

Supplementary Information for
Epitaxy of wafer-scale single-crystal MoS₂ monolayer via buffer layer control

Lu Li^{1,2}, Qinqin Wang^{1,2}, Fanfan Wu^{1,2}, Qiaoling Xu^{3,4}, Jinpeng Tian^{1,2}, Zhiheng Huang^{1,2}, Qinghe Wang⁵, Xuan Zhao^{1,2}, Qinghua Zhang^{1,2}, Qinkai Fan^{1,2}, Xiuzhen Li^{1,2}, Yalin Peng^{1,2}, Yangkun Zhang^{1,2}, Kunshan Ji^{1,2}, Aomiao Zhi^{1,2}, Huacong Sun^{1,2}, Mingtong Zhu^{1,2}, Jundong Zhu^{1,2}, Nianpeng Lu^{1,2,3}, Ying Lu^{1,2}, Shuopei Wang³, Xuedong Bai^{1,2,3}, Yang Xu^{1,2}, Wei Yang^{1,2}, Na Li³, Dongxia Shi^{1,2,3}, Lede Xian³, Kaihui Liu⁵, Luojun Du^{1,2*} & Guangyu Zhang^{1,2,3*}

¹*Beijing National Laboratory for Condensed Matter Physics, Institute of Physics, Chinese Academy of Sciences, Beijing 100190, China*

²*School of Physical Sciences, University of Chinese Academy of Sciences, Beijing 100049, China*

³*Songshan Lake Materials Laboratory, Dongguan, Guangdong 523808, China*

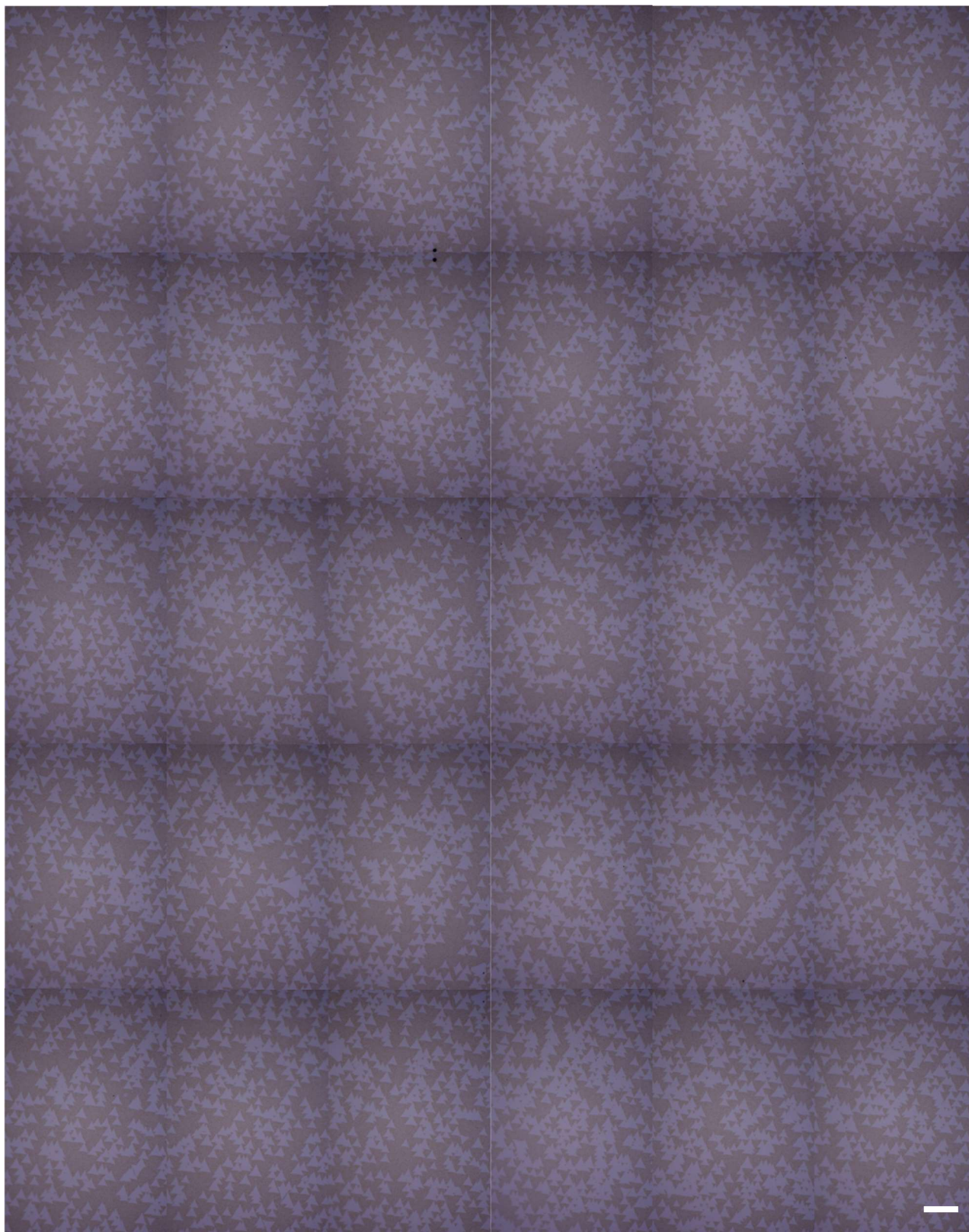
⁴*College of Physics and Electronic Engineering, Center for Computational Sciences, Sichuan Normal University, Chengdu 610068, China*

⁵*Collaborative Innovation Center of Quantum Matter and School of Physics, Peking University, Beijing 100871, China*

Email: luojun.du@iphy.ac.cn; gyzhang@iphy.ac.cn

Supplementary Note 1. The unidirectional growth of MoS₂ domains

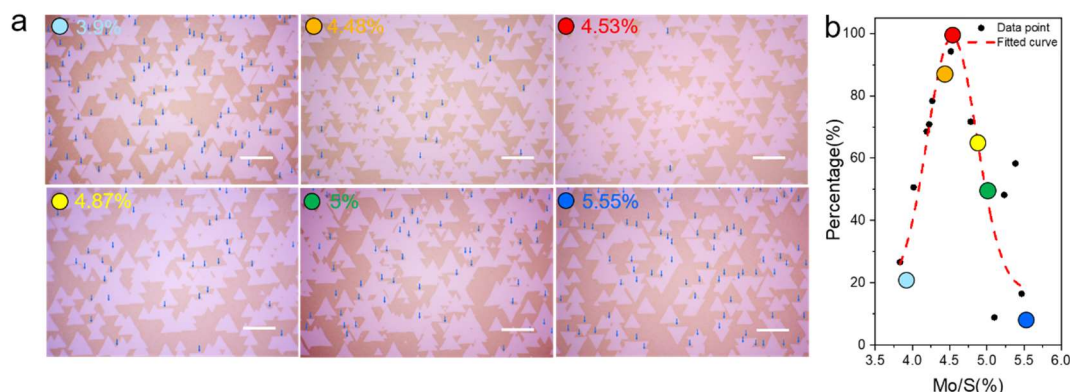
According to microscopy images over a ~ 1 mm² area (Supplementary Fig. 1), the degree of unidirectional alignment is larger than 99% for 4.5% MoO₃/S precursor ratio.



