

A clean van der Waals interface between the high- k dielectric zirconium oxide and two-dimensional molybdenum disulfide

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A clean interface between high k dielectric and two-dimensional molybdenum disulfide

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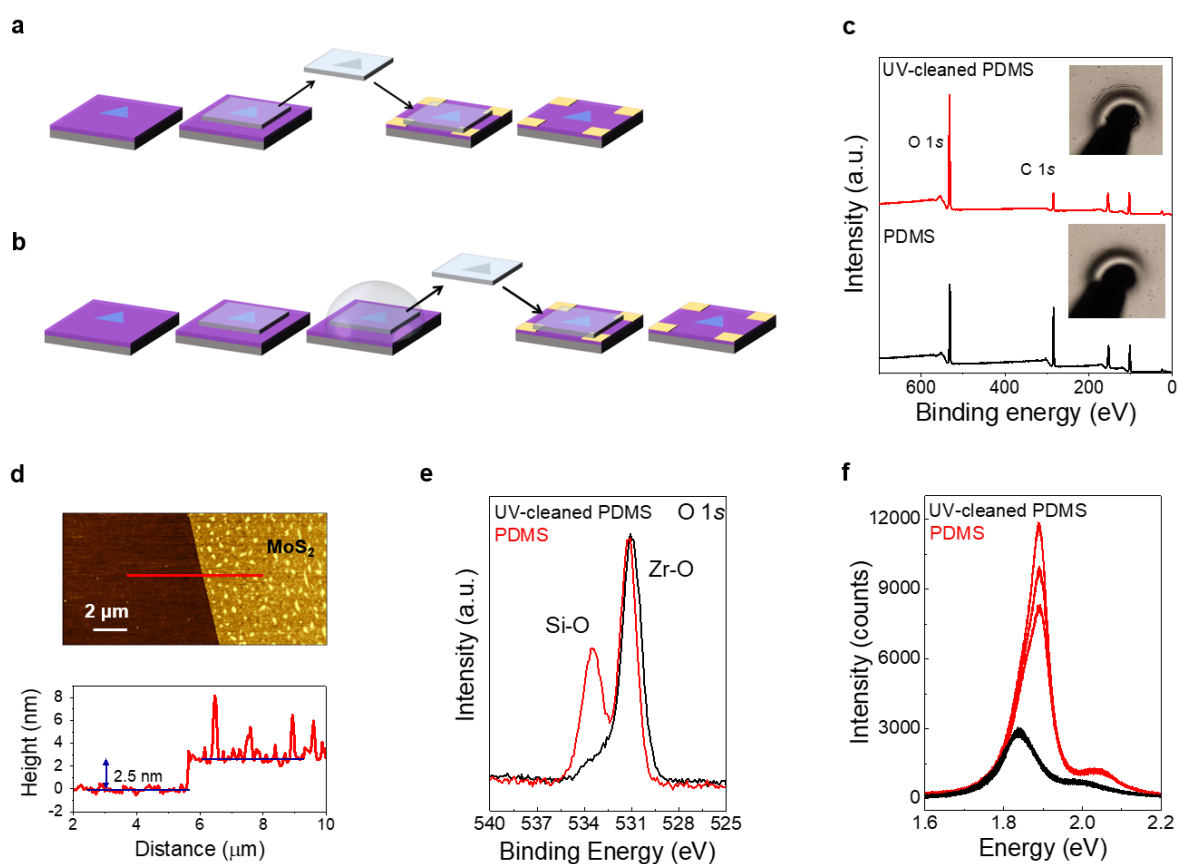
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S1: Clean sample preparation method

Polydimethylsiloxane (PDMS) dry transfer technique (schematic shown in **Supplementary figure 1a**) is widely used to transfer chemical vapor deposition (CVD) grown samples to target dielectrics. However, the viscoelastic characteristic of PDMS prevents monolayer TMD from making intimate contact with the substrate and leaves residue. In this study, we optimised the transfer process reported by Jain *et al* [1] using UV Ozone cleaning the PDMS and use water induced capillary force to separate the MoS₂ from growth substrate (schematic shown in **Supplementary figure 1b**). The XPS results in **Supplementary figure 1c** shows that the carbon contamination is reduced and the PDMS becomes more rigid. The AFM images in **Supplementary figure 1d** clearly show that the height for PMDS transferred monolayer MoS₂ is ~2.5 nm. In contrast, the UV-cleaned PDMS transferred monolayer MoS₂ shows a height of ~ 0.7 nm. XPS was performed to confirm the absence of residue from MoS₂/ZrO₂ samples transferred by UV-cleaned PDMS (**Supplementary figure 1e**). The O 1s signal from PDMS transferred sample clearly show an additional peak at higher binding energy, indicative of silicone residue, whereas the UV-cleaned PDMS transfer process result in considerably less

