

High-throughput computational design of inorganic molecular crystal-based high- κ dielectrics for two-dimensional electronics

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Abstract

Inorganic molecular crystals (IMCs) hold great promise as high- κ dielectrics for two-dimensional (2D) electronics due to their dangling-bond-free surfaces and the capability of direct integration on 2D semiconductors. However, only a limited number of IMCs have been identified so far, and interface properties between IMC-based high- κ dielectrics and 2D semiconductors remain largely unexplored. Here, we present an efficient high-throughput screening of IMC-based high- κ dielectrics from a large materials database, of which 6 IMCs ($\text{Sb}_2\text{S}_2\text{O}_9$, two Bi_2O_3 phases, $\text{As}_2\text{S}_2\text{O}_9$, Sb_2O_3 , and $\text{Te}_2\text{H}_2\text{O}_3\text{F}_4$) have been predicted to be the most promising gate dielectrics for 2D semiconductors due to their optimal trade-off between dielectric constant and band gap, as well as facile evaporation possibility. For predominant 2D semiconducting channel materials such as molybdenum disulphide (MoS_2) and black phosphorene (BP), the respective promising IMC-based high- κ dielectrics have been pinpointed. We further showcase two high-performance 2D semiconductor/IMC interfaces ($\text{BP}/\text{Sb}_2\text{S}_2\text{O}_9$ and $\text{MoS}_2/\text{Bi}_2\text{O}_3$), as evidenced by the large band offsets, high defect tolerance, and low leakage current. The downscaling capability of the IMCs to the sub-1nm equivalent oxide thickness (EOT) regime is also unravelled for both DRAM and CPU applications. Our results accelerate the exploration of IMC-based high- κ dielectrics and could promote the development of high-performance 2D electronics.

Introduction

Two-dimensional (2D) semiconductors show great potential as channel materials for high-performance nanoelectronics in the post-Moore era. This is mainly because their dangling-bond-free surfaces preserve the intrinsic carrier mobility even down to the monolayer limit, and their ultra-thin thicknesses not only minimize the short-channel effects but also enhance the gate controllability.¹⁻⁵ Diverse intriguing properties have been observed in 2D semiconductors. For instance, monolayer molybdenum disulphide (MoS₂) has tunable electronic and optical properties, high stability and large-scale growth capability.⁶⁻⁸ Black phosphorene (BP) exhibits high carrier mobilities and ambipolar behaviours.^{9,10} Indium selenide (InSe) demonstrates exceptional mechanical properties.¹¹⁻¹³ These attributes make them appealing for various electronic and optoelectronic applications.^{8,14-16}

Integration of high- κ dielectrics can further enhance the device performance of the emerging 2D electronics.¹⁷⁻¹⁹ On the one hand, high- κ dielectrics can improve the gate controllability on the channel, reduce short-channel effects, and enable continuous transistor downscaling. On the other hand, they can effectively suppress Coulomb scattering and reduce power consumption. However, it remains challenging to achieve high-performance interfaces between high- κ dielectrics and 2D semiconductors.²⁰⁻²² This is primarily attributed to the following two factors: (1) The dangling-bond-free surfaces of 2D semiconductors lack sufficient nucleation sites for direct growth of high-quality high- κ dielectric films; and (2) Conventional high- κ dielectric surfaces usually have abundant dangling bonds, which would damage the delicate 2D semiconductors and lead to a high density of interface states upon integration.²¹ Various attempts have been made to improve the integration of high- κ dielectrics and 2D semiconductors.²³⁻³² Among them, van der Waals (vdW) integrations have attracted great interest. Hexagonal boron nitride (*h*-BN) has been widely used as the gate dielectric for 2D semiconductors, where the formed vdW interface minimizes interface states and damages to the underlying 2D semiconductors. But its low dielectric constant hinders its practical device applications in the sub-1nm EOT regime.^{33,34} Besides, high-quality high- κ oxides such as strontium titanate (SrTiO₃), aluminium oxide (Al₂O₃) and hafnia (HfO₂) films have been transferred onto 2D semiconductors as gate dielectrics, showing much improved interface properties and device performances.^{28,35,36} However, vdW or quasi-vdW integrations of these high- κ oxides rely on transfer techniques which are not scalable and are incompatible with standard semiconductor fabrication processes. Thus, it is highly desired to develop high-performance high- κ dielectrics that can be directly integrated on 2D semiconductors.

Recently, inorganic molecular crystals (IMCs) have emerged as promising high- κ dielectrics which may address the aforementioned issues for 2D electronics.^{37,38} IMCs are composed of periodically ordered molecular clusters which are held together through weak vdW interactions. This endows IMCs with dangling-bond-free surfaces. Compared to other high- κ dielectric materials, more importantly, the weak inter-cluster interaction allows IMCs to be directly deposited on 2D semiconductors at relatively low temperatures and without inflicting damages on the latter, making them attractive candidates as high-performance high- κ dielectrics for 2D electronics.³⁸ Recently, antimony trioxide (Sb_2O_3) has been reported as the first IMC-based high- κ dielectric, demonstrating an impressive device performance on monolayer MoS_2 .^{37,39} Furthermore, Sb_2O_3 thin films have been used as buffer layers, which enable direct growth of HfO_2 and lead to an hybrid $\text{Sb}_2\text{O}_3/\text{HfO}_2$ dielectric layer with a low equivalent oxide thickness (EOT) of 0.67 nm and high gating efficiency.⁴⁰ Recent investigations have reported several other IMCs,^{38,41,42} yet none of them as high- κ dielectrics outperforms Sb_2O_3 . Considering the extensive repository of materials amassed in the past decades, IMCs which have comparable or even better dielectric and electronic properties than Sb_2O_3 may await to be discovered. Besides, the high-performance integration of IMCs onto 2D semiconductors requires an in-depth understanding of the interface properties, which, however, remains limited. Therefore, in this study, we develop a topology-scaling algorithm to efficiently identify potential IMCs from the Materials Project (MP) database. High-throughput first-principles calculations are subsequently applied to accelerate the screening of the high-performance IMC-based high- κ dielectric candidates and elucidate the critical interface properties with 2D semiconductors.

Results

Pre-Screening of Inorganic Molecular Crystals

For high-performance high- κ dielectrics in 2D electronics, potential synthesizability, large band gap sizes, high static dielectric constants and stability are prerequisite. In this study, we leverage the relevant properties already available in the MP database to initiate the pre-screening process for potential IMC-based high- κ dielectrics (**Figure 1**). Both legacy and new MP databases are used (accessed on 7th January 2023). We focus on the candidate materials containing up to 100 atoms per unit cell. Here, a candidate material is considered synthesizable if (i) its energy above hull (E_{hull}) is no more than 80 meV/atom or (ii) it has been assigned at least one matching entry from the Inorganic Crystal Structure Database (ICSD) by the MP database. As for the former criterion, $E_{\text{hull}} \leq 80$ meV/atom is a moderate choice. One notes that, for 90% of bulk phases without vdW bonding in ICSD, their MP energies above hull are

below 67 meV/atom.⁴³ Meanwhile, for most experimentally grown 2D materials, the analogous decomposition energies are below 100 meV/atom.⁴⁴ The next pre-screening criterion is the band gap size based on the Perdew-Burke-Ernzerhof parametrized generalized gradient approximation (PBE-GGA). Noting that the PBE functional usually underestimates band gap sizes, 2.5 eV is chosen as the threshold.⁴⁵

We then develop a topology-scaling approach to identifying IMC candidates, as illustrated in **Figure S1** in **Supplementary Information**. This approach is derived from our previous recipes used to computationally exfoliate 2D materials from layered parent bulks.⁴⁶ More specifically, given the unit cell of a candidate material, we first determine whether any two atoms are bonded by comparing their distance with the sum of the respective covalent radii of the two elements at a bond tolerance varying from 0% to 40% with an increment of 5%. We note that the upper bound of 40% is large enough to thoroughly access the likelihood of materials being classified as IMCs (**Figure S2**). The atoms within the unit cell are grouped into intra-bonded clusters whose sizes are respectively counted (N). Then, we expand the unit cell into a $3\times 3\times 3$ supercell and again count the number of atoms in each intra-bonded cluster (N') at varying bond tolerances. The candidate materials are categorized as IMCs if the topology-scaling relation of $N' = N$ and $N > 1$ are satisfied for all the intra-bonded clusters at no less than three different bond tolerances. Among the identified IMCs, those are further excluded if any constituent clusters are gaseous or liquid at room temperature or bear a net charge – an indicator of an IMC candidate being a salt and soluble in water. The above pre-screening yields 784 and 875 IMC dielectric candidates from new and legacy MP databases, respectively (**Figure 1**). After merging the two candidate sets and removing duplicates, we identify a total of 937 unique IMC candidates.