Supplementary Figure 1. The uniform and unidirectional growth of MoS₂ domains over a ~ 1 mm² area. Scale bars, 30 μ m.

Supplementary Note 2. MoS₂ domains at different Mo/S precursor ratios

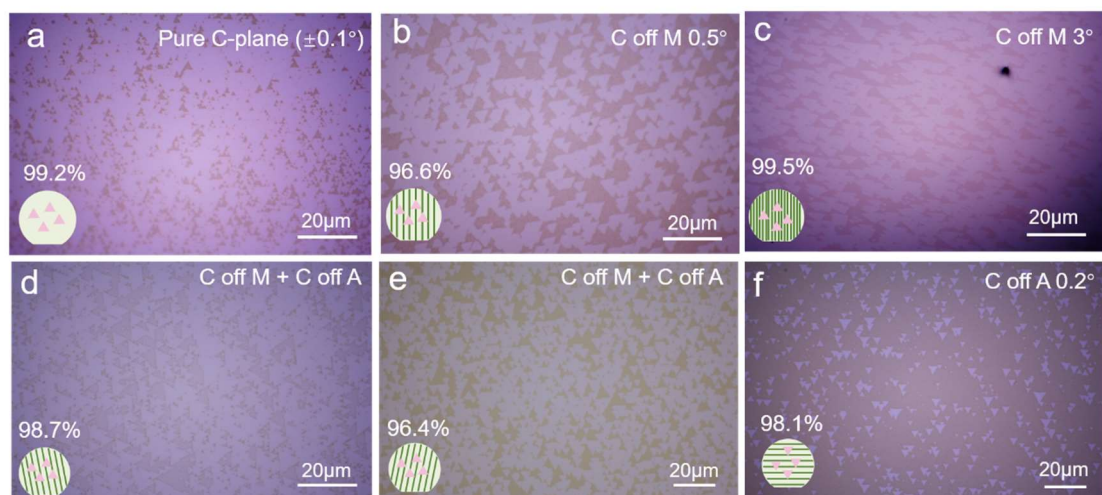
Supplementary Figure 2a presents the optical micrographs of the as-grown MoS₂ triangular domains under different MoO₃/S precursor ratios: 3.9%, 4.48%, 4.53%, 4.87%, 5% and 5.55%. The degree of unidirectional alignment can be continuously tuned from ~0 to ~100% by controlling the MoO₃/S precursor ratio (Supplementary Fig. 2b).



Supplementary Figure 2. (a) The optical microscopy images show MoS₂ domains at different Mo/S precursor ratios. Scale bar, 10 μm. (b) The degree of unidirectional alignment as a function of the MoO₃/S precursor ratio.

Supplementary Note 3. Unidirectional domain alignment on pure *c*-plane sapphires and other substrates.

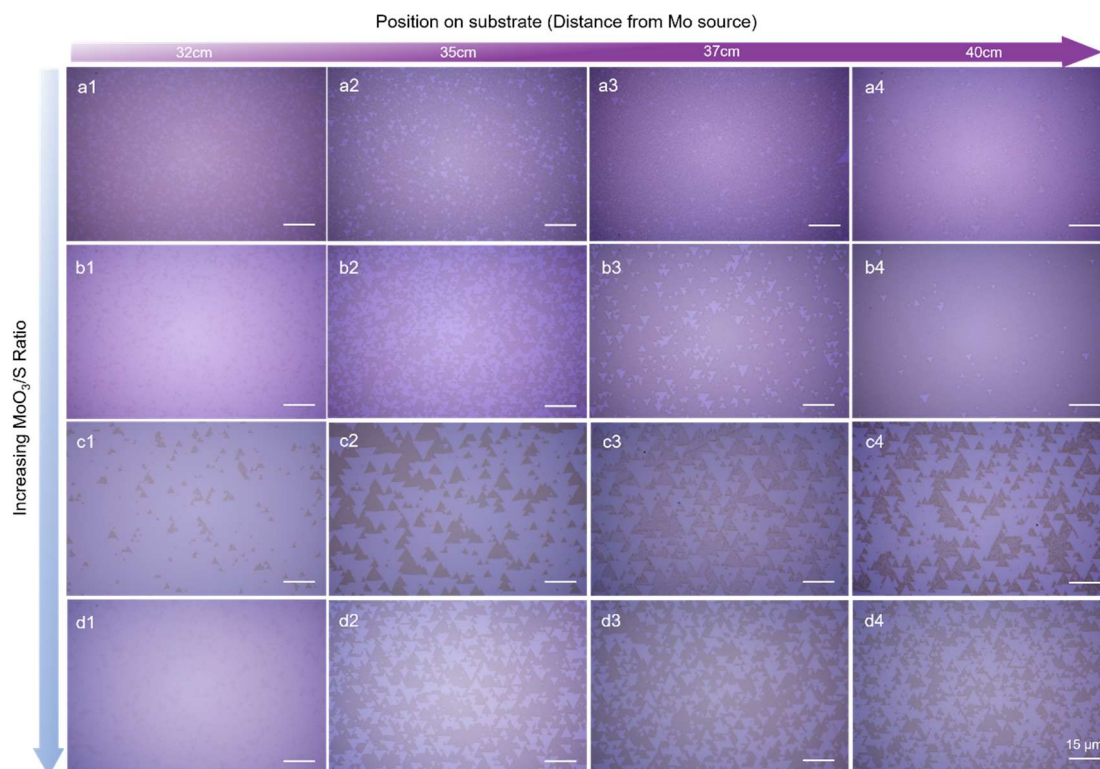
In addition to *c*-plane sapphire substrates with a major miscut angle (~0.2°) towards M-axis in the main text, the unidirectional domain alignment has also been achieved by precisely controlling the S/MoO₃ precursor ratio on pure *c*-plane sapphires without an M-axis miscut (the degree of unidirectional alignment is ~99.2%, Supplementary Fig. 3a), *c*-plane sapphire substrates with different major miscut angles towards M-axis such as C/M-0.5° (the degree of unidirectional alignment is ~96.6%, Supplementary Fig. 3b) and C/M-3° (the degree of unidirectional alignment is ~99.5%, Supplementary Fig. 3c), *c*-plane sapphire substrates with a major miscut angle (~0.2°) towards other axes (the degree of unidirectional alignment is ~98.7% in Supplementary Fig. 3d and the degree of unidirectional alignment is ~96.4% in Supplementary Fig. 3e), and *c*-plane sapphire substrates with a major miscut angle (~0.2°) towards A-axis (the degree of unidirectional alignment is ~98.1%, Supplementary Fig. 3f). Therefore, we believe that our claim is valid for pure *c*-plane sapphires without an M-axis miscut and other substrates.



