

- **Electronic Supplementary Information** -

An origin of unintentional doping in transition metal dichalcogenides: Role of hydrogen impurity

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1. Computational details for TMDs and SiO₂

We selected k-meshes to ensure the energy convergence within 10 meV/atom. To be specific, 5×5×5 and 6×6×1 k-point grid were employed for primitive cells of SiO₂ and every TMD, respectively. The gaussian smearing method with the smearing width of 0.05 eV was used for all calculations in our study. The monolayers of TMDs can have various polymorphs. In this study, we employed the phases experimentally reported; 1H phase for MoS₂, MoSe₂, MoTe₂, WS₂, WSe₂, WTe₂, and SnS₂ while the 1T phase for ReS₂. Unitcells of monolayer TMDs includes at least 10 Å of vacuum and their atomic positions and in-plane lattice were fully relaxed. The specific cell geometries for the calculations of TMDs are shown in Fig S1.

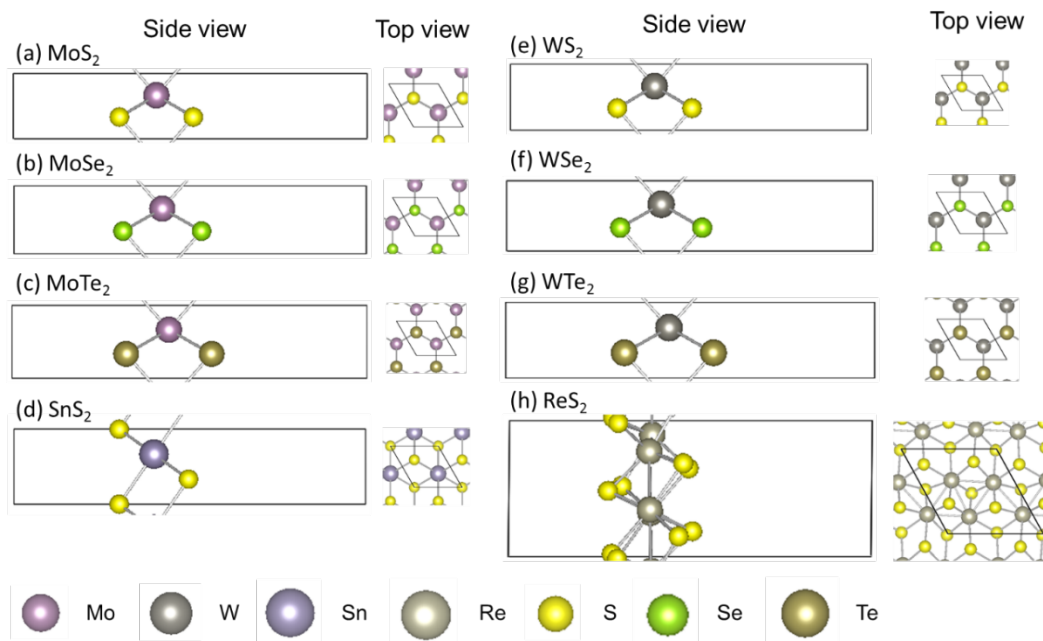


Fig S1. Unitcells of monolayer TMDs.

2. Hydrogen defect in SiO₂

For hydrogen defect calculations, the primitive cell of SiO₂ was expanded to 2×2×2 supercell and an hydrogen atom was added to it as shown in Fig. S2.

