

Supporting Information for

A Computational Study of MoS₂/HfO₂ Defective Interfaces for Nanometer-Scale Electronics

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In order to determine the thermodynamic stability of the different interface models, we investigate their formation energies. The ground state of the MoS₂/HfO₂ interface is determined by minimizing the thermodynamic potential. The relative stability of the different interface models is then obtained by comparing their formation energies, given by:

$$E^{form} = \frac{E_{tot} - n E_{Hf} - m E_S - k E_{Mo} - l \mu_O - p \mu_H}{A}, \quad (1)$$

where E^{form} is the interface formation energy, E_{tot} is the total energy of the system, A is the total interfacing area of the slab, μ_i are the chemical potentials for the respective elements and n, m, k, l and p are the number of Hf, S, Mo, O and H atoms. The total energy (DFT) is used here (instead of the Gibbs free energy) for the calculations of the formation energies since the entropy contributions and enthalpy changes due to finite temperature are insignificant for all the structures, resulting in an insignificant change in the relative interface formation.¹

The energy of bulk HfO₂ and MoS₂ can be written in terms of the gas phase reaction of an oxygen molecule and the Hafnium metal and bulk Mo and S and their respective heats of formation:

$$E_{HfO_2}(bulk) = E_{Hf}(bulk) + \mu_{O_2}(bulk) + \Delta H_{HfO_2}^f$$

$$E_{MoS_2}(bulk) = E_{Mo}(bulk) + 2\mu_S(bulk) + \Delta H_{MoS_2}^f. \quad (2)$$

Using equation (2) and setting the oxygen gas phase as a reference, the numerator of equation (1) can be re-written as follows:

$$E^{form} = E_{tot} - [n (E_{HfO_2}(bulk) - \mu_{O_2}(bulk) - \Delta H_{HfO_2}^f) + mE_S + k (E_{MoS_2}(bulk) - 2\mu_S(bulk) - \Delta H_{MoS_2}^f)] - l\mu_O - p\mu_H \quad (3)$$

Now, one can rearrange this equation to obtain the interface formation energy per unit area,

$$E^{form} = \frac{E_{tot} - nE_{HfO_2}(bulk) - kE_{MoS_2}(bulk) + n\Delta H_{HfO_2}^f + k\Delta H_{MoS_2}^f + (2n - l)\mu_O + (2k - m)\mu_S - p\mu_H}{A} \quad (4)$$

With the restriction of the chemical potential of oxygen and hafnium,

$$\mu_O \leq \mu_O(bulk) = \frac{1}{2} E_{O_2} \quad \text{and} \quad \mu_{Hf} \leq \mu_{Hf}(bulk) = E_{Hf} \quad (5)$$

The thermodynamic range of oxygen chemical potential for the interface model can then be obtained:

$$\frac{1}{2} (E_{O_2} + \Delta H^f) \leq \mu_O \leq \frac{1}{2} E_{O_2} \quad \text{which results in} \quad -10.39 \text{ eV} \leq \mu_O \leq -5.01 \text{ eV} \quad (6)$$

The interface formation energy as a function of oxygen chemical potential (μ_o) is shown in the Figure 3 of the main body of the paper. The right hand side corresponds to the O-rich limit (*i.e.*, μ_o is set to zero) whereas the left hand side of the plot represents the O-poor limit. Similar results were obtained for III-V and high- κ interfaces.^{2,3} To compare our results with realistic ALD oxide growth conditions of HfO₂ on MoS₂ at 600K, we correlate the chemical potential with the oxygen partial pressure using the following equation (plotted on the top axis of Figure 3):

$$\mu_o(T, P) = \mu_o(T, P^0) + \frac{1}{2} k T \ln\left(\frac{P}{P^0}\right), \quad (7)$$

where, P and P^0 are the pressures at T temperature and at one atmosphere, respectively.