Supplementary Figure 3. Optical microscopy image of unidirectional MoS₂ domains on pure *c*-plane sapphires without an M-axis miscut (**a**), *c*-plane sapphire substrates with a 0.5° major miscut angles towards M-axis (**b**), a 3° major miscut angles towards M-axis (**c**), with a 0.2° major miscut angles towards other axes (**d,e**), and with a 0.2° major miscut angle towards A-axis (**f**).

Supplementary Note 4. The shape evolution of MoS₂ crystals

For our home-designed three-temperature-zone chemical vapor deposition (CVD) setup (Supplementary Fig. 27), there is a long distance between the substrate and MoO₃ source (>32 cm), as well as S source (>49 cm). Therefore, the gradient of both MoO₃ and S sources is very small and the MoS₂ crystals would maintain the same shape. Supplementary Figure 4 shows the optical microscopy images of CVD MoS₂ at different locations (~32-40 cm). Clearly, the MoS₂ crystals keep the triangular shape. Furthermore, for all the MoO₃/S ratios we have investigated (ranging from ~3.83% to ~5.55%), the concentration of S source is always larger than that of MoO₃ source. Consequently, the shape of MoS₂ crystals would keep unchanged, as in our experimental results (Supplementary Fig. 4)

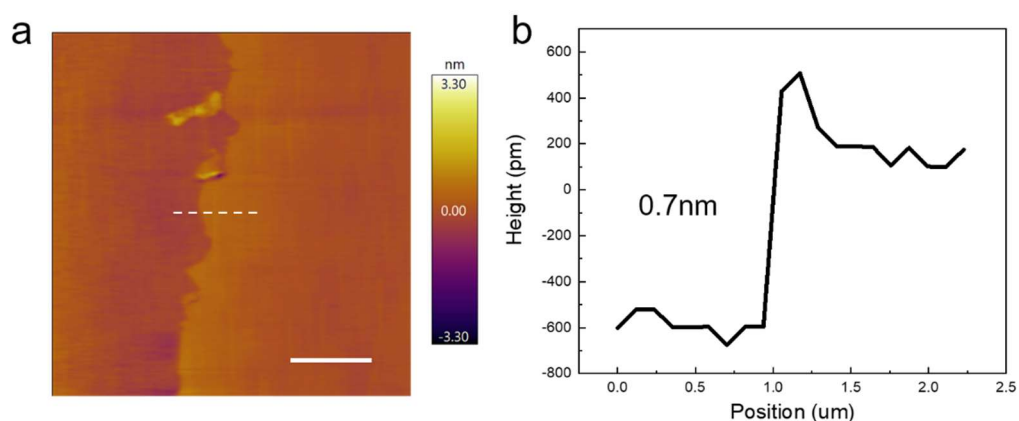


Supplementary Figure 4. Representative optical images of MoS₂ crystals grown at different MoO₃/S (a)-(d) at several different positions on the substrate (1)-(4).

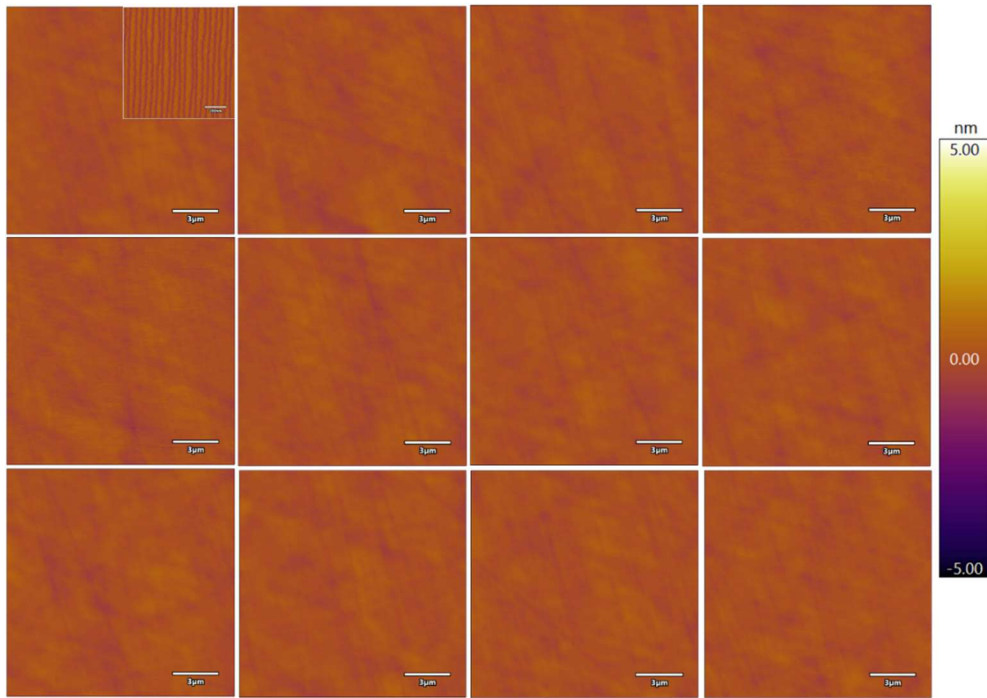
Supplementary Note 5. The AFM image of MoS₂ film

A scratch was made on a continuous MoS₂ film to measure the height of the MoS₂, and the AFM image is shown in Supplementary Fig. 5a. The height results from the dashed line (Supplementary Fig. 5b) show that MoS₂ is about 0.7 nm, indicating the monolayer nature.

