

3. Results and discussion

Antimony oxide (Sb₂O₃) is an inorganic molecular crystal consisting of Sb₂O₃ molecule clusters (Sb-O bond length of 2.01 Å) with 4 Sb and 6 O atoms in the form of a bicyclic cage, in which all the molecule clusters are bonded together by the weak vdW force. This unique structure endows Sb₂O₃ a dangling-bond-free surface, which is highly desired for the application of gate dielectrics for 2D semiconductors because it

can minimize interface state density. Furthermore, our first-principles calculations predict that the dielectric constant of Sb₂O₃ is 9.04 and its band gap is 3.93 eV (HSE), confirming its promising dielectric performance. To model the interface between Sb₂O₃ and monolayer MoS₂, we find that (2×2) Sb₂O₃ (111) supercell matches well with (5 \times 5) MoS₂ monolayer in both lattice constant and surface symmetry. A compressive lattice strain of 1.69% was applied to the Sb₂O₃ (111). This small strain does not bring a significant change in the electronic structure of Sb₂O₃ (111), as shown in Figure S1. The thickness of Sb₂O₃ (111) used in this study is three Sb₂O₃ cluster layers, which is sufficiently thick as its electronic structure in the central region recovers that of Sb₂O₃ bulk (see Figure S2). Various interface configurations have been constructed by sliding the MoS₂ on the Sb₂O₃ (111) surface, in which the energy difference among these configurations is within 33 meV (see Fig. 1(a)), inferring a weak interfacial interaction. The side and top views of the most stable interface configuration are shown in Figs. 1(b) and (c), respectively, where the structure is stabilized through maximizing the interfacial bonding tendency ^{19, 44-46}.

After the structural relaxation, the interface spacing between monolayer MoS₂ and Sb₂O₃ (111) is calculated to be 2.77 Å, which is larger than the sum of the covalent radii of S and O atoms at the interface. This suggests no covalent bonds formed at the interface, supporting the weak interfacial interaction. Adsorption energy is another important parameter to measure the interfacial interaction strength. The calculated adsorption energy E_{ad} of the MoS₂/Sb₂O₃ is -22.81 meV/Å² (see Fig. 1(d)), which is comparable to that of typical vdW interface such as bi-layer MoS₂, but is lower than those of other MoS₂/high-*k* dielectric interface is dominated by weak vdW interaction. Moreover, we also calculated the in-plane averaged electrostatic potential of MoS₂/Sb₂O₃, as shown in Figure S3. The vacuum level near the interfacial region is flat, implying the weak interaction between Sb₂O₃ and monolayer MoS₂.

To further understand the interfacial interaction, we have calculated charge density redistribution at the interface of MoS₂/Sb₂O₃. As shown in Fig. 1(b), it is apparent that the charge depletion and accumulation are mainly localized at the interface region. The

accumulated charge density is more pronounced near MoS₂, while the depleted charge density is closer to the Sb₂O₃ surface. To further clarify the charge density redistribution, we have plotted the planar-averaged charge density difference $\Delta\rho$ along the z-direction for the interface structure, as shown in Figure S4. The positive/negative values of $\Delta\rho$ correspond to the charge density accumulation/depletion, indicating a weak charge redistribution when forming the interface. This is confirmed by Bader charge analysis, which suggests insignificant charge transfer (only 0.2 electrons per interface supercell). All these calculations suggest a weak interface interaction between monolayer MoS₂ and high-*k* dielectric Sb₂O₃.



Figure 1. (a) The relative stability among various interface configurations for the MoS_2/Sb_2O_3 . (b) The visualized charge density difference of MoS_2/Sb_2O_3 with an isosurface value of 5×10^{-4} e/Å³, where the red and blue colors represent the charge accumulation and depletion, respectively. (c) The 2D contour plot of the charge density difference projected on the Mo plane. (d) The calculated adsorption energy of MoS_2/Sb_2O_3 and MoS_2/Sb_2O_3 with a Sb₂O₃ cluster vacancy.

Next, we investigate the impact of the interface interaction on the electronic

properties of monolayer MoS₂/Sb₂O₃(111). Figure 2(a) presents the calculated total density of states (TDOS) and projected density of states (PDOS) of the interface. Notably, the integration of high-*k* dielectric Sb₂O₃ does not change the intrinsic electronic properties of monolayer MoS₂ due to weak interface interaction. After interfacing with Sb₂O₃, monolayer MoS₂ preserves its semiconducting nature, and its band gap value is comparable to that of pristine monolayer MoS₂. The valence band edge is dominated by hybridized Mo *d*-orbital and S *p*-orbital contributions, while Sb₂O₃ contributions are situated 0.25 eV below the Fermi level. For the conduction band edge, it primarily originates from the Mo *d*-orbital, with Sb₂O₃ contributions commencing at 2.80 eV and above. These observations are consistent with the projected band structure depicted in Figure S5.