High-Throughput Calculations and Statistical Analyses

Since the MP database does not take the vdW correction into account, we performed high-volume first-principles calculations to optimize the crystal structures of the 937 IMC candidates using the DFT-D3 method.⁴⁷ Our in-house high-throughput first-principles calculation framework has been used to streamline and accelerate the calculations. Another round of IMC identification follows, reducing the number of IMC candidates to 879. We further check their dynamical stability. The candidates which have either acoustic phonon modes of larger than 1 meV in magnitude or imaginary optical phonon modes at the Γ point

are excluded.⁴⁸⁻⁵⁰ This further reduces the number of potential IMC candidates to 707 (**Figure 1** and **Table S1**), which will be focused on hereafter.

By choosing the corresponding volume in the MP database (V_{MP}) as a reference, we analyse the volume change of the 707 IMC candidates upon consideration of vdW corrections, as displayed in **Figure 2a**. For around 80% of the candidates, the volume decreases by at least 5%. For 50% of the candidates, the volume decrease is even above 10%. This indicates that vdW interactions play an important role in investigating loosely bound IMCs. As a result of the vdW-dominant inter-cluster interactions, IMCs tend to have low symmetries. **Figure S3** presents the crystal system distribution of the 707 IMC candidates and the entire MP database. Compared with the latter, the proportions of cubic, hexagonal, trigonal and tetragonal structures among the IMC candidates greatly decrease, while monoclinic structures become more than twice as prevalent.

Among the 707 IMC candidates, only 81 IMCs have dielectric constants available in the MP database. Therefore, we have calculated the dielectric constant of all the 707 IMC candidates. We then compare our calculated maximum polycrystalline dielectric constants (ϵ_{max}) with those in the MP database ($\epsilon_{\text{max}}^{\text{MP}}$). As shown in **Figure S4**, the difference, which is defined as $\frac{\epsilon_{\text{max}}^{\text{MP}} - \epsilon_{\text{max}}}{\epsilon_{\text{max}}} \times 100\%$, follows a Gaussian distribution with an average of -10.4% and a standard deviation of 25.7%. The significant difference indicates a substantial effect of the vdW interactions on the dielectric properties of IMCs, especially for the ionic contribution that exhibits a standard deviation of 48.1% (**Figure S4c**). Among the IMC candidates, BH_6N (MP ID: mp-675418) experiences the largest vdW correction to the dielectric constant, *i.e.*, $\epsilon_{\text{max}}^{\text{MP}} = 9.140$ versus $\epsilon_{\text{max}} = 4.548$. The dominant difference lies in the ionic contribution, *i.e.*, $\epsilon_{\text{ion. max}}^{\text{MP}} = 6.852$ versus $\epsilon_{\text{ion. max}} = 2.106$, whereas the electronic contribution is nearly the same, *i.e.*, $\epsilon_{\text{ele. max}}^{\text{MP}} = 2.289$ versus $\epsilon_{\text{ele. max}} = 2.442$. On the contrary, the vdW interactions significantly increase the ionic contribution to the dielectric constant of Sb_2O_3 to 7.098 from 4.169 in the MP database. This yields a total dielectric constant of 12.134 (versus $\epsilon_{\text{max}}^{\text{MP}} = 8.416$) for Sb_2O_3 , in good agreement with the experimental measurement of 11.5.³⁷ In general, **Figure 2b** shows that our dielectric constants calculated with vdW corrections linearly scale with the MP counterparts calculated without vdW corrections: $\epsilon_{\text{max}} = 0.876 \times \epsilon_{\text{max}}^{\text{MP}} + 0.145$ with a Pearson correlation coefficient of 0.822.

Identifications of IMC-Based High- κ Dielectrics

According to the first-order perturbation theory, the electronic susceptibility is inversely correlated with the energy difference of the transition states which on average increases with the band gap size. This leads to the widely observed inverse relation between the band gap size and the dielectric constant, especially the electronic part of the latter.^{49,51,52} Therefore, a large ionic contribution is necessary for candidate materials to concurrently achieve a large band gap and a high total dielectric constant. **Figure 2c** shows the ratio of the electronic part to the total dielectric constant of the 707 IMC candidates. One sees that the electronic contribution spans a broad range and has an average ratio of 66%, indicative of its slight dominance over the ionic part in IMCs. For experimentally reported Sb_2O_3 , the electronic part amounts to 41.5% of the total dielectric constant (vertical dashed line in **Figure 2c**). Despite the overall prevalence of the electronic part, intriguingly, **Figure 2c** reveals that there are some IMC candidates whose ionic contribution dominates and is comparable to or even higher than that of Sb_2O_3 . Among them, GeF_2 (mp-7595) and $\text{Sb}_2\text{S}_2\text{O}_9$ (mp-638424) have the lowest relative electronic contribution ($< 20\%$), which is over 50% less than that of Sb_2O_3 .

Figure 2d shows the band gap sizes (E_g) versus the dielectric constants (ϵ) of the 707 IMC dielectric candidates. The small dots represent the minimum polycrystalline dielectric constants ($\epsilon_{\min}$) of the candidates, and the vertical line attached to above a dot marks the estimated polycrystalline dielectric constant range of the corresponding candidate. The general inverse relation between dielectric constant and band gap is also clearly observable. Nevertheless, there are two most outstanding outliers, *i.e.*, GeF_2 and $\text{Sb}_2\text{S}_2\text{O}_9$. Thanks to the small electronic contribution to the dielectric properties as discussed above ($< 20\%$), which significantly weakens the inverse $\epsilon \sim \frac{1}{E_g}$ constraint, they exhibit both larger band gaps and higher dielectric constants compared with Sb_2O_3 . To screen other potential IMC-based high- κ dielectric candidates, we introduce two figures of merit: $\epsilon \cdot E_g$ and $\sqrt{\epsilon} \cdot E_g$. The former is a rough measure of current leakage across the gate dielectric and the latter of energy storage of a capacitor.^{49,53} Higher $\epsilon \cdot E_g$ and $\sqrt{\epsilon} \cdot E_g$ could suppress current leakage and maximize energy storage, respectively. Taking Sb_2O_3 as a reference ($\epsilon \cdot E_g = 35.7$ and $\sqrt{\epsilon} \cdot E_g = 10.2$), we apply the screening criteria of $\epsilon \cdot E_g \gtrsim 35$ and $\sqrt{\epsilon} \cdot E_g \gtrsim 10$ and pinpoint a total of 15 potential high- κ IMC dielectric candidates (red and blue dots in **Figure 2d**), *i.e.*, $\text{Sb}_2\text{S}_2\text{O}_9$ (mp-638424), GeF_2 (mp-7595), two Bi_2O_3 phases (mp-1196483 and mp-1188267), $\text{NiH}_8(\text{ClO}_2)_2$ (mp-1220246), Sn_4SF_6 (mp-1021490), SbH_3SO_6 (mp-720857), SbF_3 (mp-1880), ZnH_8SO_8 (mp-24708; identical to mp-1197363), $\text{Te}_2\text{H}_2\text{O}_3\text{F}_4$ (mp-1191341), Sb_2O_3 (mp-1999), $\text{BeH}_6\text{N}_2\text{F}_2$

(mp-1200927), $\text{CaH}_8(\text{ClO}_2)_2$ (mp-721047), $\text{Ge}(\text{CH}_3\text{SO}_3)_2$ (mp-1194589), and $\text{As}_2\text{S}_2\text{O}_9$ (mp-27739; identical to mp-1197011). **Figure S5** confirms that all these candidates have a small relative electronic contribution to the total dielectric constant, which is comparable to or below that of Sb_2O_3 .

