1 A dielectric-defined lateral heterojunction in a monolayer semiconductor

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21 Abstract

22 Due to their low dimensionality, two-dimensional semiconductors, such as monolayer molybdenum disulfide, 23 have a range of properties that make them valuable in the development of nanoelectronics. For example, the 24 electronic bandgap of these semiconductors is not an intrinsic physical parameter and can be engineered 25 through the dielectric environment around the monolayer. Here we show that this dielectric dependent elec-26 tronic bandgap can be used to engineer a lateral heterojunction within a homogeneous MoS_2 monolayer. We 27 visualize the heterostructure with Kelvin probe force microscopy and examine its influence on electrical 28 transport experimentally and theoretically. We observe a lateral heterojunction with ~90 meV band offset 29 due to different bandgap renormalization of monolayer MoS₂ when it is on a substrate in which one segment 30 is made from an amorphous fluoropolymer (Cytop) and another segment from hexagonal boron nitride. This 31 heterostructure leads to a diode-like electrical transport with a strong asymmetric behaviour. 32

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Atomically thin semiconductors, such as monolayer transition metal dichalcogenides (TMDs)¹⁻³, provide a 38 platform for investigating nanoscale quantum phenomena⁴⁻⁶ and have a range of potential applications in 39 40 nanoelectronics⁷⁻⁹. A freestanding monolayer of a transition metal dichalcogenide experiences a reduced 41 dielectric screening and an enhanced Coulomb interaction by virtue of its atomically thin structure. In 42 contrast to bulk materials, electric field lines between charges inside a monolayer can extend substantially outside of the layer¹⁰⁻¹². This leads to an ineffective intrinsic screening that enhances electronic interaction 43 44 and leads to large exciton binding energies between 0.2-0.7 eV in these materials¹⁰⁻¹⁸. Furthermore, the electronic band structure of atomically thin 2D layers is not completely intrinsic to the material and can be strongly affected by the surrounding environment^{13,19-23}. With both electron and hole experiencing the screening, the conduction and valence band edges shift in the opposite direction^{12,13,21,23}. *Ab initio* 45 46 47 calculations predict that there is a monotonic decrease of electronic bandgap energy with increasing 48 dielectric screening, where the reduction of bandgap can reach the order of hundreds of meV relative to the bandgap of a freestanding monolayer^{13,20,22,24-27}. Recent scanning tunnelling spectroscopy¹³ and optical 49 50 spectroscopy^{20,22} studies provided evidence that the bandgap renormalization phenomenon in atomically thin 51 52 2D semiconductors can indeed be significant. Such bandgap renormalization may have a profound effect on 53 electrical transport in atomically thin 2D semiconductors; yet, the effect has not been investigated thoroughly 54 and its implications in the development of applications based on 2D materials remains unclear.

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56 In this Article, we design lateral heterojunctions within a homogeneous MoS_2 monolayer exploiting the 57 dielectric-dependent bandgap renormalization and explore its influence on electrical transport. We prepared a 58 continuous monolayer MoS₂ which has a segment on a high- ε substrate and an adjacent segment on a low- ε 59 substrate (Fig. 1a). Due to the different degree of renormalization of the electronic bandgap introduced by the 60 two substrates on each segment, the monolayer MoS₂ forms an in-plane type-I heterojunction above the 61 boundary of the two substrates (Fig. 1b,c). We used this sample configuration to perform Kelvin Probe Force Microscopy (KPFM) and electrical transport measurements across the heterojunction. KPFM^{28,29} examines 62 63 the local variation of surface potential across the device channel³⁰ and provides a direct determination of the band offset of the MoS₂ heterojunction from the dielectric engineering. Electrical measurements show that 64 65 the presence of the heterostructure has a significant effect on electrical transport through the device, leading 66 to a strong asymmetric rectification behaviour. The experimentally observed transport phenomena can also 67 be qualitatively reproduced in a numerical simulation of the device, which exhibits several unique aspects 68 arising from the atomically thin layers. Such dielectric-defined heterostructure behaviour can be important 69 for understanding electrical transport behaviour in atomically thin 2D layers and provide a new approach for 70 engineering 2D nanoelectronic devices^{4,31}.