residue. The influence of the transfer method on the doping characterisation is also shown in **Supplementary figure 1f**. The PL spectra collected from three distinct areas on one flake are inconsistent when PDMS transfer is used. In addition, the PL spectra is more exciton dominated for PDMS transferred monolayer MoS₂, whereas the UV-cleaned sample is more trion dominated due to electron doping from SiO₂ substrate.



Supplementary figure 1. Clean transfer of CVD grown MoS₂. **a**, Schematic of PDMS assisted transfer method. **b**, Schematic of UV-cleaned PDMS transfer method. A water drop was introduced from the side of PDMS and driven by capillary force to transport underneath PDMS. The capillary force is strong enough to overcome the van der Waals force between MoS₂ and growth substrate. **c**, XPS survey spectra of PMDS and UV-cleaned PDMS clearly show that the C 1s peak is reduced after UV- Ozone cleaning. This gives less residue during

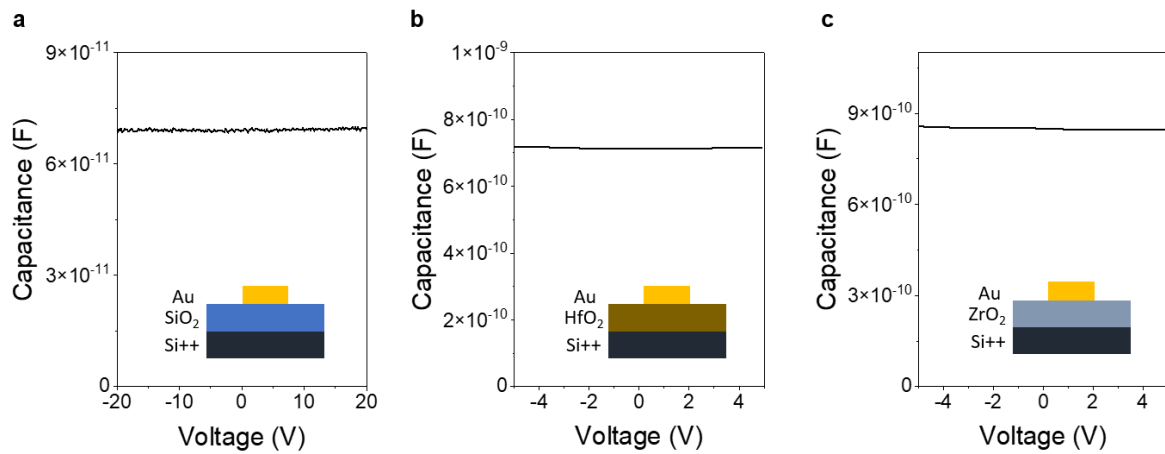
the transferring process. Inserts are photos of a tip brought in contact with PDMS and UV-cleaned PDMS, indicating the UV-cleaned PDMS is more rigid. **d**, AFM image of monolayer MoS₂ transferred onto new substrate using PDMS. The height profile shows that there is an air gap trapped between monolayer and substrate and the sample surface is not clean. **e**, O 1s of monolayer MoS₂ transferred onto ZrO₂ shows additional Si-O peak with PDMS transfer due to residue. **f**, PL of monolayer MoS₂ transferred on SiO₂ by PDMS and UV-cleaned PDMS. PDMS transferred samples are not consistent and show exciton dominant characteristics. UV-cleaned PDMS transferred samples give uniform PL signal and trion dominant signal due to intimate contact with SiO₂.