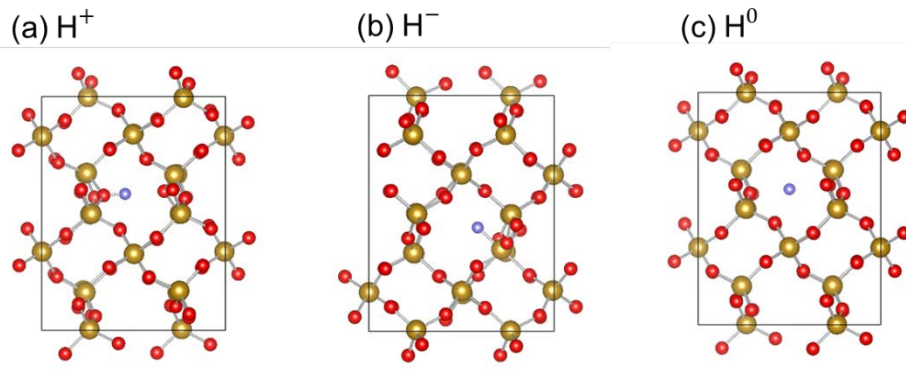


Fig S2. The atomic structures of SiO₂ supercells with a hydrogen impurity for (a) H⁺, (b) H⁻, and (c) H⁰.

All of atomic positions were relaxed using $2 \times 2 \times 2$ k-points. In the case of H⁰ which has singly occupied state, we performed spin-polarized calculation.

The band edges in quartz SiO₂ lie at different k-points indicating that its band gap is indirect, and in our calculation, the band gap is 7.54 eV which underestimates the experimental band gap of 9.3 eV. Figure S3 shows the density of states for SiO₂ supercells including hydrogen impurities. The level of a single particle state of hydrogen in SiO₂ depends on its chemical environment. The hydrogen impurity in positive state forms a bond with an oxygen atom, which causes the hydrogen level to lie somewhere above conduction band. Therefore, the corresponding defect level is not found between the band gap. In contrast, the negative hydrogen forms a bond with a Si atom, resulting in the occupied defect level relatively close to the valence band maximum (VBM). On the other hand, the neutral hydrogen does not prefer any clear chemical bond with neighboring atoms and its defect level resides inside the band gap that is singly occupied.

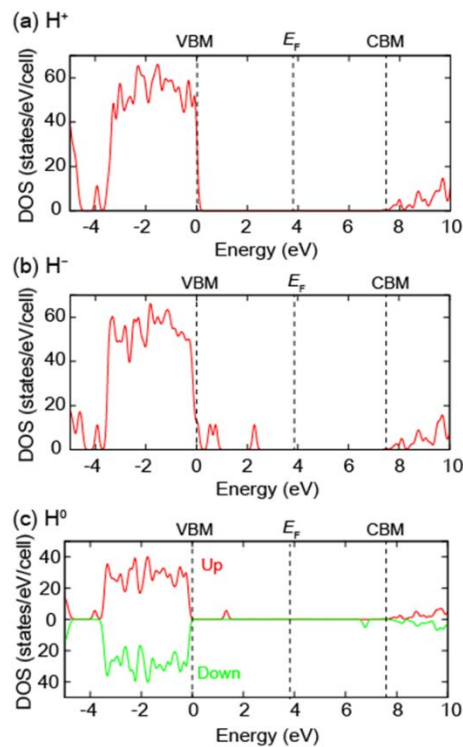


Fig S3. Density of states of SiO₂ supercells with a hydrogen impurity for (a) H⁺, (b) H⁻, and (c) H⁰.

3. Slabs of SiO₂ (0001) surface

We initially generated a slab of (0001) surface of SiO₂ including 44 atoms as well as 15 Å of vacuum and 4 hydrogen atoms were attached to surface oxygen for modelling the silanol surface as shown in Fig. S4(a). In the case of the siloxane surface, a slab geometry was constructed based on 2×2×1 supercell with 180 atoms and some atomic positions at the surfaces were shifted to make six-membered ring structures as can be seen in Fig. S4(b). In both slab calculations, two surfaces (top and bottom) were symmetrically modelled. We relaxed the positions of atoms at the surface corresponding to 2(8) SiO₂ units at the outmost regions of the silanol (siloxane) surface in our calculations while the coordinates of the others were fixed to bulk positions. We selected 4×4×1 and 2×2×1 k-points grids for the silanol and siloxane surface.