The AFM images taken from different locations across a 2-inch wafer (Supplementary Fig. 6) manifest a uniform and wrinkle-free monolayer MoS₂ film.



Supplementary Figure 5. (a) The AFM image of the scratched edge of MoS₂. Scale bar, 2 μm. (b) The height results from the dashed line.



Supplementary Figure 6. Typical AFM images of MoS₂ grown on c-Al₂O₃ at different areas.

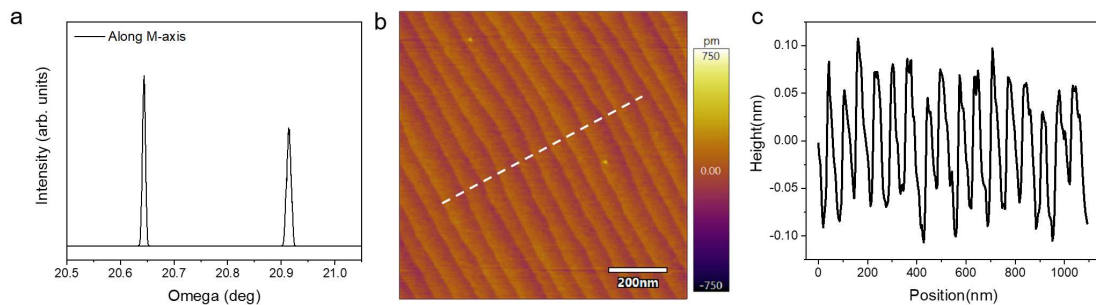
Supplementary Note 6. General *c*-plane sapphire substrates with mono-step

In a recent work¹, the bi-steps and thus single-type surface symmetry are formed by annealing at high temperatures, which enable the unidirectional alignment. However, in our studies, the used *c*-plane sapphire substrates are the general substrate with mono-step, rather than bi-steps.

1) Supplementary Figure 7a shows the XRD rocking curve of our *c*-plane sapphire substrates with unidirectional MoS₂ on it, demonstrating a major miscut angle towards M axis of 0.135°, which agrees well with the parameters provided by the supplier of HeFei crystal Technical Material Co., Ltd. (*c*-plane sapphire with a major miscut angle towards M axis of $\sim 0.2 \pm 0.1^\circ$).

2) Supplementary Figures 7b and 7c shows the AFM image of our *c*-plane sapphire substrates, indicating mono-step height H of ~ 0.16 nm and terrace width W of ~ 66.5 nm. The ratio between step height H and terrace width W , i.e., $H/W = 0.16\text{nm}/66.5\text{nm} = 0.0024$, accordance with the XRD data ($\tan 0.135^\circ = 0.002356$).

3) Our *c*-plane sapphire substrates with a major miscut angle towards M axis of $\sim 0.2^\circ$ have mono-step are quite reasonable because our substrates are annealing at 980°C, much lower than the required temperature ($>1400^\circ\text{C}$) to form bi-steps¹.



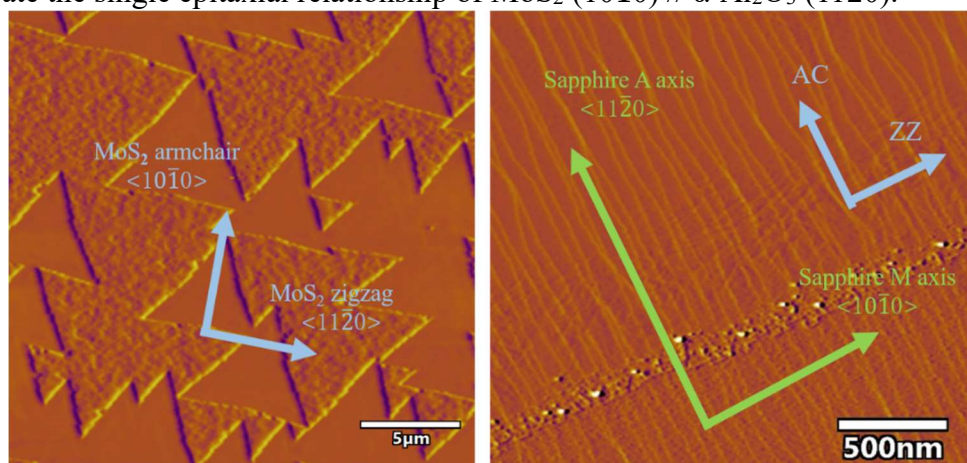
Supplementary Figure 7. (a) XRD rocking curve of *c*-plane sapphire substrates with unidirectional MoS₂ on it, demonstrating a major miscut angle towards M axis of 0.135°. (b,c) AFM characterization of sapphire substrates, indicating surface step height of ~0.16 nm and terrace width of ~66.5 nm.

Supplementary Note 7. The epitaxial relationship of MoS₂ on *c*-plane sapphire

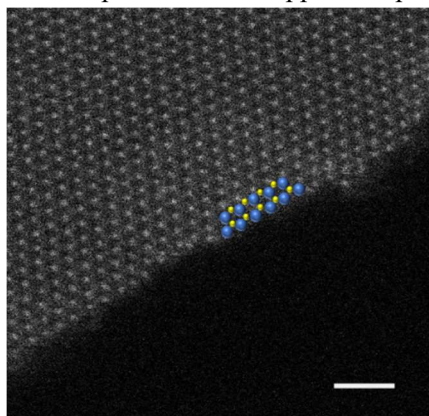
According to the AFM images (Supplementary Fig. 8), the MoS₂ $\langle 11\bar{2}0 \rangle$ direction (MoS₂ zigzag) is parallel to the $\langle 10\bar{1}0 \rangle$ direction of sapphire substrate (M axis), and the MoS₂ $\langle 10\bar{1}0 \rangle$ direction (MoS₂ armchair) is parallel to the sapphire $\langle 11\bar{2}0 \rangle$ direction (A axis).

We performed transmission electron microscopy (TEM) characterization at the atomic scale and confirmed that the triangular MoS₂ domains have zigzag edges (Supplementary Fig. 9).