Subsequent manual inspections further exclude 9 candidates, as detailed below (see **Figure S6** for their atomic structures): (i) $\text{NiH}_8(\text{ClO}_2)_2$, SbH_3SO_6 , ZnH_8SO_8 and $\text{CaH}_8(\text{ClO}_2)_2$ contain coordinate covalently bonded water molecules; (ii) $\text{BeH}_6\text{N}_2\text{F}_2$ contains coordinate covalently bonded ammonia molecules and starts to decompose at 80 °C;⁵⁴ (iii) Although GeF_2 satisfies our IMC categorization criteria under the topology-scaling approach, it in fact comprises one-dimensional (1D) chains and has a low melting point of 110 °C;⁵⁵ (iv) Sn_4SF_6 , SbF_3 and $\text{Ge}(\text{CH}_3\text{SO}_3)_2$ exhibit poor aqueous stability (**Figure S7**). Ultimately, we identify 6 IMC-based high- k dielectric candidates, as illustrated in **Figure 3** and tabulated in **Table 1**. Among the final candidate list, $\text{Sb}_2\text{S}_2\text{O}_9$, $\text{Te}_2\text{H}_2\text{O}_3\text{F}_4$ and $\text{As}_2\text{S}_2\text{O}_9$ have already been experimentally synthesized and reported as IMCs, in addition to Sb_2O_3 .⁵⁶⁻⁵⁹ On the other hand, the two solid phases of Bi_2O_3 (mp-1196483 and mp-1188267) are from theoretical predictions.⁶⁰ Bi_2O_3 (mp-1188267) is isostructural to Sb_2O_3 and comprises the cage-like Bi_4O_6 constituent cluster. Bi_2O_3 (mp-1196483) is also made up of the same cage-like constituent cluster but has a lower symmetry due to the inter-cluster distortion. A recent experimental study has demonstrated the growth of atomically thin (< 1nm), high-quality, non-layered $\beta\text{-Bi}_2\text{O}_3$ thin films.⁶¹ These two new phases of Bi_2O_3 may also be synthesized under appropriate experimental conditions. As for $\text{Sb}_2\text{S}_2\text{O}_9$ and $\text{As}_2\text{S}_2\text{O}_9$, despite different crystal systems, they contain the same constituent cluster $\text{X}_2\text{S}_2\text{O}_9$ (X=Sb, As), where the two X atoms are bridged by an oxygen atom and jointly coordinated to two SO_4^{2-} groups. For $\text{Te}_2\text{H}_2\text{O}_3\text{F}_4$, the constituent cluster comprises two Te atoms that are connected by an oxygen atom and respectively coordinated to two fluorine atoms and a hydroxide ligand. Except zigzag $\text{Te}_2\text{H}_2\text{O}_3\text{F}_4$, intriguingly, all the other 5 identified IMC candidates are either oxides or oxysulphides of group-V elements (As, Sb and Bi). Their constituent clusters $\text{X}_2\text{S}_2\text{O}_9$ (X=Sb, As) or Y_4O_6 (Y=Sb, Bi) resemble semi-open or closed cages. Despite these similarities, one notes that these identified IMC candidates exhibit markedly different electronic and dielectric properties (**Figure 2d**).

Considering the typical band gap underestimation of the PBE functional, the more accurate HSE06 band gaps of the six final candidates are calculated (see **Table 1**). In terms of the figures of merit as discussed above, **Figure S8** shows that all these final candidates still match or outperform Sb_2O_3 at the HSE06 level of theory. In addition, their inter-cluster binding energies

(E_B) are calculated and summarized in **Table 1**. For $\text{Sb}_2\text{S}_2\text{O}_9$, $\text{Te}_2\text{H}_2\text{O}_3\text{F}_4$ and $\text{As}_2\text{S}_2\text{O}_9$, their inter-cluster binding energy is similar to that of Sb_2O_3 . Bi_2O_3 exhibits stronger inter-cluster binding strength, but it still falls within the typical vdW regime. Thus, these newly identified IMCs might display sublimation behaviours similar to Sb_2O_3 under high-vacuum, elevated-temperature conditions.

For nanoscale field effect transistors (FETs), a large operating field is expected across the dielectric layer. Therefore, we also estimate the intrinsic breakdown field (F_{BD}) of the six potential high- κ IMC dielectrics (**Table 1**). According to the previous machine-learning (ML) assisted investigation, the intrinsic breakdown field (unit: $\text{MV} \cdot \text{cm}^{-1}$) can be calculated as $F_{\text{BD}} = 0.24442 \times \exp(0.315 \times \sqrt{E_g \omega_{\text{max}}})$, where E_g is in eV and ω_{max} is the maximum vibrational frequency in THz.⁶² As shown in **Table 1**, $\text{Sb}_2\text{S}_2\text{O}_9$, $\text{Te}_2\text{H}_2\text{O}_3\text{F}_4$ and $\text{As}_2\text{S}_2\text{O}_9$ have relatively high breakdown fields ($\geq 10 \text{ MV} \cdot \text{cm}^{-1}$), whereas it is relatively low for Bi_2O_3 and Sb_2O_3 . Nevertheless, we stress that these breakdown field values are only rough estimates because (i) the maximum vibrational frequency used here is approximated by that at the Brillouin zone centre; (ii) the ML-derived formula is not unique; and (iii) it was derived from conventional 3D elemental and binary materials.⁶² More advanced yet expensive methods will be in need to accurately predict the intrinsic breakdown field of the identified IMC candidates where the vdW interactions dominate in between their constituent clusters.⁶³

IMC-Based High- κ Dielectrics for 2D Electronics

Among thousands of 2D semiconductors, BP,⁹ MoS_2 ,² molybdenum diselenide (MoSe_2),⁶⁴ tungsten disulphide (WS_2),⁶⁵ tungsten diselenide (WSe_2),⁶⁶ bismuth oxyselenide ($\text{Bi}_2\text{O}_2\text{Se}$),⁶⁷ indium selenide (InSe),⁹ tin disulphide (SnS_2)⁶⁸ and tin diselenide (SnSe_2)⁶⁹ have been experimentally investigated as promising channel materials. Here, we employ Anderson's rule to evaluate the valence band offset (VBO) and the conduction band offset (CBO) of these potential 2D channel semiconductors with the screened IMC candidates as the high- κ dielectrics (see **Figure S9** and **Table S2** for their surface models). The monolayer (ML) of these nine 2D semiconductors is considered. **Table S2** shows that the band gaps of these IMC candidates' surfaces are very close to their bulk counterparts. This similarity is consistent with the vdW-dominated interactions between constituent clusters and underscores the dangling bond-free or self-saturation nature of these IMC surfaces. **Figures 4a** and **S12-S13** display the band alignment of the considered 2D semiconductors with the IMC candidates. To suppress current leakage across the gate dielectric layer, a band offset of at least 1 eV is often

required.^{17,29} **Figure 4a** shows that CBO between Sb_2O_3 and MoS_2 meets this requirement, in good agreement with the recent experimental measurement of the low leakage current.³⁷ The 1eV-CBO threshold is also satisfied when MoS_2 is interfaced with $\text{Sb}_2\text{S}_2\text{O}_9$ and both Bi_2O_3 phases. Notably, the 1eV-VBO requirement can be simultaneously reached for $\text{Sb}_2\text{S}_2\text{O}_9$. It also fulfils the 1eV-offset requirement for MoSe_2 and BP. Sb_2O_3 may serve as an effective dielectric for BP as well. **Figure 4b-c** compile calculated CBOs and VBOs for all 2D semiconductors studied. Notably, there is at least one IMC candidate which exceeds the 1eV offset for almost every 2D semiconductor studied. Therefore, the leakage current is likely to be significantly suppressed when these IMCs are used as gate dielectrics for the 2D semiconductors.

High-Performance BP/ $\text{Sb}_2\text{S}_2\text{O}_9$ and $\text{MoS}_2/\text{Bi}_2\text{O}_3$ Interfaces

Noting their large band offsets, near-perfect lattice and symmetry matching, the explicit interfaces between BP and $\text{Sb}_2\text{S}_2\text{O}_9$ (001) and between MoS_2 and the (111) surface of Bi_2O_3 (mp-1188267) are built to further scrutinize their interface properties. **Figure 5a** shows the optimized BP/ $\text{Sb}_2\text{S}_2\text{O}_9$ interface. While the interlayer spacing (2.67 Å) is near the lower bound of the typical vdW gap, the calculated interlayer binding energy (-15.80 meV/Å²) and the barely perturbed BP lattice imply a weak interaction between BP and $\text{Sb}_2\text{S}_2\text{O}_9$. In addition, the charge redistribution is mainly localized around the BP layer, indicative of negligible charge transfer or interface hybridization across the vdW gap. The projected density of states (PDOS) in **Figure 5b** shows clear valence and conduction band offsets between BP and $\text{Sb}_2\text{S}_2\text{O}_9$. We notice that the valence (conduction) band offset of 2.29 eV (1.57 eV) based on the explicit interface model is very close to that determined by Anderson's rule (VBO: 2.39 eV; CBO: 1.62 eV), thereby further confirming their weak interaction and validating the applicability of this rule in the present study. On the other hand, the weak vdW-dominant inter-cluster interaction implies that cluster vacancies are prone to form, especially around the interface (**Figure 5c**). This is confirmed by the calculated formation energies of intrinsic defects in $\text{Sb}_2\text{S}_2\text{O}_9$ (see **Table S3**), where the molecular defect $\text{Sb}_2\text{S}_2\text{O}_9$ at the interface exhibits the lowest formation energy. Intriguingly, this interfacial molecular defect does not bring significant effects on the interface properties, as evidenced by the nearly unchanged charge redistribution, electronic structure, and the band offsets (see **Figures 5c** and **5d**). These results highlight the great defect tolerance of IMC-based high- κ dielectrics, which is another inherent advantage of IMCs and is beneficial to high-performance 2D electronics.