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Theoretical calculations^{21,23,32,33} show that the change in the bandgap of the 2D layer due to dielectric 72 screening effect by the substrate(s) is most dramatic when the 2D layer has a low intrinsic dielectric constant 73 74 (ε). In addition, a high contrast from the dielectric screening environment involving a low- ε substrate and a 75 high- ε substrate is desirable to introduce a significant change in the bandgap of the 2D layer at the heterojunction. We choose the fluoropolymer Cytop ($\varepsilon = 2.0-2.1$) and hBN ($\varepsilon(0) = 6.9$, $\varepsilon(\infty) = 5.0$ normal to 76 *c*-axis³⁴) to serve as the ε_{low} and ε_{high} substrates respectively. The fluoropolymer Cytop substrate is one of 77 78 the materials with the lowest dielectric constant that still allows ease of processing and device fabrication. Meanwhile, the straight edges of as-exfoliated thin hBN flake provide a boundary that is atomically sharp for 79 a well-defined junction area. Moreover, both Cytop³⁵ and hBN³⁶ are known to be insulating layer with a low 80 81 density of surface trap states.

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83 Heterojunction device design and electrical measurement

84 We transferred a monolayer of MoS_2 atop the boundary of an hBN flake on a Cytop film and then fabricated 85 electrical contacts onto the monolayer to form a device channel that is perpendicular to the Cytop/hBN 86 substrate boundary (Fig. 2a). The electrical measurements are then performed in 4-terminal configuration to 87 minimize the influence of contacts. Fig. 2b shows the I-V measurement of the device for different back gatesource voltages (which we shall refer to as "gate voltage" for brevity) $V_{gs} > 0$ V, which correspond to electron 88 89 doping. With the MoS₂ segment on Cytop grounded, the device exhibited a rectification behavior that is 90 reminiscent of a diode. This rectification behaviour is consistent with the expected type-I heterojunction formation drawn in Fig. 1c, where the MoS₂ segments above the ε_{low} and ε_{high} substrates have different 91 92 electronic bandgap due to dielectric screening. This behaviour is similar to an n-n heterojunction with MoS₂

93 segment on Cytop (hBN) containing the depletion (accumulation) regime³⁷.

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In comparison, the reference MoS_2 monolayer device on a uniform Cytop film exhibits linear Ohmic-like behaviour (Fig. 2c), suggesting that the rectification arises from the presence of the heterojunction at the boundary between high- ε and low- ε substrates. Furthermore, we also conducted control experiments with MoS₂ monolayer on a step edge of an hBN flake that otherwise supports a uniform dielectric environment (Supplementary Fig. 7). Such control device shows symmetric output curves, which also substantiates that the rectification cannot be attributed only to the presence of step edge (*e.g.*, strain-induced or otherwise) without introducing dielectric contrast.

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103 A prominent feature of our MoS₂ heterojunction device behaviour is that the *I-V* curve at forward bias that is 104 higher than $V_{ch} \approx 0.1$ V is mostly linear. This behaviour is commonly found in a real diode, which can be 105 described by a piecewise linear model with a "turn-on" voltage (V_t) before the device appears to be Ohmic-106 like³⁸. The turn-on voltage is often correlated to the potential landscape of the diode (*e.g.*, built-in voltage in 107 Si p-n diode), and it provides an estimate of conduction band offset across the heterojunction. Our low-108 temperature transport measurements yield a turn-on voltage $V_t \sim 90$ mV in the device (17 K, Fig. 2d).

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111 KPFM characterization

Fig. 3a illustrates the KPFM measurement configuration, where lift mode with a constant tip height (h = 30nm) is used and the DC component of bias voltage (V_{bias}) is applied to the sample. Fig. 3b displays the topography scan of atomic force microscope (AFM) from the MoS₂ heterojunction area at the Cytop/hBN substrate boundary. The averaged height profile (Fig. 3c) shows that the thickness of the hBN is around 10 nm. The exposed top surface in our devices allows for direct KPFM characterization.