S2: Dielectric depositions and characterisations

90 nm of thermally grown SiO₂, 40 nm of ALD grown HfO₂, and 40 nm of ALD grown ZrO₂ on boron degenerately doped silicon substrates were used in this study. The ALD process was carried out using 60 sccm Ar as the carrier gas. Deposition of HfO₂ proceeded at 200 °C using TDMAHf and H₂O as precursors. The TDMAHf precursor container was heated to 75 °C. The pulse/purge times for TDMAHf and H₂O precursors were 60 ms/10 s and 250 ms/10 s, respectively. The ALD of ZrO₂ was carried out at 275 °C, and tetrakis(dimethylamino)zirconium (TDMAZr) and H₂O were the precursors. The TDMAZr precursor container was heated to 75 °C. The pulse/purge times for TDMAZr and H₂O were 60 ms/8 s and 250 ms/12 s, respectively.

The breakdown voltage of SiO₂ is over 20 V for 90 nm SiO₂ and 8 V for both HfO₂ and ZrO₂. The capacitance versus voltage (CV) measurements of SiO₂, HfO₂, and ZrO₂ were characterized with MIM structures, shown in **Supplementary figure 2**. The top contacts were made by metal deposition, with a shadow mask of 500-μm-diameter pattern. The CV

measurements were done at frequency of 10 kHz. The dielectric constant for HfO₂ and ZrO₂ are extracted to be 16 and 19, respectively.



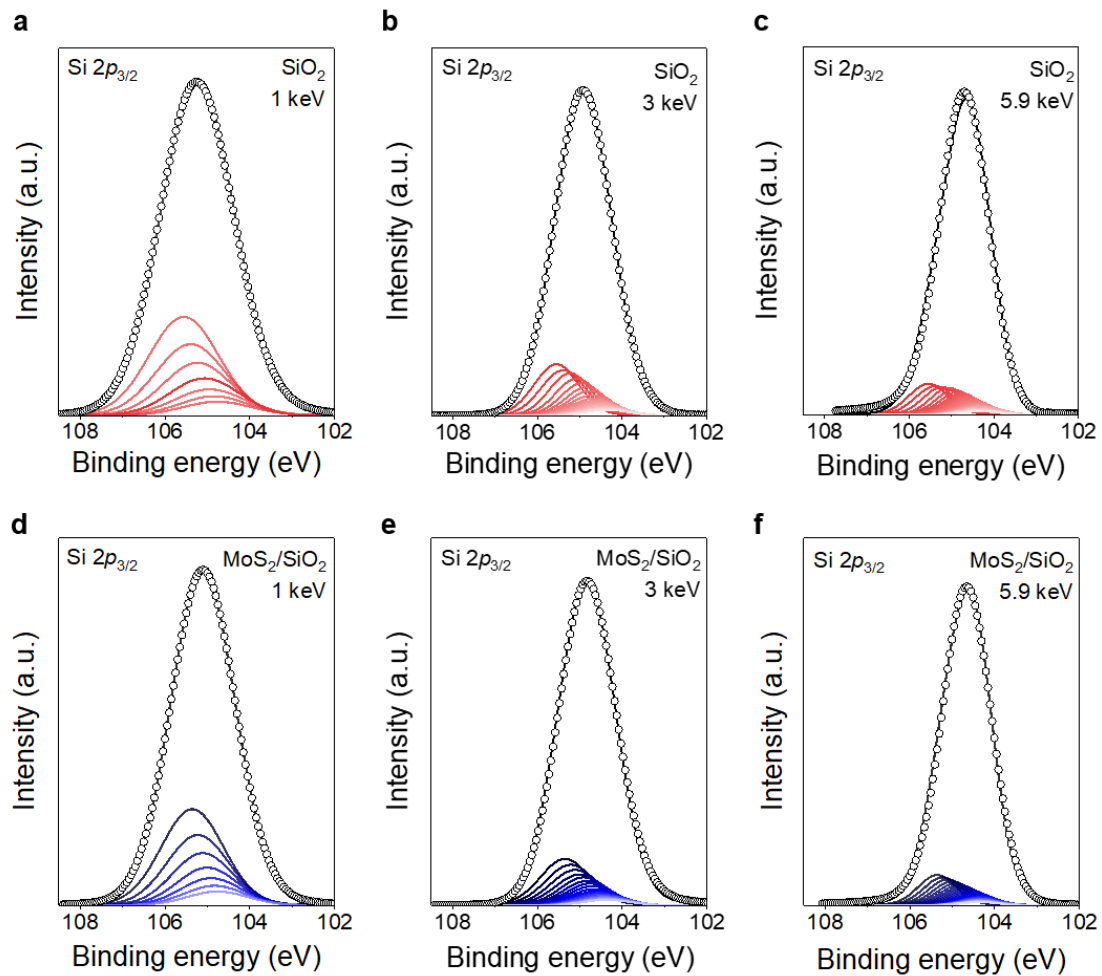
Supplementary figure 2. Capacitance- voltage measurements of the MIM structure for different substrates used in this study.