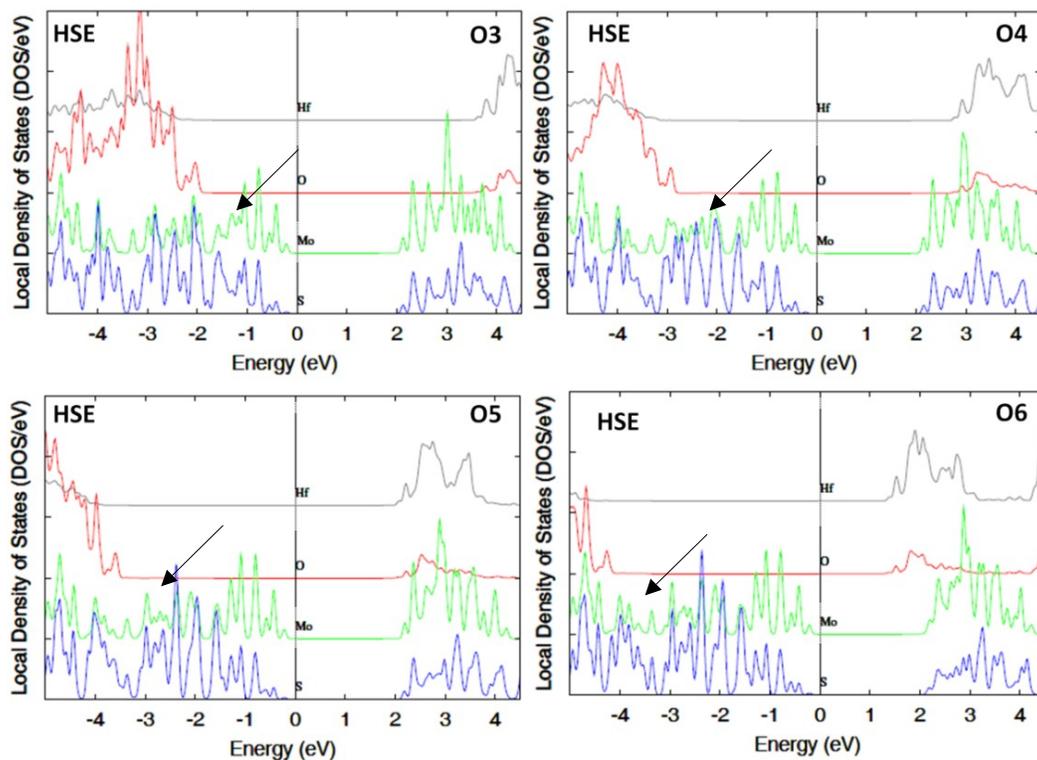


Figure S1. Estimation of the band offsets from local DOS for the MoS₂/HfO₂ interface, as obtained from HSE calculations for various interfacial O concentrations. The zero of the energy is aligned to the Fermi level. The arrows mark the VBOs (with respect to the Fermi level). CBOs can always be easily obtained from VBOs and band gaps (see Table S1).