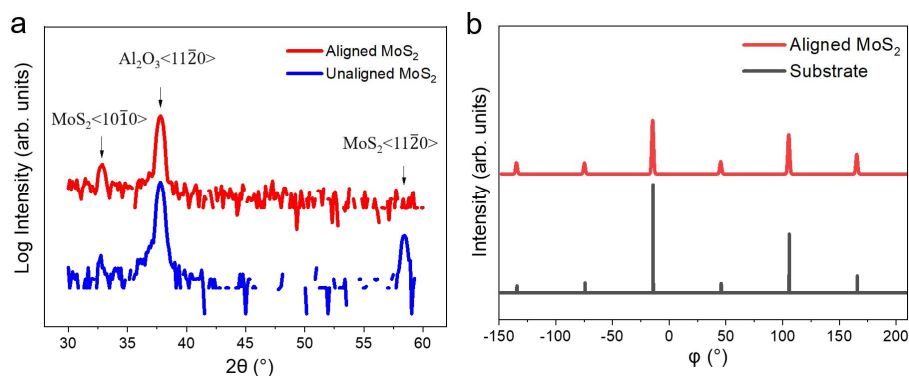
The epitaxial relationship of MoS₂ on *c*-plane sapphire is further confirmed by in-plane X-ray diffraction (XRD) measurements. In the XRD θ - 2θ scan, only the diffraction peak of MoS₂ (10 $\bar{1}$ 0) plane and α -Al₂O₃ (11 $\bar{2}$ 0) plane are detected simultaneously in the single oriented MoS₂ film at the same ϕ angle (red line, Supplementary Fig. 10a). Furthermore, the XRD ϕ scan (Supplementary Fig. 10b) show that the peaks of MoS₂ (10 $\bar{1}$ 0) plane coincide with that of α -Al₂O₃ (11 $\bar{2}$ 0) plane, indicate the single epitaxial relationship of MoS₂ (10 $\bar{1}$ 0) // α -Al₂O₃ (11 $\bar{2}$ 0).



Supplementary Figure 8. The AFM images of triangular domains show that the zigzag $\langle 11\bar{2}0 \rangle$ direction of single oriented MoS₂ is parallel to the $\langle 10\bar{1}0 \rangle$ direction of sapphire substrate, and the armchair $\langle 10\bar{1}0 \rangle$ direction of MoS₂ is parallel to the sapphire step $\langle 11\bar{2}0 \rangle$ direction.

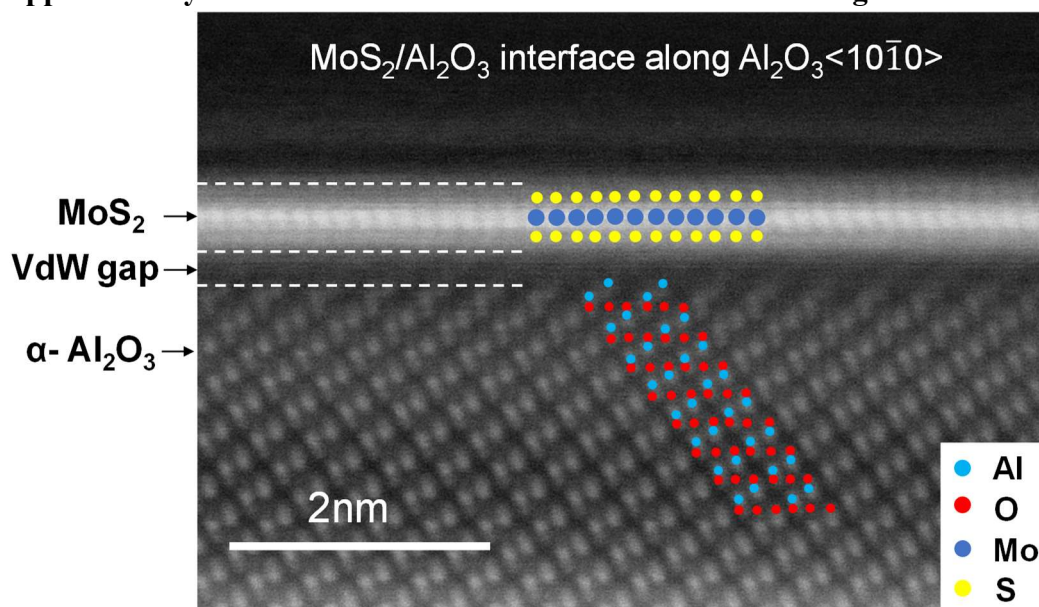


Supplementary Figure 9. STEM images show the Mo-Zigzag edges of MoS₂ domains. Scale bars, 1 nm.

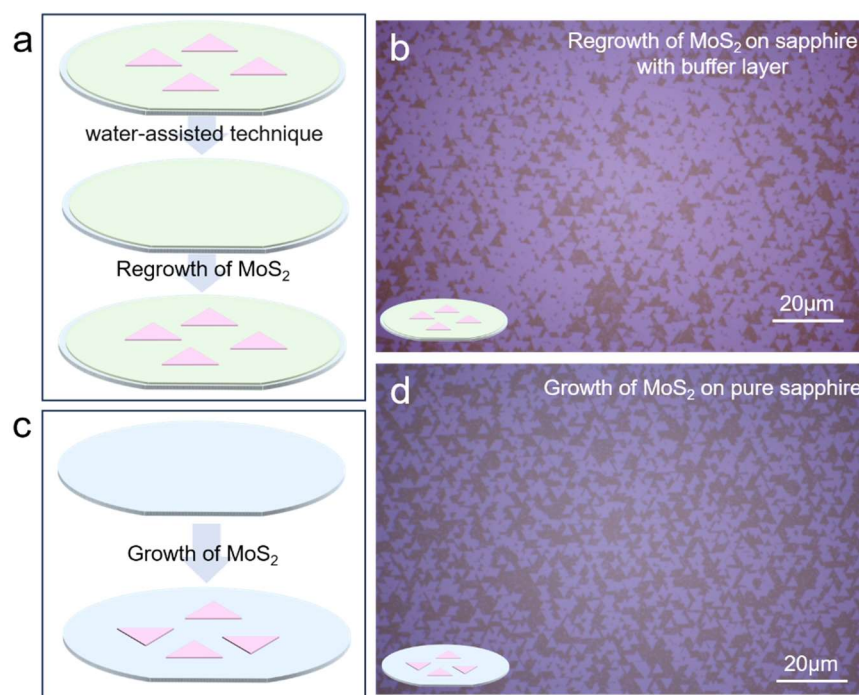


Supplementary Figure 10. (a) In-plane XRD θ - 2θ diffractogram. (b) In-plane XRD ϕ scan of the (10 $\bar{1}$ 0) planes of MoS₂ and the (11 $\bar{2}$ 0) planes of α -Al₂O₃.