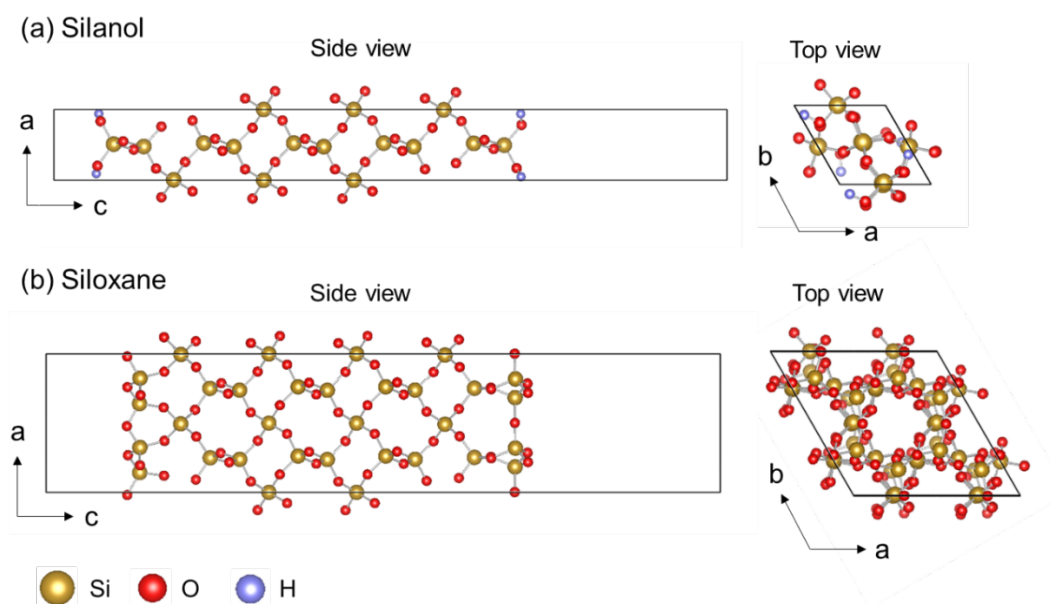


Fig S4. The atomic structures of (a) silanol and (b) siloxane surfaces of SiO₂

4. SiO₂/MoS₂ interface modelling

We modelled an interface of SiO₂/MoS₂ where MoS₂ lies on oxygen-terminated SiO₂(0001) surface with the silanol group (Si-OH) as shown in Fig. S5(a). Since the theoretical lattice parameters of MoS₂ and SiO₂ are 3.18 and 5.01 Å, respectively, a supercell is constructed on the basis of 3×3 cell of MoS₂ monolayer and 2×2 cell of SiO₂(0001) surface. In this calculation, 32 formula units of SiO₂ are included and dangling bonds of Si at the bottom are passivated by hydrogen. The positions of 8 formula units of SiO₂ on the surface including hydrogen atoms are relaxed before forming the interface. The in-plane lattice parameter of the supercell is set to that of MoS₂. To determine the optimum separation between SiO₂ and MoS₂, we computed the binding energy (E_b) defined by $E_b(d) = E_{\text{SiO}_2/\text{MoS}_2}(d) - (E_{\text{SiO}_2} + E_{\text{MoS}_2})$ where $E_{\text{SiO}_2/\text{MoS}_2}$ is the total energy of SiO₂/MoS₂ system at the given separation, d , and E_{SiO_2} and E_{MoS_2} are the total energies of isolated SiO₂ and MoS₂, respectively. The van der Waals energy was considered based on the non-local van der Waals density functional (vdW-DF) scheme as implemented in VASP. For the calculation of $E_{\text{SiO}_2/\text{MoS}_2}$, we used 4×4×1 k-points grid. Figure S5(b) shows the change of the binding energy with respect to d considering and the optimum separation was determined by the point giving the minimum binding energy.