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As KPFM typically requires the sample to be sufficiently conducting, we performed KPFM on the MoS₂ when it is electrostatically gated to its on-state (electron accumulation) at high gate voltage. Fig. 3d shows the map of V_{bias} that was applied to the sample to cancel the electrostatic force between the tip and the sample, which is imaged at $V_{gs} = 50$ V. Meanwhile, Fig. 3e shows the corresponding averaged V_{bias} profile. The V_{bias} magnitude is related to the work function of the sample and that of the tip by $W_{f,\text{sample}} = eV_{\text{bias}} + W_{f,\text{tip}}$ (see Supplementary Fig. 8). Therefore, the difference in local work function between two segments of the sample that are imaged by the same tip is given by:

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$$\Delta W_{f,\text{sample}} = e \Delta V_{\text{bias}}$$

Two distinct areal regions of V_{bias} are seen in Fig. 3d that correlates well with the two segments of MoS₂ on Cytop and hBN from the topographic image (Fig. 3b). By using the averaged line profile in Fig. 3e, we therefore conclude that the work function difference ($\Delta W_f = W_{f,\text{low}} - W_{f,\text{high}}$) of MoS₂ on the Cytop and hBN substrate is -90 ± 20 meV at $V_{gs} = 50$ V. Here, the negative sign means that the vacuum level of MoS₂ on Cytop is lower than that on hBN.

- 134 The conduction band offset can be obtained from the work function difference by
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$$\Delta E_c = -\Delta W_f - kT \ln \left[\frac{\exp\left(\frac{\pi \hbar^2 n_{\text{low}}}{m^* kT}\right) - 1}{\exp\left(\frac{\pi \hbar^2 n_{\text{high}}}{m^* kT}\right) - 1} \right]$$
(2)

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138 with the carrier density $n = C_g (V_{gs} - V_{th})/e$, where V_{th} is the gate threshold voltage, and m^* is the effective 139 mass of electrons. Because the serial gate capacitance (C_g) at ε_{high} and ε_{low} side of the device does not differ 140 significantly (the geometric capacitance of the 285 nm SiO₂ substrate dominates the serial capacitance), the 141 ratio $n_{\rm low}/n_{\rm high}$ becomes closer to unity at high gate voltage. Applying these considerations to equation (2) 142 in combination with (1) suggests that performing the measurement at the high gate voltage provides two 143 major benefits: first, it counters the doping contribution from the environment to allow the relative carrier 144 density on both sides of the junction to be more balanced since the charge density is dominated by that 145 induced by the gate. Secondly, as the consequence of $n_{\rm low}/n_{\rm high} \approx 1$, KPFM measurements at high gate

(1)

146 voltage allow direct interpretation of the conduction band offset from the V_{bias} contrast. Fig. 3e therefore 147 implies that $\Delta E_c \approx -e\Delta V_{\text{bias}} \sim 90$ meV for our experimental condition, *i.e.*, E_c for MoS₂ on Cytop is 148 positioned higher than that on hBN.

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150 The heterojunction measured by KPFM is consistent with the electrical transport data. It suggests that 151 dielectric engineered bandgap difference is around $\Delta E_g \approx 2\Delta E_c = -180\pm40$ meV (illustrated in Fig. 1c), 152 assuming electron-hole symmetry. We compare this experimental result with the theoretical calculation of the electronic bandgap of MoS₂ within the *ab initio* GW₀ approach as implemented in the BerkeleyGW 153 package^{39.41} and account for the dielectric screening effect from the substrates using the in-plane substrate 154 155 averaging approach (details regarding the GW_0 calculation is in Supplementary Note 4)^{13,33}. The GW_0 calculation shows that the bandgap of MoS₂ on a similar dielectric fluoropolymer as Cytop, after accounting 156 157 of surface roughness (Supplementary Fig. 3), is larger than that of MoS₂ on hBN by 120±40 meV, of which 158 the CBM offset is $\sim 70\pm 20$ meV (Fig. 3f). Our calculations reveal that the roughness of the Cytop surface 159 decreases the effective dielectric screening experienced by MoS₂: the same calculation performed on a 160 perfectly smooth Cytop-like substrate results in a CBM offset of ~40 meV. The calculated bandgap and CBM 161 offset agree well with the experimental results, with overlapping error bars. The CBM and VBM offsets are 162 also approximately symmetric.