Supplementary Note 8. The mechanism of unidirectional MoS₂ growth



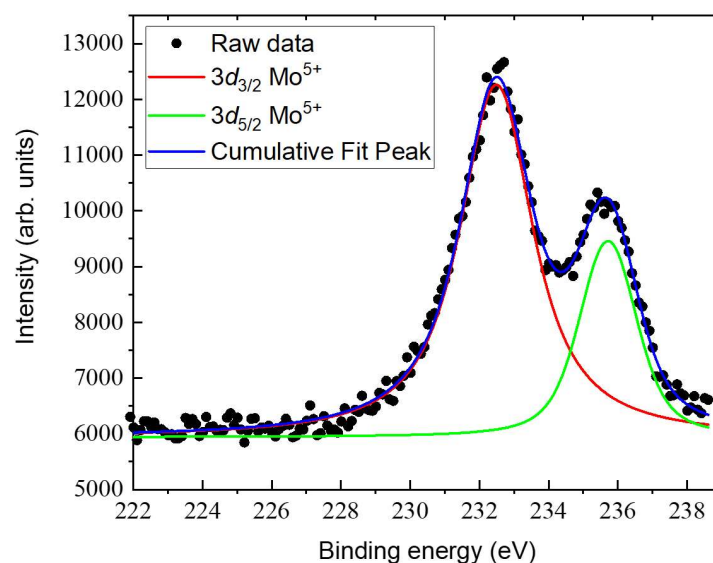
Supplementary Figure 11. Cross-sectional HAADF-STEM images of a MoS₂ grown on the α -Al₂O₃ (0001) substrate along the α -Al₂O₃ <10 $\bar{1}$ 0> direction, where the degree of unidirectional alignment is ~ 0 .



Supplementary Figure 12. (a) Schematic illustration of removal and regrowth of unidirectional MoS₂. The as-grown unidirectional MoS₂ is removed from *c*-plane sapphire substrate by water-assisted transfer method, which would perfectly maintain the formed buffer layer. (b) Optical micrographs of the regrown MoS₂ with unidirectional domain alignment. (c,d) Illustration and optical micrographs of MoS₂ domains grown on an unused new sapphire substrate, showing two antiparallel domains.

Supplementary Note 9. The structure of the buffer layer

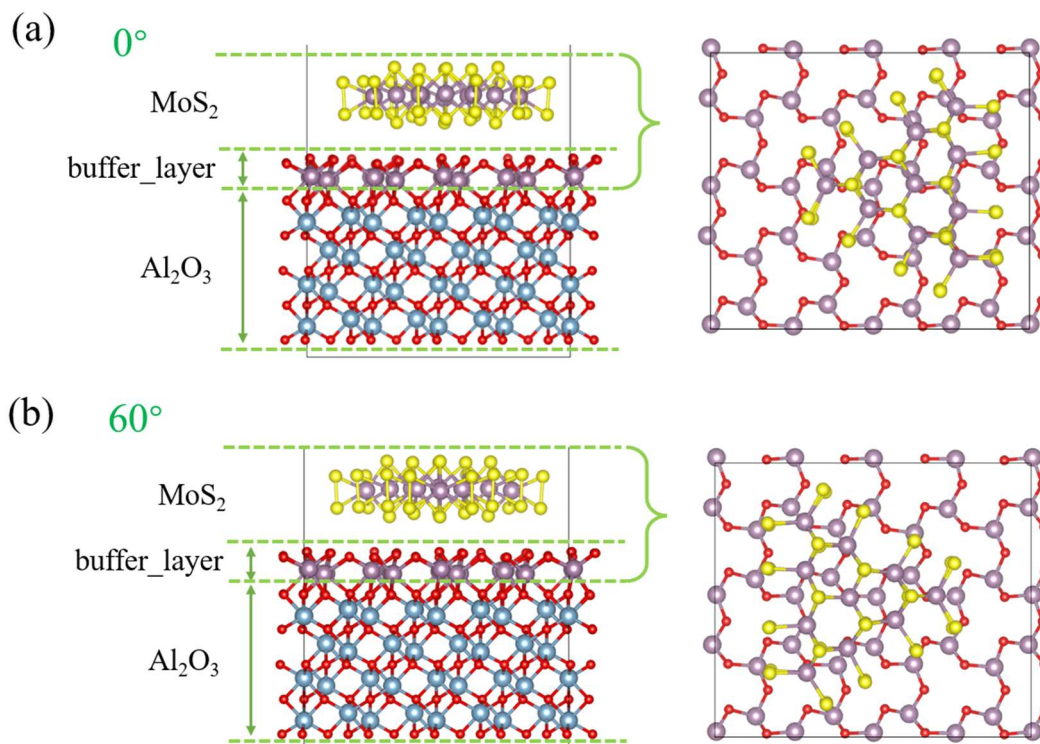
Supplementary Figure 13 shows the high-resolution XPS spectrum of Mo 3*d*, after removing the as-grown unidirectional MoS₂ by a non-destructive water-assisted technique. A deconvolution and curve fitting reveal that the Mo 3*d* spectrum can be decomposed into a doublet corresponding to 3*d*_{5/2} Mo⁵⁺ (3*d*_{3/2} Mo⁵⁺).



Supplementary Figure 13. The high-resolution XPS spectrum of Mo 3*d*.

Based on the XPS results and previous results of MoS₂ epitaxy on β -Ga₂O₃ (001)², we infer that one possible configuration of the buffer layer is O–Mo–O–Al, with Mo exhibiting a (+5) oxidation state. To determine the detailed structure of the O–Mo–O–Al buffer layer, we perform density functional theory (DFT) calculations with the Vienna ab initio software package³. The Perdew-Burke-Ernzerhof (PBE) exchange-correlation functionals are employed⁴, along with DFT-D2 method of Grimme van der Waals corrections⁵. An energy cutoff of 520 eV for the plane wave basis sets and a Γ -centered k-mesh of $1\times 1\times 1$ is used for geometry optimization and electronic structure calculations. The convergence of total energy with respect to these parameters is examined and found to reach the level of less than 0.001 eV/f.u. To prevent artificial interactions between periodic slab images, a vacuum thickness greater than 15 Å was applied. The Al₂O₃ (001) surfaces are modeled using large supercell slabs containing 9 atomic layers. The bottom 5 layers of atoms are kept fixed at their optimized bulk positions and other atomic positions are fully optimized with the lattice constant for the supercell kept fixed at a value corresponding to the experimental lattice constant for a 1×1 unit cell.