To evaluate the interface performance more quantitatively, we further calculate the leakage current density resulting from both the quantum tunnelling and the thermionic emission (see **Methods** for more information).^{45,70} **Figure 5e** shows the calculated leakage current density of the BP/Sb₂S₂O₉ interface as a function of EOT for both electrons (*e*) and holes (*h*) in BP, where *n*-MOS/HfO₂ is selected as a reference. Within 2-nm EOT, the pristine BP/Sb₂S₂O₉ interface can suppress the leakage current more efficiently than *n*-MOS/HfO₂. This improvement primarily stems from the large carrier effective mass in Sb₂S₂O₉ (*e*: 0.727 m_e ; *h*: 0.862 m_e) versus in HfO₂ (*e*: 0.11 m_e), which significantly reduces the quantum tunnelling current. For hole carriers, the quantum tunnelling is further suppressed by the large VBO of 2.29 eV. Notably, in the sub-1nm EOT regime required for state-of-the-arts MOSFETs, the pristine BP/Sb₂S₂O₉ interface is able to reach the stringent dynamic random access memory (DRAM) limit ($< 10^{-7}$ A/cm²; horizontal dashed line in **Figure 5e**). Even when molecular defects are present, the interface remains below this limit, owing to the excellent defect tolerance of Sb₂S₂O₉. All these analyses thus suggest that the BP/Sb₂S₂O₉ interface may hold promise for 2D electronics.

The remarkable tolerance to interfacial defects has also been demonstrated at the MoS₂/Bi₂O₃ (mp-1188267) interface using explicit interface models, as shown in **Figure 6**. Analogous to the BP/Sb₂S₂O₉ interface, the vdW interaction dominates at the MoS₂/Bi₂O₃ interface, as evidenced by (i) the interlayer spacing of 2.73 Å, (ii) localized charge redistribution around the MoS₂ layer, (iii) the interlayer binding energy of -26.77 meV/Å², and (iv) the similarity of band offsets determined by the explicit interface model (VBO: 0.52 eV; CBO: 0.91 eV) and Anderson's rule (VBO: 0.25 eV; CBO: 1.05 eV). Also, **Figures 6c-d** imply that these characteristics persist after molecular defects are introduced at the interface. **Figure 6e** displays the simulated leakage current density of the pristine and defective MoS₂/Bi₂O₃ interface. In the sub-1nm EOT regime where quantum tunnelling dominates, the MoS₂/Bi₂O₃ interface matches *n*-MOS/HfO₂ in terms of the leakage current. Such comparability originates from the relatively large electron effective mass in Bi₂O₃ (0.426 m_e versus 0.11 m_e in HfO₂), which compensates for the relatively small CBO of MoS₂/Bi₂O₃ (~0.9 eV) versus that of *n*-MOS/HfO₂ (1.5 eV). One notes that the MoS₂/Bi₂O₃ interface meets the central processing unit (CPU) limit of $< 10^{-1}$ A/cm² at sub-1nm EOT, regardless of interfacial defects (**Figure 6e**). In addition, the ab initio molecular dynamics simulations further confirmed the thermal and chemical stability of both BP/Sb₂S₂O₉ and MoS₂/Bi₂O₃ interfaces (see **Figures S18-S19**).

Downscaling Capability to Sub-1nm EOT

Based on Anderson’s rule, we further estimate the leakage current density for each identified IMC candidate as a gate dielectric layer on the 2D semiconductors considered. **Figures 7a** and **7b** correspond to BP and MoS₂ at EOT=0.5, 1.0, 1.5 and 2.0 nm, respectively (analogous data for the other 2D semiconductors in **Figures S20-S26**). **Figures 7c** and **7d** compile the leakage current density of all interfaces considered at EOT = 1 nm for electrons and holes, respectively. For electron carriers in both BP and MoS₂, **Figures 7a-b** show that Sb₂S₂O₉ and Bi₂O₃ (mp-1196483) can reach the DRAM limit at the sub-1nm EOT, and most identified IMCs can fulfil the more relaxed leakage current requirement for CPU applications. As for hole carriers in BP and MoS₂, more IMC candidates turn out to be capable of suppressing leakage below both DRAM and CPU limits in the sub-1nm EOT regime (bottom panel of **Figure 7a-b**). This electron-hole asymmetry in the leakage current is also observed when these identified IMC candidates are in contact with the other 2D semiconductors except InSe, SnS₂ and SnSe₂ (**Figures 7c-d**). It is attributable to (i) generally larger VBO than CBO (see **Figure 4b-c**) and (ii) heavier hole effective masses than the electron counterparts in these IMC candidates (**Table S4**). As mentioned above, the state-of-the-arts MOSFETs require EOT to scale down within 1 nm. From **Figures 7c-d**, one sees that for each 2D semiconductor considered and carrier polarity, the stringent DRAM limit at sub-1nm EOT is reachable when appropriate gate dielectrics are selected from the identified IMC candidate list. This clearly underscores the downscaling potential of IMC-based high- k dielectrics for 2D electronics.

Discussion

In summary, we report the high-throughput computational screening of inorganic molecular crystal-based high- κ dielectrics for 2D electronics. From the Materials Project database, we single out 6 potential IMC-based high- κ dielectrics that optimally balance band gaps with dielectric constants, and exhibit aqueous stability and propensity to facile sublimation, *i.e.*, Sb₂S₂O₉ (mp-638424), Bi₂O₃ (mp-1196483 and mp-1188267), Te₂H₂O₃F₄ (mp-1191341), Sb₂O₃ (mp-1999) and As₂S₂O₉ (mp-27739). For 9 experimentally reported promising 2D channel materials (BP, MoS₂, MoSe₂, WS₂, WSe₂, Bi₂O₂Se, InSe, SnS₂ and SnSe₂), our calculations predict the respective potential IMC-based high- κ dielectrics which exhibit large enough band offsets (> 1 eV). By selecting BP/Sb₂S₂O₉ and MoS₂/Bi₂O₃ (mp-1188267) as representative systems, our explicit interface simulations demonstrate the desirable sharp vdW interfaces, large band offsets, low leakage current and excellent defect tolerance. These merits are mainly attributed to the intrinsic dangling-bond-free nature of the IMC surfaces and their weak inter-cluster interactions. In addition, our leakage current density simulations further

reveal that when appropriately paired with 2D semiconductors, these identified IMCs may achieve the sub-1nm EOT downscaling for both DRAM and CPU applications. These findings could stimulate further investigations on the IMC-based high- κ dielectrics identified in the present study and beyond, contributing to the direct high-performance integration of high-quality high- κ dielectrics in 2D electronics.

Methods

Computational methods. All first-principles calculations were carried out using the Vienna Ab initio Simulation Package (VASP) with the core-electron interactions described by the projector wave-augmented (PAW) method.⁷¹⁻⁷³ The Perdew-Burke-Ernzerhof parametrized generalized gradient approximation (PBE-GGA) was used for the exchange-correlation interaction.⁷⁴ Calibrated Hubbard U values were applied to the d orbitals of the transition metal elements in transition metal oxides and fluorides,^{75,76} and can be found in Ref. ⁷⁷. The kinetic energy cutoff of the plane wave basis was chosen to be 600 eV. The Brillouin zone was sampled by a k -point mesh of 3000 per reciprocal atom. The total energy and structural relaxation convergence criteria were set to 1×10^{-6} eV and 0.01 eV/Å, respectively. A previous investigation has demonstrated that these parameters could reach a good balance between calculation efficiency and computational convergence.⁴⁸ In addition, DFT-D3 method with the Becke-Johnson damping function was included to account for the weak inter-cluster interactions in inorganic molecular crystals.⁴⁷

The total dielectric tensor consists of the electronic and ionic contributions. The former was calculated using the density-functional perturbation theory (DFPT). As for the ionic contribution, we resorted to the finite difference approach owing to the incompatibility of DFPT with the DFT-D3 method in VASP. The DFT-calculated dielectric tensor corresponds to that of a single crystal. Based on the single crystalline result, we derive the scalar polycrystalline dielectric constant. Its lower and upper bounds can be estimated as follows:⁷⁸

$$\frac{3}{\frac{1}{\lambda_1} + \frac{1}{\lambda_2} + \frac{1}{\lambda_3}} < \varepsilon < \frac{\lambda_1 + \lambda_2 + \lambda_3}{3}$$

where λ_1 , λ_2 and λ_3 are the eigenvalues of the single crystalline dielectric tensor. All high-throughput first-principles calculations were performed using our in-house VASP-based high-throughput calculation framework (https://github.com/bitsoal/VASP_HTC_framework).