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164 Energy band modelling

165 We model the electrical potential and charge transport through the junction numerically to understand the 166 unusual electrical transport from an atomically thin 2D heterojunction. While the rectification behaviour of 167 the heterojunction is consistent with the predicted band alignment in Fig. 1c, the transport data cannot be 168 aptly modelled with a thermionic emission theory commonly used to describe a Schottky diode, in which the 169 current level predicted from a thermionic emission mechanism is several orders of magnitude larger than that 170 measured herein (Supplementary Note 1 and Supplementary Fig. 1-2). The thermionic emission model fails 171 in atomically thin 2D layers because these 2D materials tend to have rather low mobility, and the drift-172 diffusion behaviour of charge carriers plays a dominant role in the transport across the heterojunction 37 . To 173 accurately model the device behaviour, we introduce a carrier density dependent electron mobility in MoS₂ 174 by $\mu(n) = \mu_0 / [1 + \exp(\alpha^{-n+n_0})]$. Here, the mobility has a constant value of μ_0 at high doping but drops 175 significantly at low doping. This functional form is reminiscent to an activated behaviour with a certain 176 density of trap states, and the relevant parameters are obtained through gate-dependent transport data from a 177 homogeneous MoS₂ monolayer (Supplementary Fig. 5f-g). The density-dependent mobility is especially 178 relevant at the depletion region, which would experience increased local electrical resistance due to lowered 179 carrier density (Fig. 4d).

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181 Fig. 4 shows the calculated band diagram and the associated band bending of MoS_2 around the Cytop and 182 hBN substrates for the conduction band edges at zero, forward, and reverse applied bias (see method in 183 Supplementary Note 2). The electron density n_0 at x < 0 (at Cytop) is assumed to be ~2×10¹² cm⁻². The zero bias calculation result (Fig. 4a) captures the built-in potential on each side of the junction (ψ_1 and ψ_2 for 184 185 MoS₂ on hBN and Cytop, respectively) because of the work function differences between the two segments 186 of MoS₂. In the case of a biased channel, the current flow is a response of a voltage drop over the whole channel: $V_{ch} = E_F(z = -L) - E_F(z = L)$ that shifts the Fermi level out of equilibrium. However, we see 187 188 from both Fig. 4b and 4c that the voltage drop primarily transpires at the heterojunction, ensuring that the 189 heterojunction property to define the *I-V* behaviour of the device.

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191 In the forward bias (Fig. 4b), the voltage drop across the heterojunction reduces the net built-in potential into 192 $\psi_1 - V_1$ and $\psi_2 - V_2$, respectively. A net current will flow with the electrons moving from the segment on 193 Cytop to that on hBN. At a finite temperature, electrons moving in this direction will see an energy barrier 194 for transport across the heterojunction. However, this energy barrier becomes negligible at a sufficiently large applied bias $V_{ch} > V_t$, as illustrated in Fig. 4b. In other words, $\psi_2 - V_2 \approx 0$ and the transport across the junction should be mostly dominated by the sheet resistance of MoS₂ away from the junction and appears 195 196 197 Ohmic-like. As an approximation, the $\psi_2 - V_2 \approx 0$ condition is achieved when the total built-in voltage across the junction: $\psi_i = \psi_1 + \psi_2 \approx V_t$. We believe that this picture might explain the *I-V* behaviour for the 198 199 heterojunction as discussed in Fig. 2. An equivalent diode circuit for the junction is shown in the inset of Fig. 200 4b: the heterojunction is comprised of an internal built-in potential V_t that needs to be compensated by 201 applying an external potential, following which the current-voltage behaviour is dictated by a resistance R_s

202 in series due to the MoS₂ segment away from the junction. Our simulated *I-V* plot (Fig. 4e) reproduces the

- 203 threshold-like behavior of the device.
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205 Conclusions

We have reported an operational device application of bandgap renormalization in 2D materials via dielectric screening, and shown that a dielectric-engineered lateral heterojunction can strongly modify electrical transport in monolayer MoS₂. Since heterostructures are fundamental building blocks in electronics, such dielectric engineering can provide a powerful new route for realizing more complex device architecture. Our findings also have implications for the efforts to incorporate 2D materials in optoelectronics, in order to improve functionality (for example, spin-valley current for information encoding⁴²) and drive miniaturization^{43,44}.