Supplementary Figure 14 shows the calculated the structure of the O–Mo–O–Al buffer layer on Al₂O₃ surface after fully structural relaxation. Generally, every O atom under the Mo layer is connected to two Al and two Mo atoms, and every Mo atom is connected to 3 O atoms under it. Meanwhile, every O atom above the Mo layer is connected to two Mo atoms and 3 O atoms are assigned to 1 Mo atom. Further, MoS₂ triangles with different orientations are positioned on the surface of the Al₂O₃ substrate with O–Mo–O–Al buffer layer. The DFT results reveal that the 60° structure, compared to the 0° structure, has a lower free energy of 110 meV, demonstrating a preferred growth orientation for MoS₂ triangles.

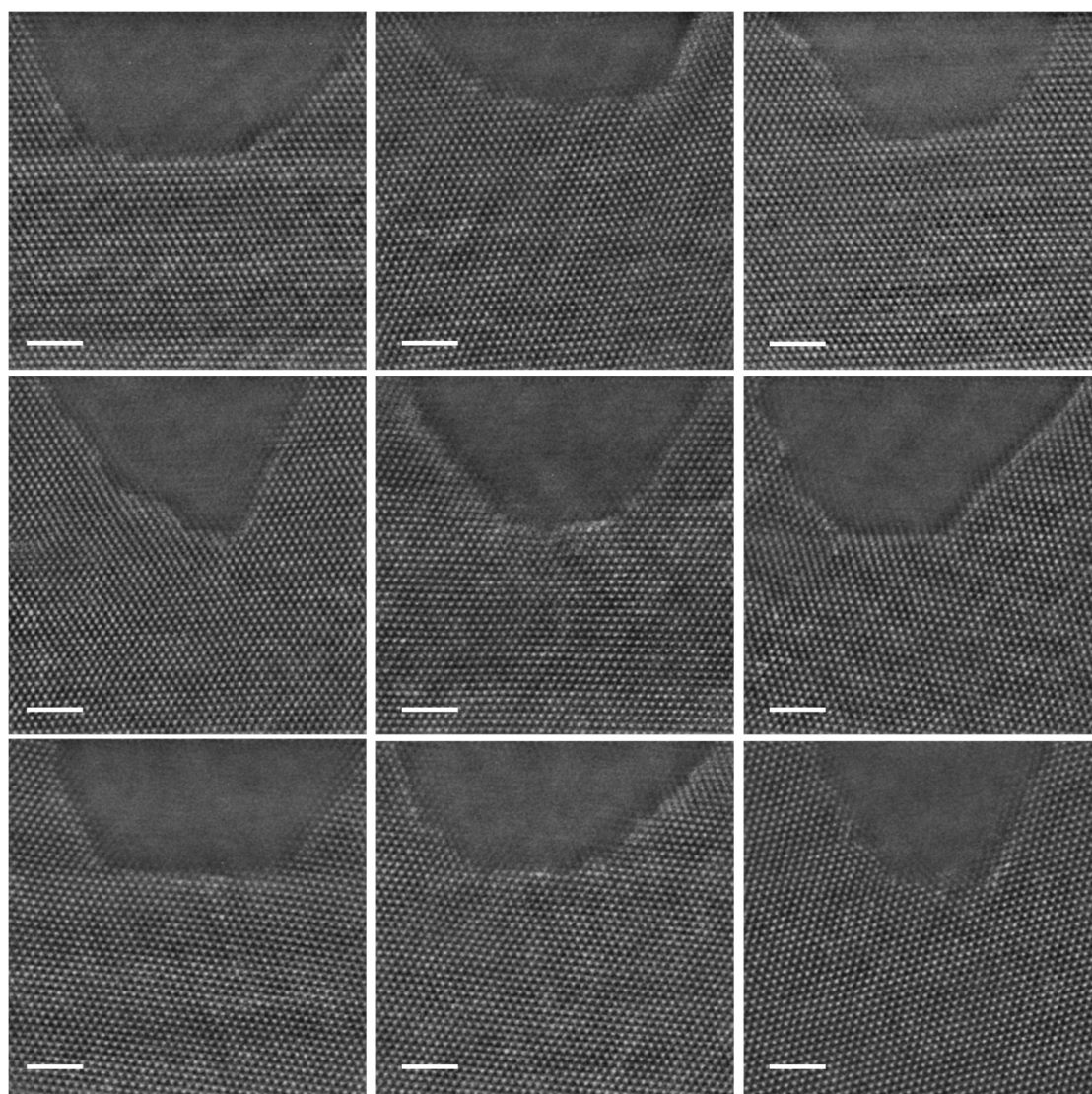


Supplementary Figure 14. The atomic structures of MoS₂ growth on α -Al₂O₃ (001) with buffer layer. The side view of the relaxed MoS₂ layer in 0° (a) and 60° (b) directions grown on Mo⁺⁵/Al₂O₃ substrate and the corresponding top view of MoS₂ on the buffer layer. The Mo, S, O and Al atoms are shown in purple, yellow, red, and blue respectively.