Inter-cluster binding energy estimation. The binding energy between constituent clusters (E_B) of an IMC is defined as:

$$E_B = \frac{E(\text{IMC}) - \sum_i E_i}{\sum_i S_i},$$

where $E(\text{IMC})$ and E_i are the energies of the bulk-phase IMC and its i -th constituent cluster in a large supercell box, respectively. S_i is the surface area of the i -th constituent cluster. Note that unlike two-dimensional materials it remains challenging to precisely define the surface of a zero-dimensional cluster and calculate its exact surface area. For the sake of simplicity, we approximate the i -th molecular cluster's surface using an ellipsoid fully enclosing that cluster. A two-step procedure is taken to uniquely determine the i -th ellipsoid. First, both the orientation and shape of the i -th ellipsoid are optimized to minimize its volume (V_i^0) under the constraint that the i -th cluster is fully contained. Second, a uniform scaling factor C is applied to all ellipsoids so that their total volume is equal to the bulk IMC volume ($V(\text{IMC})$), namely, $V(\text{IMC}) = C \times \sum_i V_i^0$, ensuring that the entire bulk IMC is roughly fully filled by the constituent clusters.

Leakage current estimation. The leakage current density arising from the direct tunnelling (J_{tun}) and the thermionic emission (J_{therm}) can be calculated as:⁷⁹

$$J_{\text{tot}} = J_{\text{tun}} + J_{\text{therm}}$$

$$J_{\text{tun}} = \frac{q^3 E^2}{8\pi h V_g} \exp \left(\frac{-4\sqrt{2m^*} \left(\varphi^{\frac{3}{2}} - (\varphi - V_g)^{\frac{3}{2}} \right)}{3q\hbar E} \right)$$

$$J_{\text{therm}} = \frac{4\pi q m^* k_B^2}{h^3} T^2 \exp \left(\frac{-q \left(\varphi - \sqrt{\frac{qE}{4\pi\epsilon}} \right)}{k_B T} \right)$$

where q , E , h ($\hbar$), φ , V_g , m^* , T , ϵ and k_B are the elementary charge, the electric field across the dielectric layer, the Planck constant (the reduced Planck constant), the barrier height (band offset), the applied voltage, the carrier effective mass, the temperature, the dielectric constant, and the Boltzmann constant, respectively. In the simulation, the temperature is set to 300 K and the dielectric constant to the minimum polycrystalline dielectric constant. The electric field can be calculated as the ratio of the applied voltage (V_g) to the dielectric layer thickness (t): $E = \frac{V_g}{t}$. According to the International Roadmap for Devices and Systems (IRDS), we assume

$V_g = 355$ mV.⁴⁵ The equivalent oxide thickness (EOT) of a dielectric layer is defined as $EOT = \frac{t \times \epsilon_{SiO_2}}{\epsilon}$, where $\epsilon_{SiO_2} = 3.9$ is the dielectric constant of SiO_2 and ϵ of the dielectric layer. Therefore, both J_{tun} and J_{therm} are functions of EOT, so is J_{tot} .

The band offset between the screened IMCs and 2D semiconductors was estimated based on Anderson's rule. The valence and conduction band offsets are defined as $VBO = E_{VBM}(2D) - E_{VBM}(IMC)$ and $CBO = E_{CBM}(IMC) - E_{CBM}(2D)$, respectively, where $E_{VBM/CBM}(2D)$ and $E_{VBM/CBM}(IMC)$ are the valence band maximum (VBM)/conduction band minimum (CBM) of the 2D semiconductor and the IMC candidate, respectively. Here, the vacuum level, which was estimated by calculating the planar average electrostatic potential, was used to align the band edges between IMCs and 2D semiconductors. The adopted symmetric IMC surface models were summarized in **Table S2** and **Figure S9**. In **Figure S10** the symmetric $Sb_2S_2O_9$ surface model was taken as an example to illustrate the determination or alignment of its VBM and CBM with respect to the vacuum level. The middle one-third of the IMC surface models were fixed during structural relaxations. In order to alleviate the spurious interaction between periodic images, a vacuum layer of no less than 20 Å was inserted along the out-of-plane direction of all slab models.

The carrier effective mass of the dielectric layer was extracted from the PBE bulk band structure along the out-of-plane direction of the respective surface model for the band offset estimation (**Table S2**). More specifically, the out-of-plane k -path was sampled by 100 k -points for the bulk band structure calculation. The N nearest eigenvalues $E(k)$ near the band edge extremum from each side were used to perform the parabolic fitting. The effective mass can be determined from the coefficient of the quadratic term according to $\frac{1}{m^*} = \frac{1}{\hbar^2} \frac{d^2 E(k)}{dk^2}$. By varying N from 10 to 1, we extrapolated the effective mass to $N = 0$. The extracted effective mass of the screened IMC candidates is summarized in **Table S4**. For n -MOS/ HfO_2 , the conduction band offset of 1.5 eV, the electron effective mass of $0.11m_e$ and the dielectric constant of 25 were directly retrieved from literatures.^{80,81}

The explicit BP/ $Sb_2S_2O_9$ interface model. The unit cell of bulk $Sb_2S_2O_9$ has a tetragonal lattice (space group: $P4_12_12$) housing four $Sb_2S_2O_9$ clusters. The optimized lattice parameters for bulk $Sb_2S_2O_9$ are $a = b = 6.60$ Å and $c = 17.10$ Å, while for monolayer BP $a = 3.29$ Å and $b = 4.44$ Å. To model the BP/ $Sb_2S_2O_9$ interface, a supercell of 1×2 $Sb_2S_2O_9$ along the (001) orientation with three cluster layers and a supercell of 2×3 BP monolayer was employed.

Consequently, the lattice mismatches between them amount to 0.22 % and 0.88 % along the a and b directions, respectively. The vacuum layer is set to 20 Å.

The asymmetry of the $\text{Sb}_2\text{S}_2\text{O}_9$ slab allows for the construction of two distinct interfaces for BP/ $\text{Sb}_2\text{S}_2\text{O}_9$ (see **Figure S14a-b**). For each interface, while maintaining the $\text{Sb}_2\text{S}_2\text{O}_9$ fixed, the BP monolayer is shifted along one in-plane axis first with a step of 0.5 Å. Once the position with the lowest energy is identified, the BP monolayer is shifted again along the other in-plane axis with a step size of 0.5 Å. The calculated energies of these configurations are shown in **Figure S14c**. Observably, the energy analysis reveals that the optimal configuration for interface 2 is lower in energy than that of interface 1. Consequently, the optimal configuration of interface 2 is adopted for all subsequent simulations of the explicit BP/ $\text{Sb}_2\text{S}_2\text{O}_9$ interface.

The explicit $\text{MoS}_2/\text{Bi}_2\text{O}_3$ interface model. The unit cell of bulk Bi_2O_3 (mp-1188267) has a cubic lattice (space group: $Fd\bar{3}m$) and comprises two Bi_4O_6 clusters. The optimized lattice constants of bulk Bi_2O_3 are $a = b = c = 7.910$ Å, whereas for monolayer MoS_2 $a = b = 3.151$ Å. The $\text{MoS}_2/\text{Bi}_2\text{O}_3$ interface was constructed by putting a 5×5 supercell of monolayer MoS_2 atop a 2×2 supercell of the three-layered Bi_2O_3 (111) surface. Consequently, the lattice mismatch between them amounts to 0.40%. The vacuum layer is set to 20 Å.

Analogous to the BP/ $\text{Sb}_2\text{S}_2\text{O}_9$ interface, the most stable $\text{MoS}_2/\text{Bi}_2\text{O}_3$ interface was determined by shifting the MoS_2 layer first along the in-plane b -axis direction with a step size of 0.5 Å and then along the in-plane a -axis direction based on the b -axis lowest-energy configuration, where only the MoS_2 layer was relaxed. The calculated energies of these configurations are shown in **Figure S15**. The most stable stacking configuration was adopted for all subsequent simulations of the explicit $\text{MoS}_2/\text{Bi}_2\text{O}_3$ interface,

Data availability

Relevant data supporting the key findings of this study are available within the article and the Supplementary Information file. All raw data generated during the current study are available from the corresponding authors upon request.

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Author Contributions

M. Y. conceived the idea. M. Y., T. Y., and J. Z. designed the study. T. Y. performed high-throughput calculations. T. Y., J. Y. H, K. D., K. Y., and J. Z. performed the explicit interface simulations and leakage current simulations. T. Y., J. Z., W. H., J. Z., Y. Y., Y. C., K. P. L., and M. Y. performed the analysis. T. Y. prepared the manuscript. All the authors read and corrected the final manuscript.