S3: Synchrotron data modelling

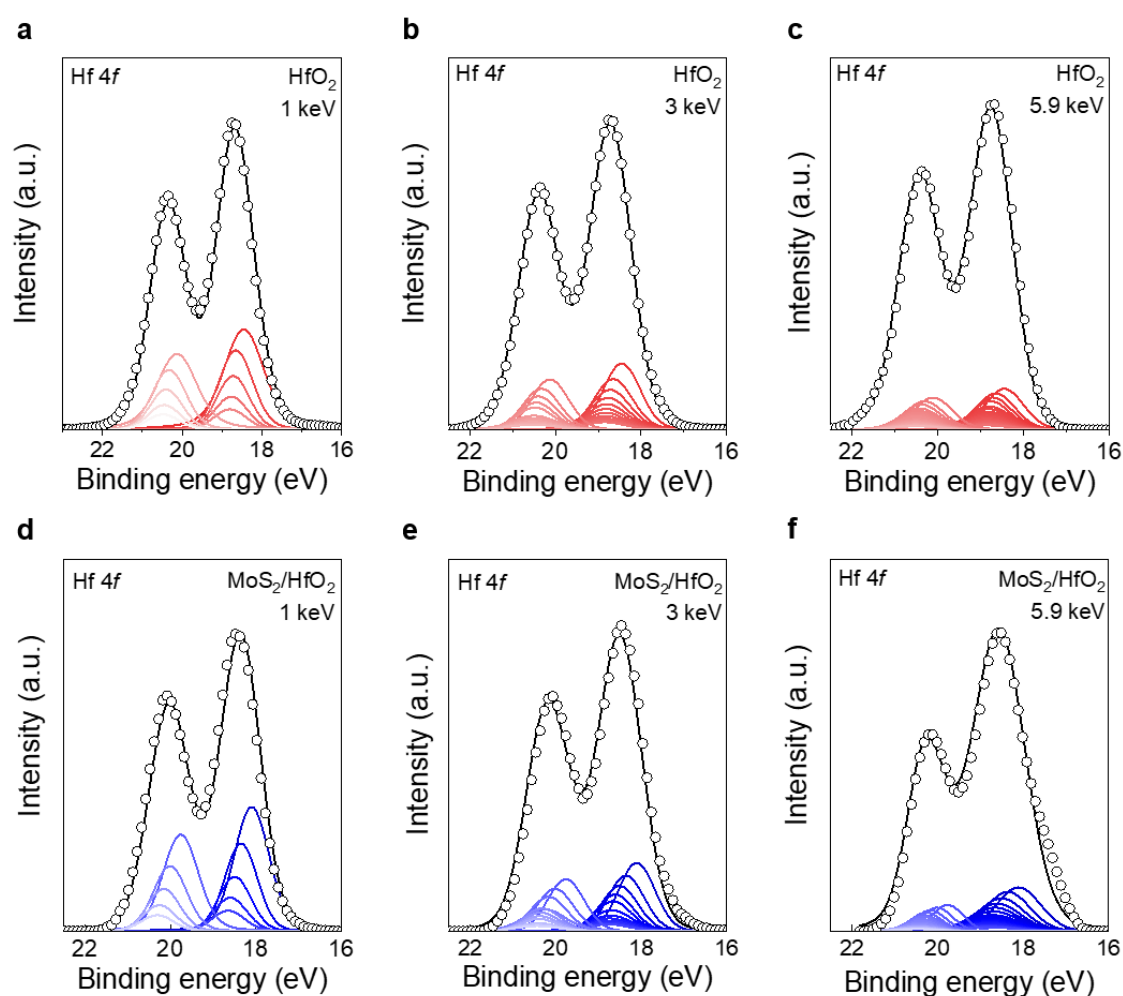
The method adopted in the present work for extracting band edge profiles is similar to those reported [2, 3]. The photoelectron inelastic mean free paths (λ) for different dielectrics and different X-ray excitation energies were obtained from NIST database [4]. For the same dielectric, a higher incident beam energy would result in a longer λ . The interface band bending profile can be extracted by soft and hard X-ray photoelectron spectroscopies.