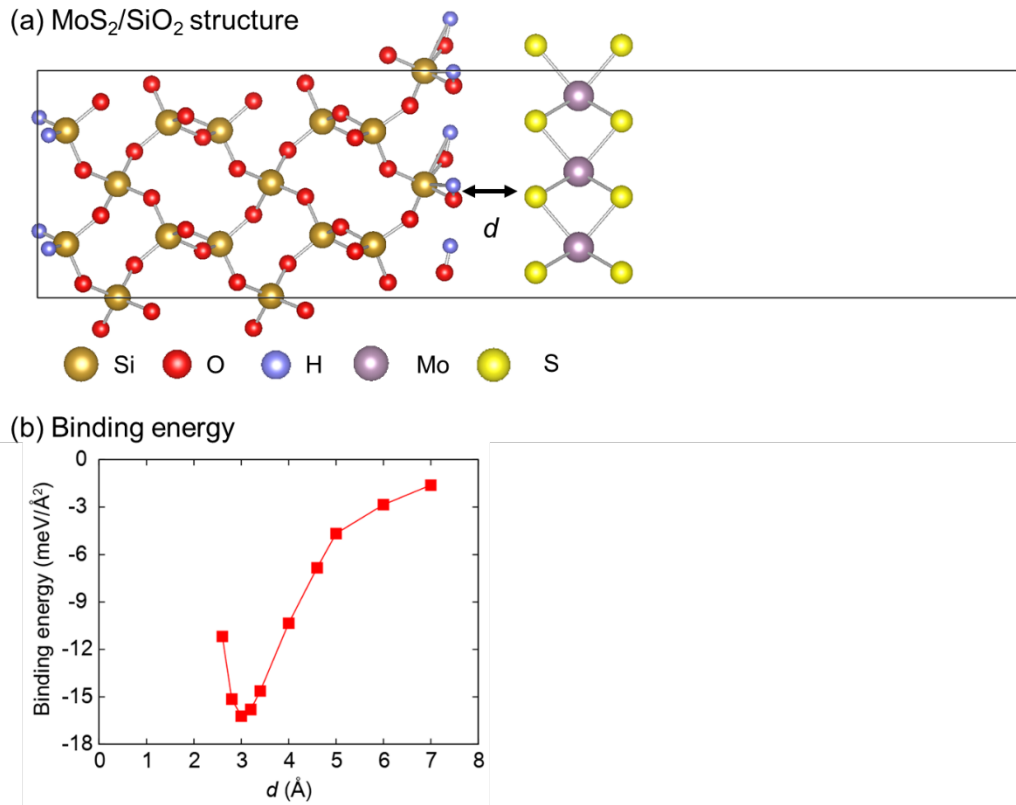


Fig S5. (a) The atomic structure of MoS₂/SiO₂ interface. (b) Binding energy of MoS₂/SiO₂ as a function of the separation, d .

5. Modelling of an hydrogen impurity in MoS₂/SiO₂ interface

We calculated the hydrogen transition level in MoS₂/SiO₂ interface as shown in Fig. S6. For this computation, we used 4×4×1 k-points grid and atomic positions were relaxed within PBE calculations.

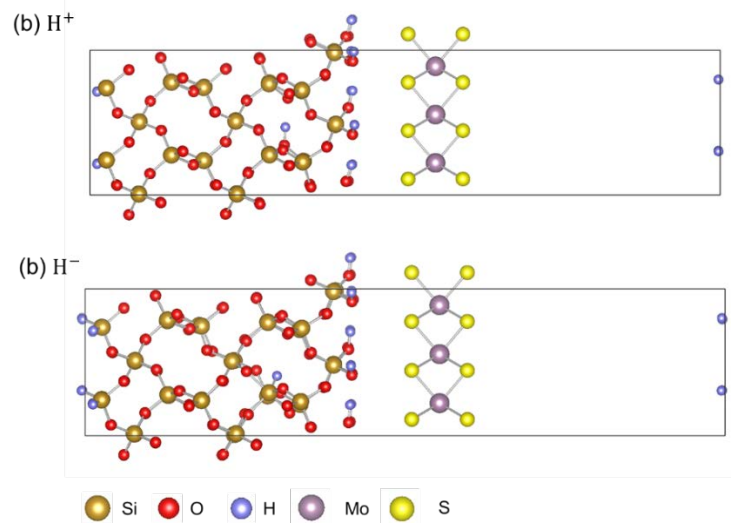


Fig S6. The atomic structures of for (a) H⁺ and (b) H⁻ in MoS₂/SiO₂ interface.