Competing Interests

The authors declare no competing interests.

Additional information

Supplementary information The online version contains supplementary material available at [xxx](#)

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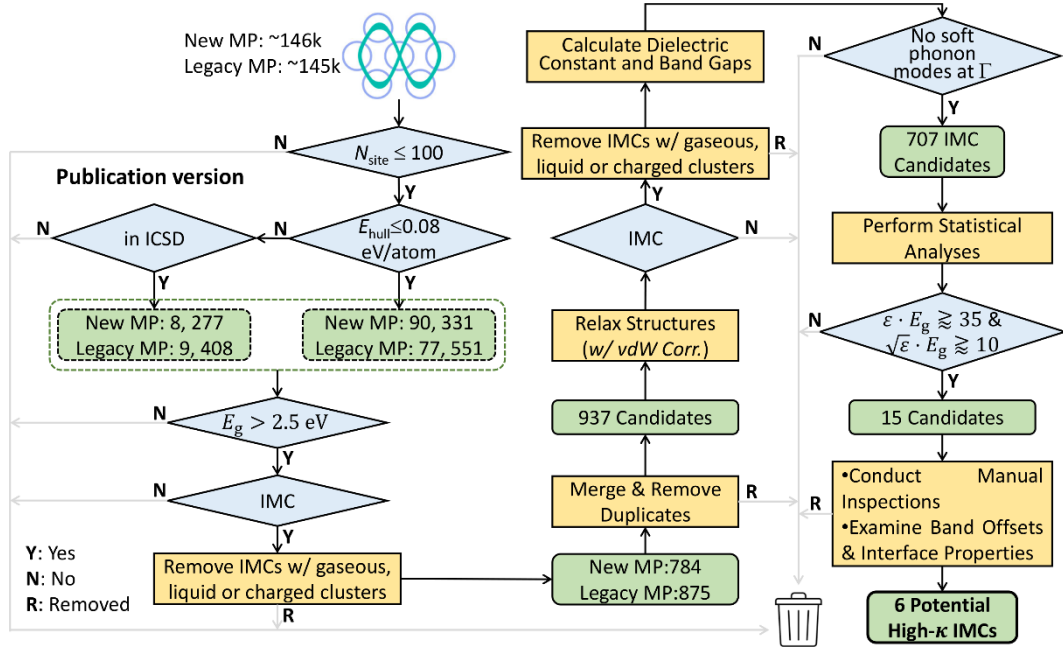


Figure 1. The workflow for pre-screening and high-throughput computational screening of IMC-based high- κ dielectrics for 2D electronics.

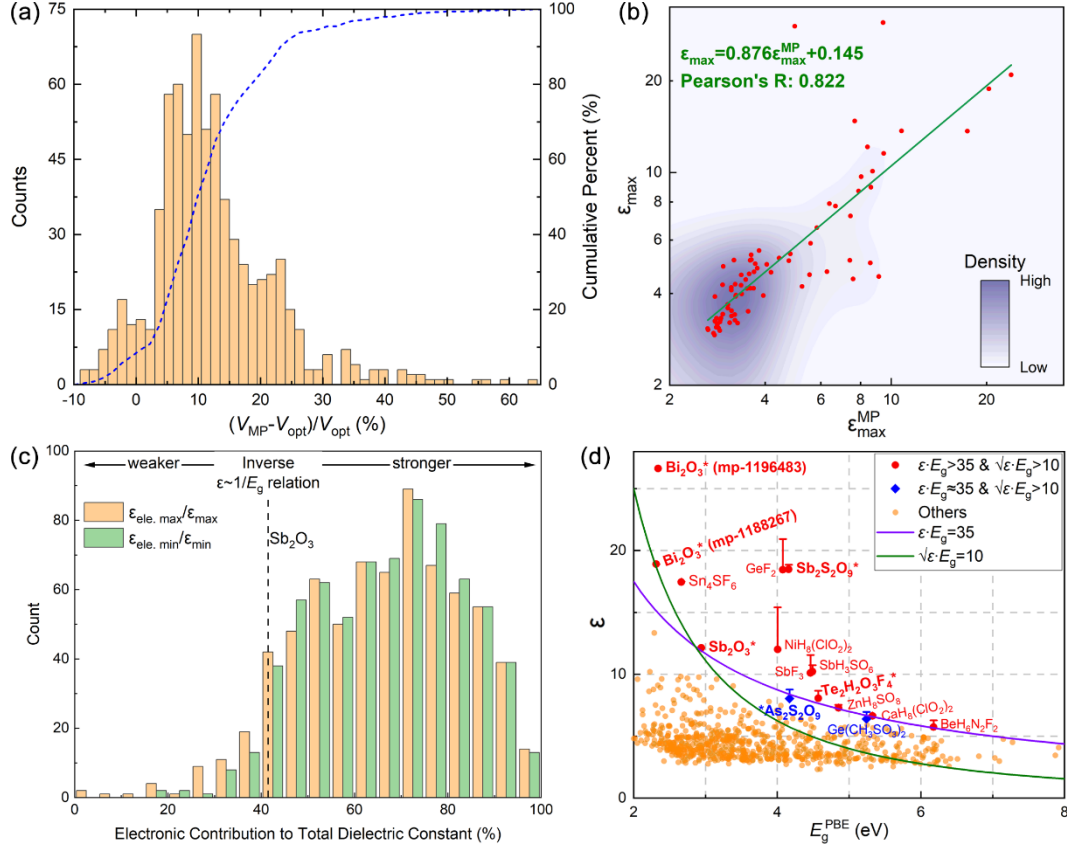


Figure 2. Statistics on the 707 IMC candidates. (a) The volume change upon consideration of the vdW interaction; (b) Comparison of calculated dielectric constants (ϵ_{max}) with the counterparts available in the Materials Project database (ϵ_{max}^{MP}); (c) The histogram of the electronic contribution to the calculated total dielectric constant. The vertical dashed line corresponds to Sb_2O_3 (mp-1999). The polycrystalline dielectric constants are used in (b-c). (d) The minimum polycrystalline dielectric constant (ϵ_{min} ; dots) versus the PBE band gap (E_g^{PBE}). The vertical line attached to above a dot denotes the estimated range of the polycrystalline dielectric constant of that IMC candidate. The six identified potential IMCs are highlighted in the bold font and with asterisks.

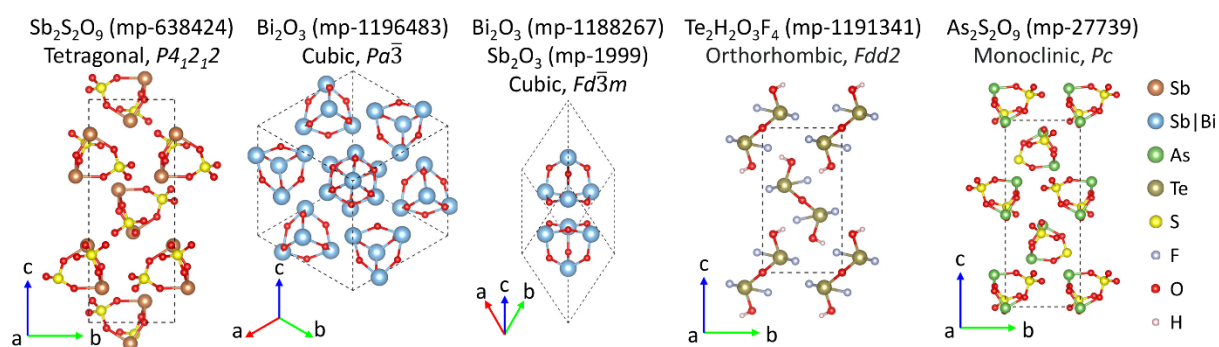


Figure 3. Atomic structures of the six identified IMC candidates. Bi_2O_3 (mp-1188267) is isostructural to Sb_2O_3 .