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214 In practical applications, all aspects of manufacturing must be considered. For instance, the monolithic 215 integration of 2D materials in circuitry requires interfacing with other components, such as substrate, 216 electrodes, and interconnections. Each component may screen the 2D materials, resulting in different degree 217 of bandgap renormalization across the channel. Notably, the bandgap of MX_2 should decrease significantly 218 upon interfacing with electrodes due to the high permittivity of metals and thus a heterojunction is expected 219 to form at each border between the MX₂ segments with and without metal contact. Although the behaviour of 220 metal-MX₂ junction is dominated by other mechanisms such as Fermi-level pinning^{45,46}, recent work 221 suggests the possibility to prevent pinning by minimizing disorders and interface states at the metal-MX₂ 222 junction^{47,48}. At such limit, accounting for bandgap renormalization is essential to fully understand the 223 physics of electrical contact to MX₂ monolayers.

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225 Although we have used Cytop and hBN substrates in order to simplify fabrication, the bandgap 226 renormalization is a general phenomenon in 2D semiconductors and the heterojunction should form with other combinations of dielectrics. The constraint for low ε_{low} substrate may be satisfied by other established materials in industry, such as electronic-grade plastic substrates^{49,50} with well-developed scalability and 227 228 229 processability. Additionally, an advantage of such polymeric surfaces is the absence of dangling bonds, 230 leading to a low density of surface trap sites. If conventional high- ε dielectrics are used, an abrupt 231 heterojunction is affordable by patterning with state-of-the-art microfabrication technology. Another scalable 232 approach also includes using CVD-grown 2D lateral heterojunction as the substrate if the material combination has a significant dielectric contrast^{51,52}. We also believe that the influence from interface 233 234 trapping and substrate doping for non-optimized surface can be minimized if the heterojunction is operated at 235 high carrier density as defined by the electrostatic gating, where the difference in the work functions between 236 low- and high- ε channel segments are primarily due to the bandgap renormalization.

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243 Methods

244 Device fabrication. Cytop (CYTOP CTL-809M, Asahi Glass Co.) is mixed into CTL180 (Asahi Glass Co.) 245 in 2:7 v/v and spincoated at 1000 rpm for 1 min to a uniform thickness of \sim 70 nm on highly doped Si 246 substrates with 285 nm SiO₂. The Cytop-coated substrate is then heated at a hotplate for 5 min at 100°C and 247 then 5 min at 150°C. Crystal of hBN is then exfoliated on the Cytop surface. The hBN flakes with thickness of 5-15 nm that have a flat side edge are identified from optical microscopy and confirmed with AFM 248 imaging. Monolayers of MoS₂ are exfoliated onto a PDMS stamp and dry-transferred^{53,54} to the flat edge of 249 250 such hBN flake (Supplementary Fig. 4a,b). For all devices, 100 nm Au film is deposited for the electrode of 251 MoS₂ using a standard electron beam lithography (EBL) process with two layers of EBL resist (495PMMA 252 A4 and 950PMMA A4, MicroChem). We found that exposing the Cytop film to a short, low power N_2 253 plasma (10 sccm, 5 W for 1 s) before the hBN exfoliation can help to produce better spincoating of the 254 resists on Cytop. 255

KPFM. KPFM were performed using a Multimode AFM with grounded tip and biased sample. A blunted Si cantilever with \sim 50 nm Au film coating was used for the imaging. The measurement was performed in surface potential mode with a lift-height of 30 nm and a drive amplitude of 2 V. The high lift-height was chosen to avoid interaction between the metal tip and the monolayer MoS₂ that can introduce additional screening effect. The AFM instrument is housed inside a home-made enclosure that is flushed with a constant fluer of demonstrates an inset structure.

constant flow of dry nitrogen to provide an inert atmosphere.

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263 Data availability

The data that support the plots within this paper and other findings of this study are available from the corresponding author upon reasonable request

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387 Author contribution

F.W., M.I.B.U., H.K. conceived the project and designed the experiments. M.I.B.U. and H.K. performed sample preparation, device fabrication, electrical transport measurements, and data analysis. W.Z., M.I.B.U.,

- and S.W. performed KPFM measurement. M.I.B.U. conducted optical spectroscopy. R.K., S.Z., and A.Z.
- contributed in the device fabrication process. F.W., M.I.B.U., H.K. simulated the energy band diagram of the
- heterojunction. C.S.O., F.H.d.J., and D.Y.Q. performed GW calculations on and together with S.G.L. did the
- analyses of the quasiparticle band structures. H.C., H.L., and S.T. grown the MoS₂ single crystal. K.W. and
- T.T. grew the hBN single crystal. F.W., S.G.L., and A.Z. supervised the project.
- 395