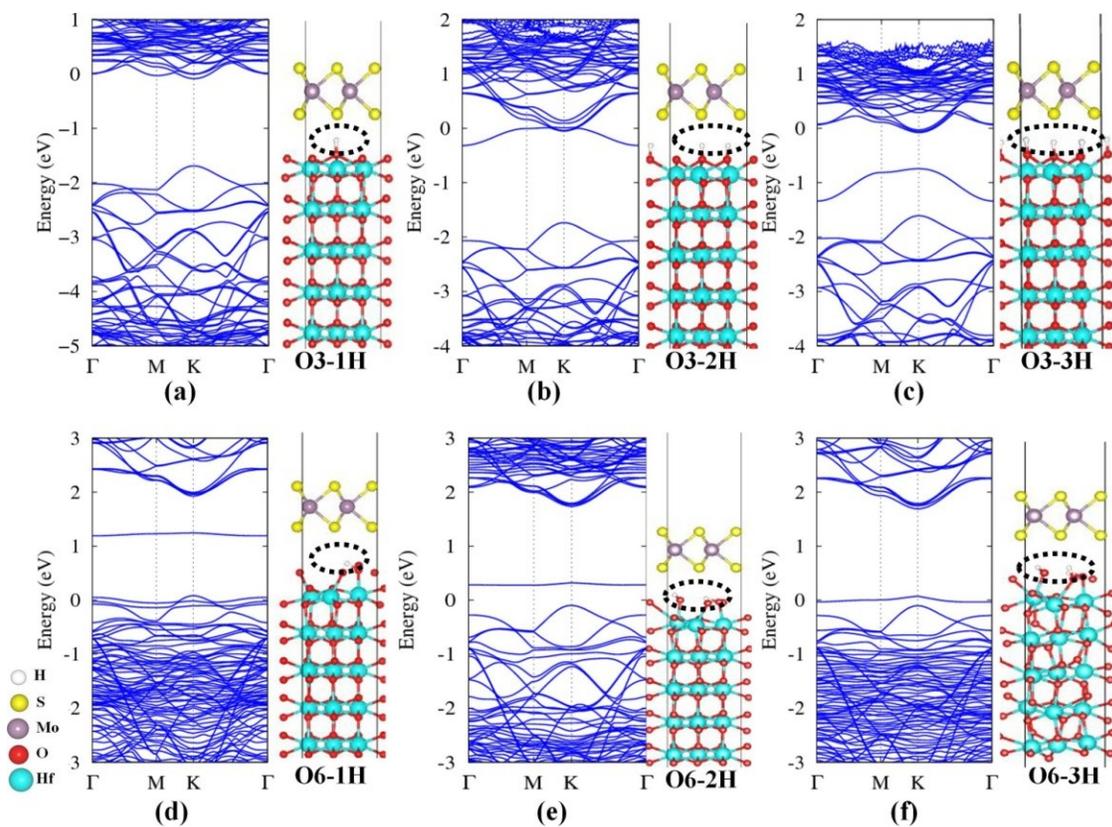


Figure S2. Electronic band structures of $\text{MoS}_2/\text{HfO}_2$ interface with H and OH bonding defects, for low (O3, shown in panels a-c) and high oxygen concentrations (O6, shown in panels d-f). The zero of the energy is aligned to the Fermi level. The atomic structures of the $\text{MoS}_2/\text{HfO}_2$ interfaces for several interfacial hydrogen concentrations (1H-3H) are also shown. Hafnium, oxygen, molybdenum and sulfur are represented by turquoise, red, purple and yellow spheres, respectively (H impurities at the interface result in OH bonding).