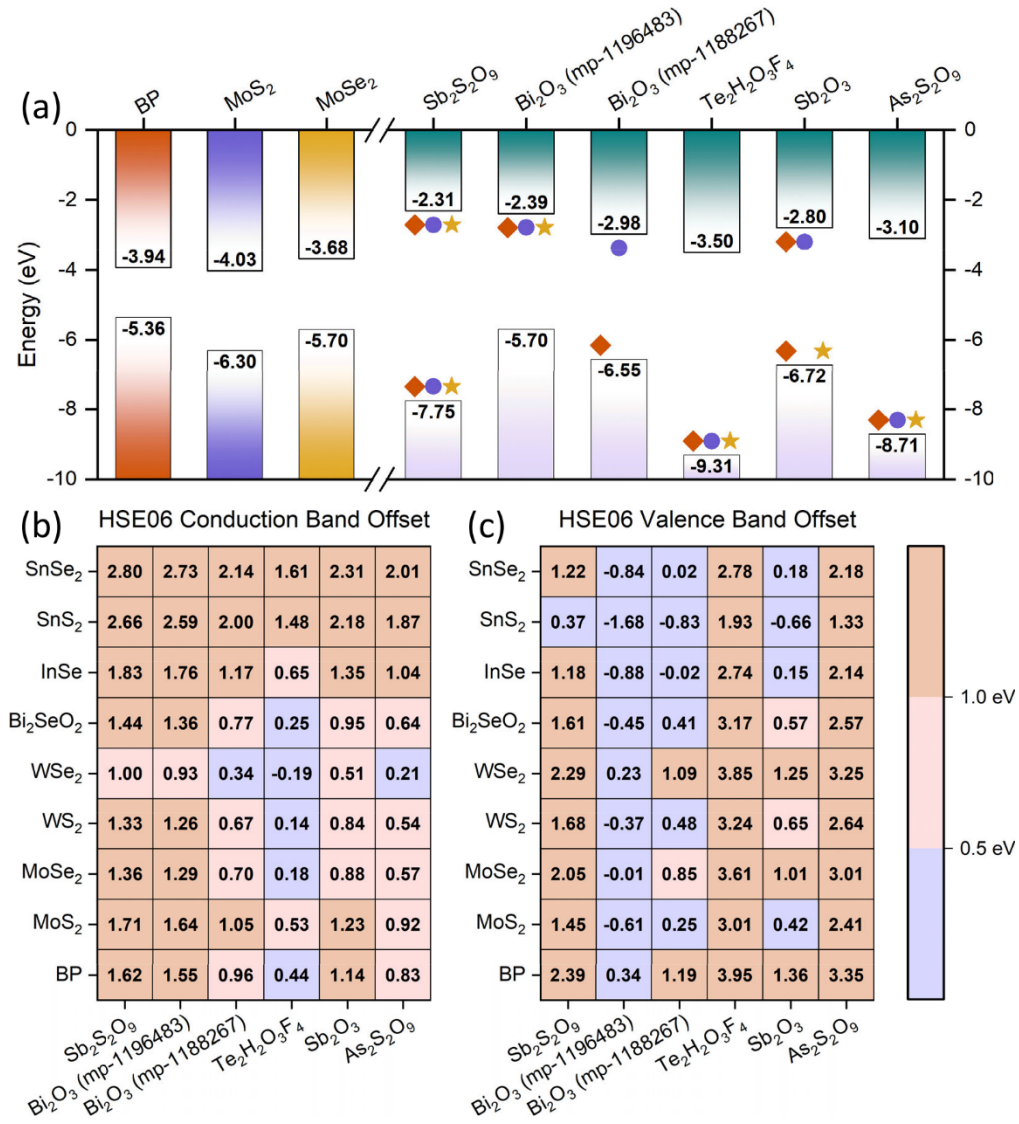


Figure 4. Band alignment between identified IMCs and 2D channel materials. (a) Band alignment of the 6 identified IMC candidates with monolayer black phosphorene (BP), MoS₂ and MoSe₂ at the HSE06 level of theory. The alignment is based on the calculated vacuum level which is set to 0 eV. The orange diamonds, the purple circles and the yellow stars mark the band edges of IMCs satisfying the 1-eV band offset requirement with respect to those of BP, MoS₂ and MoSe₂, respectively. (b) The conduction band offset and (c) the valence band offset of the 6 IMC candidates with 9 potential 2D semiconducting channel materials.

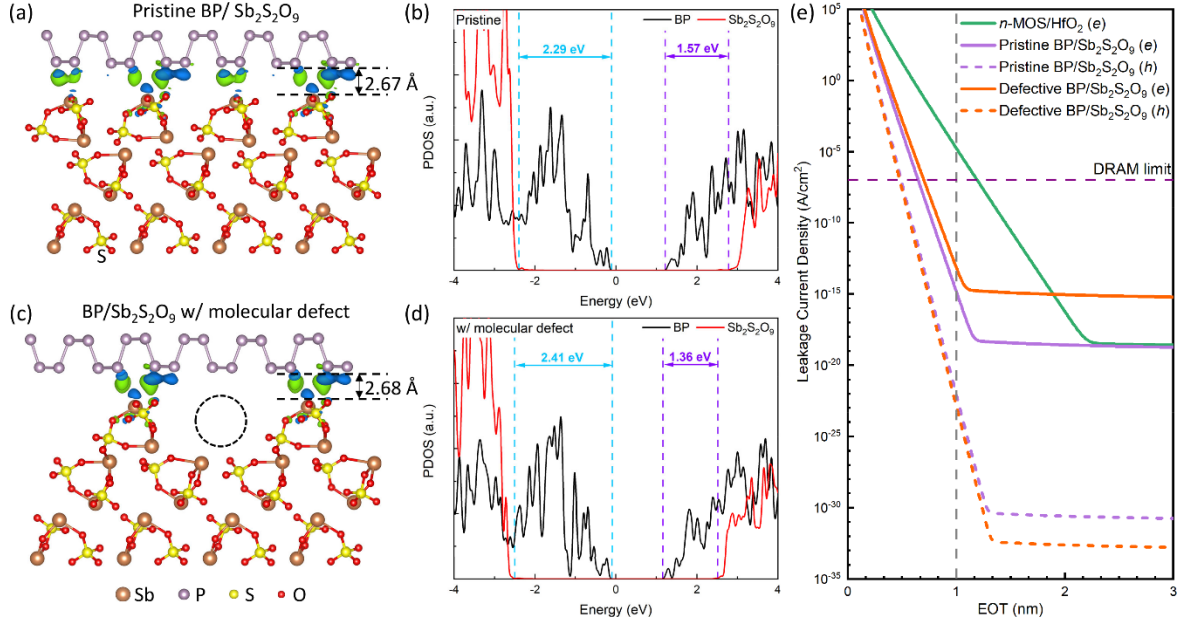


Figure 5. The interface between the $\text{Sb}_2\text{S}_2\text{O}_9$ (001) surface and BP monolayer. (a) The side view of the interface with the charge redistribution superimposed; (b) the projected density of states of the interface; (c-d) the counterparts of (a-b) in the presence of an interfacial $\text{Sb}_2\text{S}_2\text{O}_9$ molecular defect (the dashed circle). The green (blue) iso-surface with an iso-value of $0.001 e/\text{\AA}^3$ in (a) and (c) denotes charge accumulation (depletion) upon interface formation. (e) The leakage current density of BP/ $\text{Sb}_2\text{S}_2\text{O}_9$ based on the band offset estimated by the interface models in panels (a-d) as a function of the equivalent oxide thickness (EOT). e and h in the parentheses denote the carrier type (e for electron and h for hole). $n\text{-MOS}/\text{HfO}_2$ is also included for comparison. The DRAM limit ($< 10^{-7} \text{ A}/\text{cm}^2$) is marked using the purple dashed line.