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399 Additional information

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409 Figure 1 | Engineering 2D heterojunction through dielectric-dependent bandgap renormalization. a, 410 Schematic illustration of the heterostructure. Two substrates with different dielectric constant ($\varepsilon_{low} < \varepsilon_{high}$) 411 are used to locally vary the MoS₂ electronic bandgap. b, The expected band alignment of isolated monolayer 412 MoS₂ situated on ε_{low} substrate (Cytop) and on ε_{high} substrate (hBN), respectively. The segment of MoS₂ 413 monolaver on Cytop and that on hBN are assumed to have the same electron doping density from the 414 electrostatic gating. c, The band alignment from (b) if the MoS_2 segments at the two substrates are in contact 415 and reach equilibrium following Anderson's rule. A type-I lateral heterojunction forms with an energy barrier 416 for electron transport in the conduction band.

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418 Figure 2 | Current-voltage characteristics of MoS₂ heterojunction device. a, Optical micrograph of an 419 MoS₂ monolayer that is partially situated on Cytop and on hBN substrates. The white dashed line denotes the 420 location of the monolayer that acts as the device channel. The MoS₂ segment on hBN received the high bias 421 potential (drain). Scale bar: $2 \mu m$. **b**, The output characteristics of the device with various back gating at the 422 temperature of 200 K. c, The output characteristics of a reference MoS_2 monolayer device on a uniform 423 Cytop substrate measured at 200 K. Inset: The micrograph of the reference device. Scale bar: 2 µm. d, The 424 output characteristics of the heterojunction device at 17 K in log-log scale. The forward bias current is fitted 425 with a straight line that extrapolates to a turn-on voltage of 90 mV. Inset: the same data in linear scale.

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427 Figure 3 | KPFM characterization of the MoS_2 heterojunction formation from differences in the degree 428 of local dielectric screening. a, Schematic of the KPFM setup with V_{bias} applied to the sample. For the 429 measurements herein, the device is back gated to $V_{gs} = 50$ V and the lift height of the tip is set to h = 30 nm. 430 b, The topography image recorded in tapping mode AFM. c, The height profile, averaged from the area 431 inside the white-dashed rectangle in (b). d, The spatially mapped V_{bias} from the same area as in (b). e, The 432 V_{bias} profile from (**d**), also averaged similarly from the same area as in (**c**). Given that $\Delta E_c = -e\Delta V_{\text{bias}}$ in the 433 measurement configuration, the KPFM result demonstrates that the conduction band edge of MoS₂ on Cytop 434 substrate is higher by 90 meV than that of MoS_2 on hBN. f, Results from GW calculations of the bandgap 435 and band alignment of monolayer MoS_2 that is freestanding without substrate screening effect (left), that is 436 placed on a surface of a fluoropolymer (middle), and that is placed on a hBN substrate (Scale bars in (b) and 437 (d) corresponds to 500 nm).

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439 Figure 4 | Simulation results of the energy band bending at the 2D heterojunction. a,b,c The conduction 440 band edges and Fermi levels are calculated at (a) zero bias, (b) forward biased (current: 80 nA/ μ m), and (c) 441 reverse biased condition (current: -6 nA/ μ m). In the three cases, the MoS₂ segment on Cytop is assigned to be electrically grounded. Under small forward bias ($V_{ch} = V_1 + V_2$), an electron traversing the heterojunction from the segment on Cytop to that on hBN experiences an energy barrier due to the built-in voltage. 442 443 444 However, for large enough bias beyond the turn-on voltage ($V_{ch} > V_t$), electrons traversing the heterojunction 445 (blue circle) do not experience significant energy barrier and the current-voltage characteristic is determined 446 by the resistance of the channel instead of the junction. Inset in (b): a schematic of the diode modelling 447 according to piecewise linear model. d, Carrier density distribution across the junction under different bias 448 condition. e, Simulated current-voltage characteristics with a carrier density-dependent mobility. All calculations are performed using carrier density of 2.0×10^{12} cm⁻² at 140 K. 449

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