For modelling the interface, the dielectrics were divided into a finite number of 0.5 nm-thick slices, of which the photoelectron signal (fitted with Voigt profiles) at depth d is damped by the factor of $e^{-\frac{d}{\lambda \cos \theta}}$, where λ is the photoelectron inelastic mean free path and θ is the photoelectron emission angle with respect to the surface normal. Thus, the intensity proportion from each slice could be determined. The slice model captures around 90% of the total

photoelectrons, the last 10% is fitted with a single Voigt profile. In the modelling for each substrate, the line shape is shared across all slices and the binding energy position of each slice is shared across all photon energies. The binding energies of the core level in the individual slices are allowed to shift to reflect the Fermi level shifts and to reproduce the measured line shape. The Si $2p$ and Hf $4f$ spectra are deconvoluted first before modelling. The depth-resolved Si $2p_{3/2}$ peaks from SiO₂ with and without MoS₂ on top are shown in **Supplementary figure 3**. Hf $4f$ spectra from HfO₂ and MoS₂/HfO₂ are summarized in **Supplementary figure 4**. The Hf $4f$ peaks recorded with 5.9 keV X-rays show significant differences, indicating that the influence of MoS₂ extends well into HfO₂.



Supplementary figure 3. XPS of SiO₂ and MoS₂/SiO₂ with different probing energy. a - c, Si 2*p* of SiO₂ probed with 1 keV, 3 keV, and 5.9 keV. **d - f,** Si 2*p* of MoS₂/SiO₂ probed with 1 keV, 3 keV, and 5.9 keV. Qualitatively, the Si 2*p* spectra collected from top surface is broader and has higher binding energy compared to the spectra collected from bulk region. The Si 2*p* of SiO₂ is higher than Si 2*p* of MoS₂/SiO₂ at all probing energies due to more band bending at the surface.



Supplementary figure 4. XPS of HfO₂ and MoS₂/HfO₂ with different probing energy. a - c, Hf 4*f* of SiO₂ probed with 1 keV, 3 keV, and 5.9 keV. **d - f,** Hf 4*f* of MoS₂/HfO₂ probed with 1 keV, 3 keV, and 5.9 keV. The peak shifts after contacting MoS₂ at lower probing energy but

gets broadening at higher probing energy, indicating the influence of MoS₂ extends to bulk HfO₂.

S4. Raman analysis of MoS₂ on different dielectric substrates.

Summary of Raman peak positions and full widths at half maximum (FWHM) for the A_{1g} mode of MoS₂ on different dielectric substrates. The values are extracted from five independent Raman measurements for each sample type, demonstrating the influence of the underlying dielectric on the doping of MoS₂.

	Peak position of A _{1g}	FWHM of A _{1g} peak
MoS ₂ on SiO ₂	403.82 ± 0.07 cm ⁻¹	4.81 ± 0.61 cm ⁻¹
MoS ₂ on HfO ₂	404.38 ± 0.32 cm ⁻¹	4.76 ± 0.37 cm ⁻¹
MoS ₂ on ZrO ₂	405.23 ± 0.45 cm ⁻¹	4.19 ± 0.20 cm ⁻¹

Reference:

1. Jain, A. et al. Minimizing residues and strain in 2D materials transferred from PDMS, *Nanotechnology*, 29, 265203, (2018)
2. Sushko, P. V. & Chambers, S. A. Extracting band edge profiles at semiconductor heterostructures from hard-x-ray core-level photoelectron spectra. *Sci. Reports* 10, 1–10 (2020)
3. Stübinger, M. et al. Hard x-ray photoemission spectroscopy of LaVO₃/SrTiO₃: Band alignment and electronic reconstruction. *Phys. Rev. B* 103, 235128 (2021)
4. NIST Standard Reference Database 71 | NIST. doi:10.18434/T48C78.