Effective mass is another crucial property for semiconductor device applications, as lower effective mass typically corresponds to higher carrier mobility. We examine the influence of integrated high-k dielectric Sb₂O₃ on the effective masses of monolayer MoS₂. Figure 2(c) shows the calculated effective masses of electron (m_{e}^{*}) and hole (m_{h}^{*}) for the pristine monolayer MoS₂ and the monolayer MoS₂/Sb₂O₃ (111) interface. The m_e^* and m_h^* of the pristine monolayer MoS₂ are estimated to be 0.46 m₀ and 0.55 m₀, respectively, which are consistent with previous calculations ^{49, 50}. With the presence of Sb₂O₃ (111), the m_h^* of monolayer MoS₂ increases slightly to 0.72 m₀, while the m_e^* remains nearly unchanged. This marginal increase in the effective masses of monolayer MoS_2 upon Sb_2O_3 integration aligns well with the 2D contour plot of charge density difference projected on the Mo plane, as illustrated in Figure 1(c). The presence of Sb₂O₃ results in negligible spatial variations in charge density redistribution on monolayer MoS₂, thereby suppressing the impact of electron-hole puddles on device performance. Overall, the calculated DOS, band structure, effective mass, and electronhole puddles demonstrate that employing Sb₂O₃ as the gate dielectric does not bring noticeable harmful effects to the electronic properties of monolayer MoS₂.

In high-performance semiconductor devices, the band offset between the gate dielectric and the semiconductor is of critical importance. Both valence band offset (VBO) and conduction band offset (CBO) should exceed 1 eV to minimize the static

tunneling current ^{19, 51, 52}. A viable method for estimating band offset involves calculating PDOSs of the interface structure, which yields band offsets based on the relative shift of the band edges between the semiconductor and the gate dielectric. This approach considers the effect of interface interaction on band offsets and is applicable to hybrid structures with weak interfacial interactions, such as the MoS₂/Sb₂O₃ interface. As depicted in Fig. 3(a), a type-I band offset forms at the interface between monolayer MoS₂ and Sb₂O₃ (111). The VBO and CBO are strongly asymmetric, with values of 0.25 eV and 1.07 eV at the PBE level, respectively. The CBO is large enough for minimizing the electron tunning. However, the VBO is much smaller than 1 eV, thus insufficient for practical applications. In a previous study ²⁹, a symmetric band offset with a large VBO (~1.02 eV) was predicted for the MoS₂/Sb₂O₃ interface, which however was not calculated in a self-consistent way.



Figure 2. (a) The total DOS and the projected DOS of MoS_2/Sb_2O_3 . (b) LDOS of monolayer MoS_2 on Sb_2O_3 (111) and the pristine monolayer MoS_2 . (c) The effective electron and hole masses (in unit of electron mass m_0) for monolayer MoS_2 and monolayer MoS_2 on Sb_2O_3 (111).

To verify the effectiveness of our predicted band offsets between MoS2 and Sb2O3

(111) with weak interface interaction, we utilized Anderson's rule to estimate the band offsets, in which the band edges of monolayer MoS₂ and Sb₂O₃ (111) with the vacuum level and the interaction between them is ignored. As shown in Fig. 3(b), the Anderson's rule also leads to asymmetric band offsets, in which the VBO and CBO are estimated to be 0.07 and 1.19 eV, respectively, very close to those determined by the interface model. It is noted that all these calculations are based on PBE functionals, which lead to underestimated band gaps and might cause a wrong prediction on the band offset. Therefore, we have employed HSE calculations to verify the band offsets between monolayer MoS₂ and Sb₂O₃ (111) using Anderson's rule. As Figure S6 shows, the HSE calculations produce larger band gaps of monolayer MoS₂ (2.14 eV) and Sb₂O₃ (111) (3.93 eV). Importantly, the HSE calculations also predict asymmetric type-I band offsets between MoS₂ and Sb₂O₃, in which VBO and CBO are estimated to 0.23 eV and 1.57 eV, respectively, consistent with the band offsets predicted by the PBE calculations.



Figure 3. (a) The projected DOSs of monolayer MoS_2 and central Sb_2O_3 layers in the MoS_2/Sb_2O_3 interface model, where the Fermi level is shifted to 0 eV. (b) Band offsets between monolayer MoS_2 and Sb_2O_3 (111) calculated by the Anderson's rule using vacuum level as the reference, in which vacuum level is set to 0 eV. (c) Band offset diagram of the MoS_2/Sb_2O_3 interface with an 8 Å interface spacing.