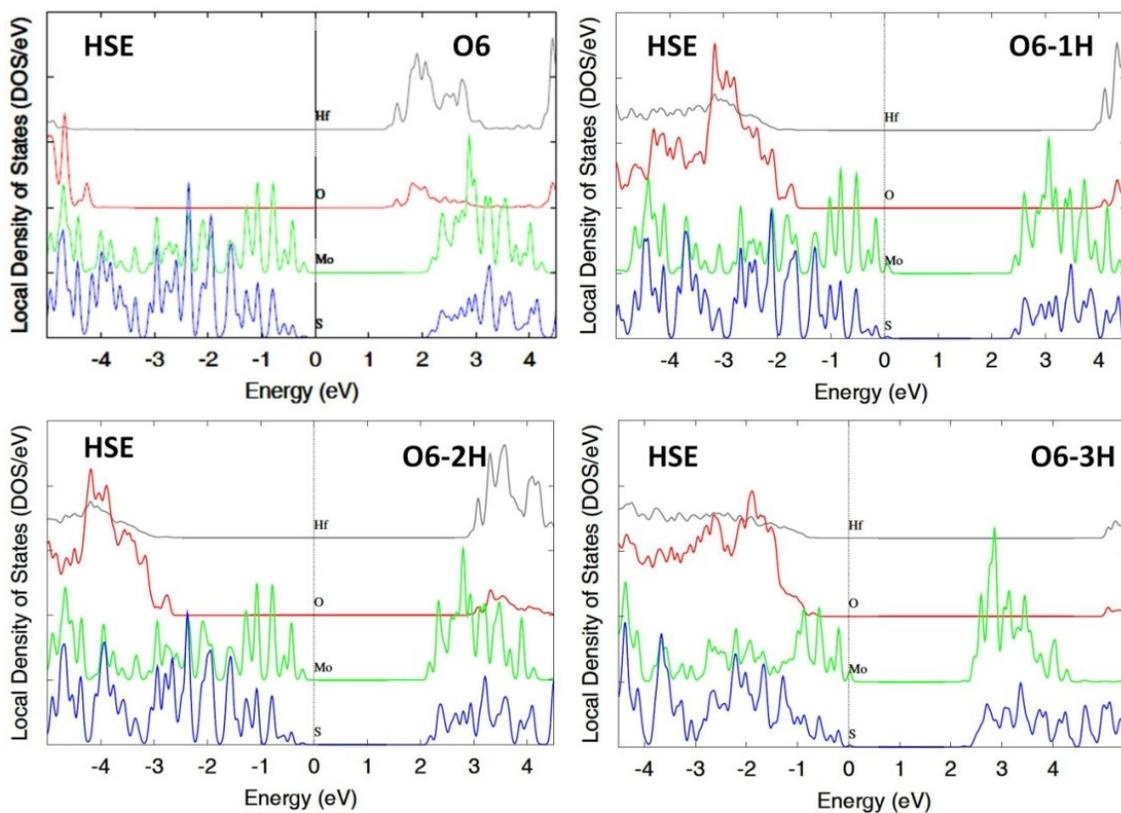


Figure S3. Estimation of band offsets from local DOS for the MoS₂/HfO₂ interface with H defect incorporation to the O6 model, as obtained from HSE calculations. The zero of the energy is aligned to the Fermi level.

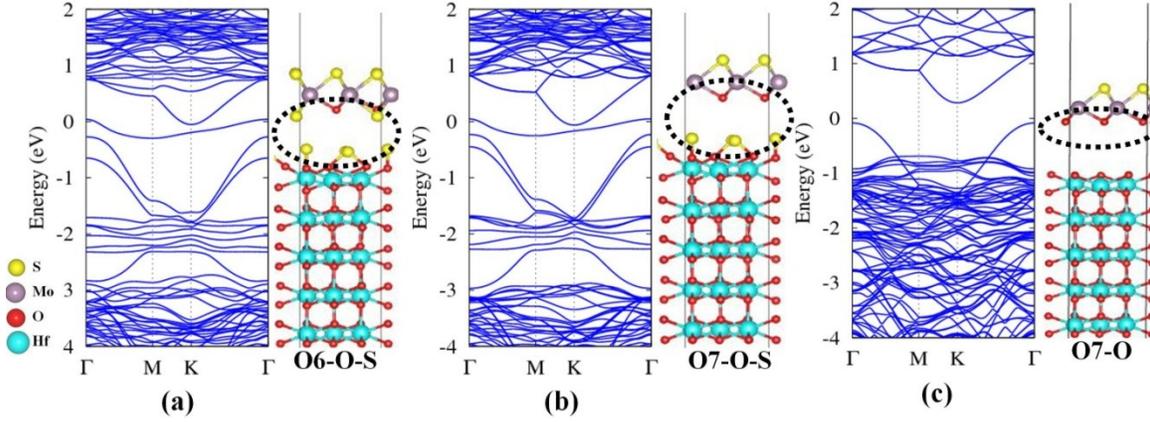


Figure S4. Electronic band structures of the $\text{MoS}_2/\text{HfO}_2$ interface with several S-O bonding defects at the interface (see text for details): a) O-S exchange, b) S layer replaced by O, along with O-S interfacial bonding and c) single S-M-O layer and HfO_2 interface. The zero of the energy is aligned to the Fermi level. The corresponding atomic structures of the $\text{MoS}_2/\text{HfO}_2$ interfaces with S-O bonding defects are also shown. Hafnium, oxygen, molybdenum and sulfur are represented by turquoise, red, purple and yellow spheres, respectively.

TABLE S1: Band offsets between MoS_2 and HfO_2 for various interfacial oxygen concentrations.

Interface Model	Concentration (#O atoms/cm ²)	VBO (GGA) (eV)	VBO (HSE) (eV)	E _g (GGA) (eV)	E _g (HSE) (eV)	CBO (GGA) (eV)	CBO (HSE) (eV)
O ₃	0.88×10^{15}	1.0	1.8	1.84	2.34	1.16	1.82
O ₄	1.18×10^{15}	1.8	2.6	1.83	2.37	0.37	1.03
O ₅	1.48×10^{15}	2.3	3.2	1.43	2.28	0.27	0.52
O ₆	1.76×10^{15}	2.8	4.1	1.0	1.59	0.20	0.40

References:

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- 2 KC, S.; Dong, H.; Wang, W.; Longo, R. C.; Xiong, K.; Wallace, R. M.; Cho, K. Electronic Properties of InP(001)/HfO₂(001) Interface: Band Offsets and Oxygen Dependence. *J. Appl. Phys.* **2014**, *115*, 023703.
- 3 Xiong, K.; Wang, W.; Zhernokletov, D. M.; Longo, R. C.; Wallace, R. M.; Cho, K. Interfacial Bonding and Electronic Structure of HfO₂/GaSb Interfaces: A First Principles Study. *Appl. Phys. Lett.* **2013**, *102*, 022901.