The below figure shows atomically resolved density of states for the interface structures shown in Fig. S6. It is noted that there is a clear difference in a position of a defect state induced by hydrogen impurity between (a) and (b); for H^+ , there is no in-gap state and the defect level resides above the conduction band of SiO_2 as well as MoS_2 while a localized level trapping electrons is created 0.2 eV below the conduction band minimum of MoS_2 for H^- . In general, the transition level of a defect lies somewhere between defect levels formed in different charge states, and therefore, we can understand why the resulting Fermi level appears close to the conduction band minimum of MoS_2 . (The specific value of the transition level is determined by the total energy in which the relaxation effects is considered together.)

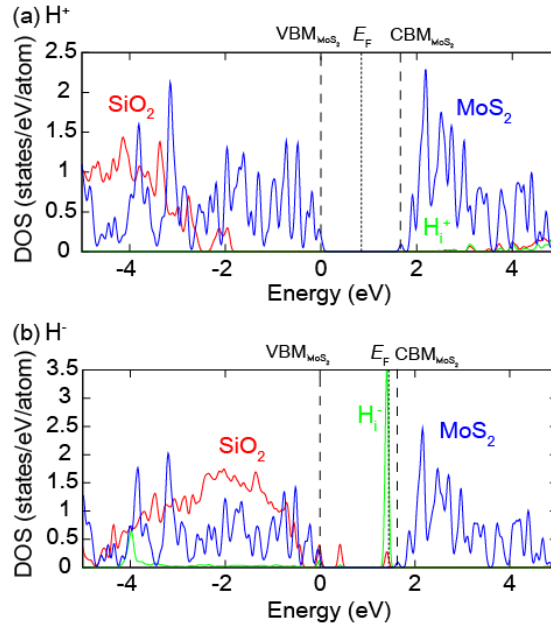


Fig S7. Atomically resolved density of states for the corresponding structures shown in Fig. S6.

6. A solver of Poisson's equation

We developed a solver of the Poisson's equation for MoS_2 - SiO_2 interfaces that calculates the Fermi level of MoS_2 in a self-consistent way considering the charge transfer and resulting interface dipole. The density of states of MoS_2 was described by the two dimensional free electron model and the effective mass is quoted from Cheiwchanchamnangij *et al.*, (*Phys. Rev. B* 2012, **85**, 205302). The hydrogen concentration is assumed to be 10^{12} cm^{-3} . The below figures show the Fermi level of MoS_2 before and after the charge transfer occurs.

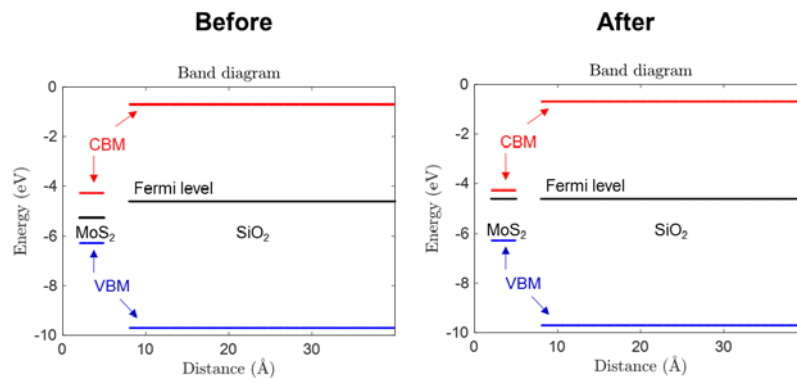


Fig S8. The Fermi level of MoS₂ before and after the charge transfer happens.