To further elucidate the interface interaction effect on the band offset, we employed the interface model, but the interface spacing between MoS₂ and Sb₂O₃ was increased to 8 Å to reduce the interface interaction. The predicted band offsets are shown in Fig. 3(c), with 0.1 and 1.11 eV for the VBO and CBO, respectively. All these results suggest strongly asymmetric band offsets between MoS₂ and Sb₂O₃ and the interface interaction only leads to slight variation of the band offsets.

During the deposition of high-k dielectric film on 2D semiconductors, defects often form within the high-k dielectric layer, leading to degraded device performance. In the case of Sb₂O₃, vacancies of Sb₂O₃ clusters are found to be the most dominant intrinsic defects, as suggested by the calculated lowest defect formation energy in Fig. 4(a). The formation energy of Sb₂O₃ cluster vacancies is significantly lower than those of other defects, such as oxygen and antimony vacancies. This can be understood by the weak interactions among the Sb2O3 cluster, while within the Sb2O3 cluster, the Sb-O forms strong ionic bonds. Despite their dominance, Sb₂O₃ cluster vacancies do not bring detrimental effects to the electronic properties of the MoS₂/Sb₂O₃ (111) interface. Figure 1(d) displays the calculated interface adsorption energy in the presence of the defect, indicating that the weak interface interaction remains unaffected. Furthermore, Figures. 4(b) and (c) show visualized charge density redistribution for the interface structure containing Sb₂O₃ cluster vacancies, which demonstrate minimal charge redistribution and negligible electron-hole puddles at the Mo basal plane. Importantly, the total density of states (DOS) comparison in Fig. 4(d) confirms that the electronic properties are not adversely affected by the presence of the Sb₂O₃ cluster vacancy at the interface. The Sb₂O₃ vacancies do not introduce the undesired mid-gap states, and the resulting electronic structures are nearly the same as the ones without the defects. These findings underscore the exceptional defect tolerance exhibited by the MoS₂/Sb₂O₃ interface with respect to the dominant defect in Sb₂O₃, an attribute that is highly desirable for electronic device applications.



Figure 4. (a) The formation energy of intrinsic defects (O vacancies, Sb vacancies and Sb₂O₃ vacancies) in a $2 \times 2 \times 2$ Sb₂O₃ supercell. (b) The side view of interface structure for MoS₂/Sb₂O₃-v with visualized charge density redistribution using an iso-surface value of 5×10^{-4} e/Å², where the red and blue colors denote the accumulated and depleted charge density, respectively. (c) The charge puddles distribution on the Mo plane. The green dashed circles in (b) and (c) indicate a Sb₂O₃ vacancy at monolayer MoS₂/Sb₂O₃ (111) interface. (d) The DOS of the MoS₂/Sb₂O₃ (111) interface with/without the interfacial Sb₂O₃ cluster vacancy.

4. Conclusions

In conclusion, with in-depth DFT calculations, we have revealed the interfacial properties between high-*k* dielectric Sb₂O₃ and 2D semiconductor monolayer MoS₂. We demonstrate that the IMC Sb₂O₃ can form a high-performance interface with monolayer MoS₂, owing to the absence of interface states, weak interface interaction, and the preserved electronic properties for the 2D semiconductor. Significantly, the MoS₂/Sb₂O₃ (111) interface exhibits exceptional defect tolerance capability, in which the dominant defect in Sb₂O₃ does not lead to noticeable degradation on the interface

properties. We also reveal strongly asymmetric interface band alignment, in which VBO at the MoS₂/Sb₂O₃ (111) interface is insufficient to minimize hole tunneling. This insight could be useful in understanding the experimentally observed sizeable gate leakage currents in MoS₂/Sb₂O₃-based electronic devices ⁵³. Our study suggests that IMCs hold great promise as high-performance high-*k* dielectrics for 2D semiconductors. Further research is highly desired to explore alternative IMCs with larger band gap and higher dielectric constant, which would enable a much-improved interface performance for 2D-semiconductors-based nanoelectronics.

Supporting Information: s1-s4 (DOS of Sb₂O₃ w/o strain; PDOS of Sb₂O₃ bulk and (111) surface; Averaged electrostatic potential of MoS₂/Sb₂O₃; Planar-averaged charge density difference and project band structure of MoS₂/Sb₂O₃; HSE calculations on the band offsets)

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Conflict of Interest

The authors declare no conflict of interest.

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