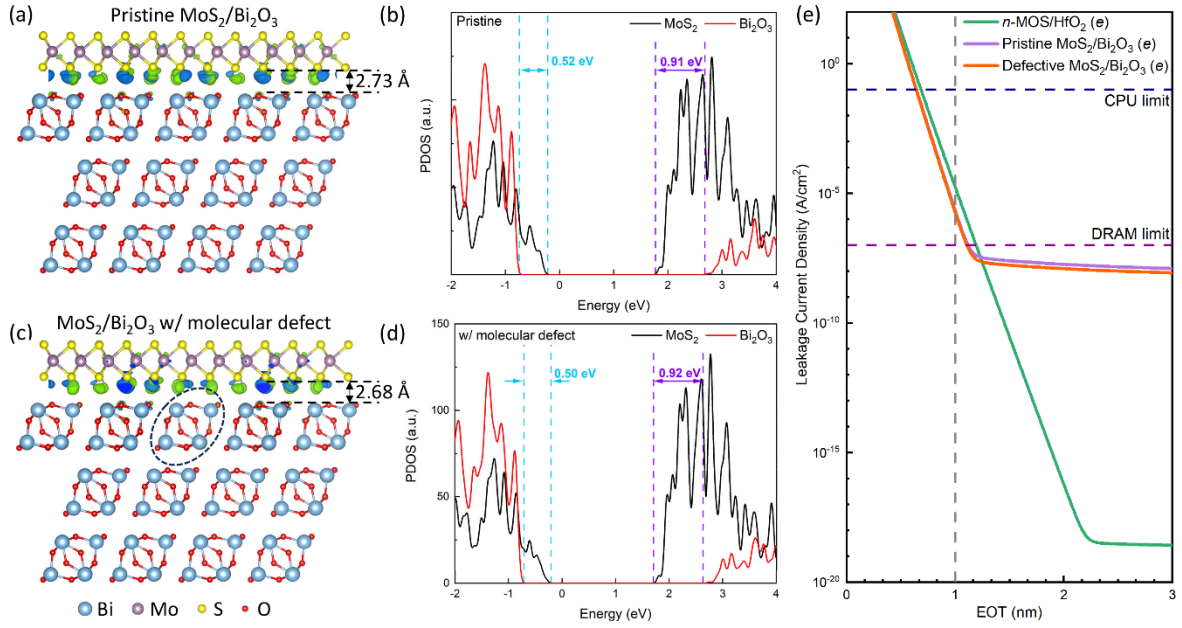


Figure 6. The interface between the (111) surface of Bi_2O_3 (mp-1188267) and MoS_2 monolayer. (a) The side view of the interface with the charge redistribution superimposed; (b) the projected density of states of the interface; (c-d) the counterparts of (a-b) in the presence of an interfacial Bi_2O_3 molecular defect (the dashed ellipse). The green (blue) iso-surface with an iso-value of $0.001 \text{ e}/\text{\AA}^3$ in (a) and (c) denotes charge accumulation (depletion) upon interface formation. (e) The leakage current density of $\text{MoS}_2/\text{Bi}_2\text{O}_3$ based on the band offset estimated by the interface models in panels (a-d) as a function of the equivalent oxide thickness (EOT). e and h in the parentheses denote the carrier type (e for electron and h for hole). $n\text{-MOS}/\text{HfO}_2$ is also included for comparison. The CPU limit ($< 10^{-1} \text{ A}/\text{cm}^2$) and the DRAM limit ($< 10^{-7} \text{ A}/\text{cm}^2$) are marked using the navy and purple dashed lines, respectively.

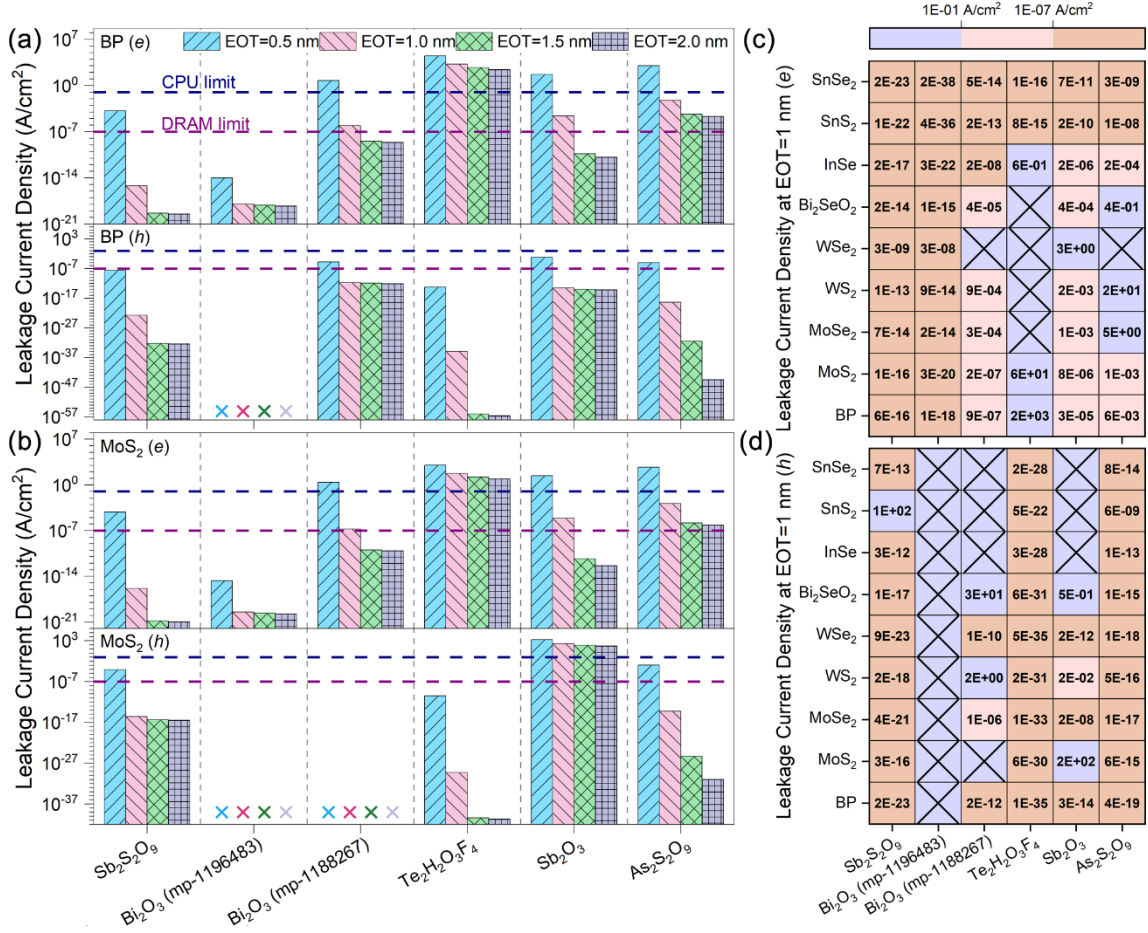


Figure 7. The leakage current density for 2D semiconductors/IMCs. (a-b) The leakage current density across IMCs interfaced with (a) BP and (b) MoS₂, respectively. The charge carrier in the top (bottom) panel is electron (hole). The equivalent oxide thickness (EOT) of IMCs is set to 0.5, 1.0, 1.5 and 2.0 nm. The CPU limit ($< 10^{-1}$ A/cm²) and the DRAM limit ($< 10^{-7}$ A/cm²) are marked using the navy and purple dashed lines, respectively. (c-d) the leakage current density across IMCs interfaced with the nine selected 2D semiconductors at EOT=1 nm with the charge carrier being (c) electron and (d) hole, respectively. The crosses mark the interfaces where the band offset is so small that quantum tunnelling across IMCs is significant under the applied gate voltage of 355 mV.

Table 1. The calculated electronic ($\epsilon_{\text{ele.}}$) and ionic contribution ($\epsilon_{\text{ion.}}$) to the polycrystalline total dielectric constant (ϵ), electronic band gap (E_g in eV), the product of the minimum polycrystalline total dielectric constant (ϵ_{min}) with E_g , the energy storage indicator ($\sqrt{\epsilon_{\text{min}}} \cdot E_g$), the inter-cluster binding energy (E_B in meV/Å²), the maximum vibrational frequency (ω_{max} in THz), and the breakdown field (F_{BD} in MV · cm⁻¹) of the six screened IMC candidates in a descending order of $\epsilon_{\text{min}} \cdot E_g$. The value in the first (second) row of $\epsilon_{\text{ele.}}$, $\epsilon_{\text{ion.}}$ and ϵ denotes the estimated minimum (maximum) of the polycrystalline dielectric constant. The values in parentheses correspond to the HSE06 counterparts.

	$\epsilon_{\text{ele.}}$	$\epsilon_{\text{ion.}}$	ϵ	E_g	$\epsilon_{\text{min}} \cdot E_g$	$\sqrt{\epsilon_{\text{min}}} \cdot E_g$	E_B	ω_m	F_{BD}
Sb₂S₂O₉ (mp-638424)	3.496 3.504	14.850 15.345	18.479 18.849	4.160 (5.555)	76.866 (102.640)	17.881 (23.877)	-18.622	33.258	9.936 (17.681)
Bi₂O₃ (mp-1196483)	6.228 6.228	20.399 20.399	26.627 26.627	2.342 (3.316)	62.355 (88.307)	12.084 (17.113)	-26.136	17.325	1.818 (2.661)
Bi₂O₃ (mp-1188267)	5.962 5.962	12.937 12.937	18.898 18.898	2.314 (3.574)	43.727 (67.539)	10.059 (15.536)	-23.195	18.216	1.889 (3.104)
Te₂H₂O₃F₄ (mp-1191341)	3.116 3.134	4.724 5.547	8.066 8.681	4.572 (5.936)	36.877 (47.878)	12.984 (16.858)	-13.558	96.063	179.900 (451.624)
Sb₂O₃ (mp-1999)	5.036 5.036	7.098 7.098	12.134 12.134	2.941 (3.907)	35.689 (47.406)	10.246 (13.609)	-16.512	20.441	2.811 (4.080)
As₂S₂O₉ (mp-27739)	3.215 3.237	4.481 5.539	8.039 8.777	4.173 (5.729)	33.545 (46.057)	11.831 (16.244)	-10.954	36.750	12.084 (23.613)