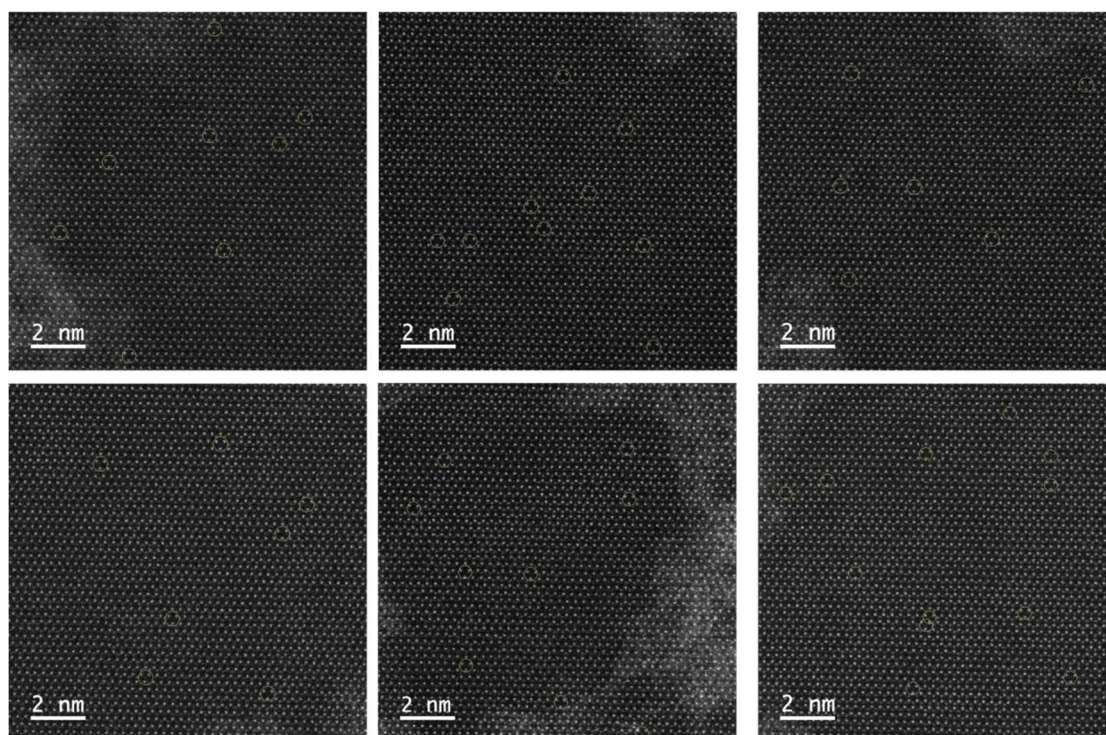
Supplementary Note 10. The atomic-resolution HAADF-STEM images of MoS₂ samples

Supplementary Figure 15 show more atomic-resolution HAADF-STEM images from different merging areas, the atomic-resolution HAADF-STEM images are filtered to enhance the contrast and no stitched grain boundary is found.

The Vs were denoted in the yellow circles in Supplementary Figure 16, and the average concentration of sulfur vacancy is about $\sim 5.2 \times 10^{12} \text{ cm}^{-2}$, which is an order of magnitude lower than that of previously reported exfoliated MoS₂.



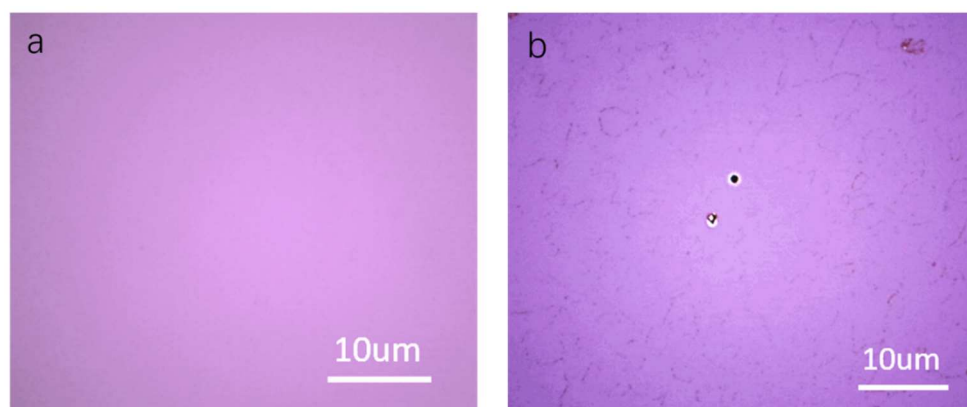
Supplementary Figure 15. HAADF-STEM images of the merging areas between neighboring unidirectional domains. Scale bar, 2 nm.



Supplementary Figure 16. The atomic-resolution STEM images of MoS₂ samples.

Supplementary Note 11. Etching results verify seamless stitching

The samples are heated at 150°C for 30 minutes under moisture-rich ambient conditions for thermal oxidation. No boundaries are observed for single oriented MoS₂ films (Supplementary Fig.17a), but boundaries can be clearly seen in multiple oriented MoS₂ films under the same condition (Supplementary Fig. 17b).

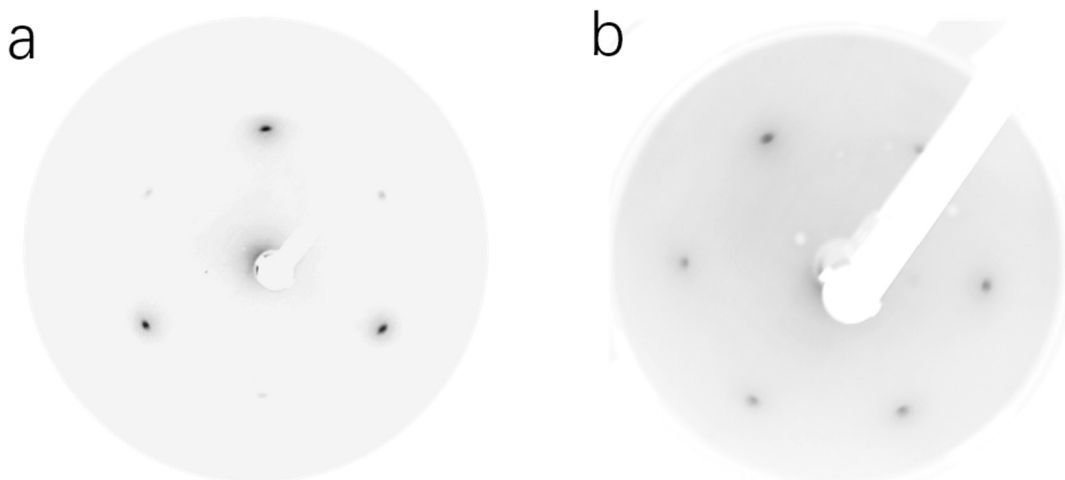


Supplementary Figure 17. Optical images of single oriented MoS₂ films (a) and multiple oriented MoS₂ films (b) after hot H₂O vapour etching.

Supplementary Note 12. The LEED patterns of MoS₂ films

Due to the three rotational symmetry of MoS₂, the intensity of three diffraction points in LEED diffraction are much higher than those of the other three points, indicating that the obtained MoS₂ films have a single domain orientation (Supplementary Fig. 18a). By contrast, the intensities of the six diffraction points in

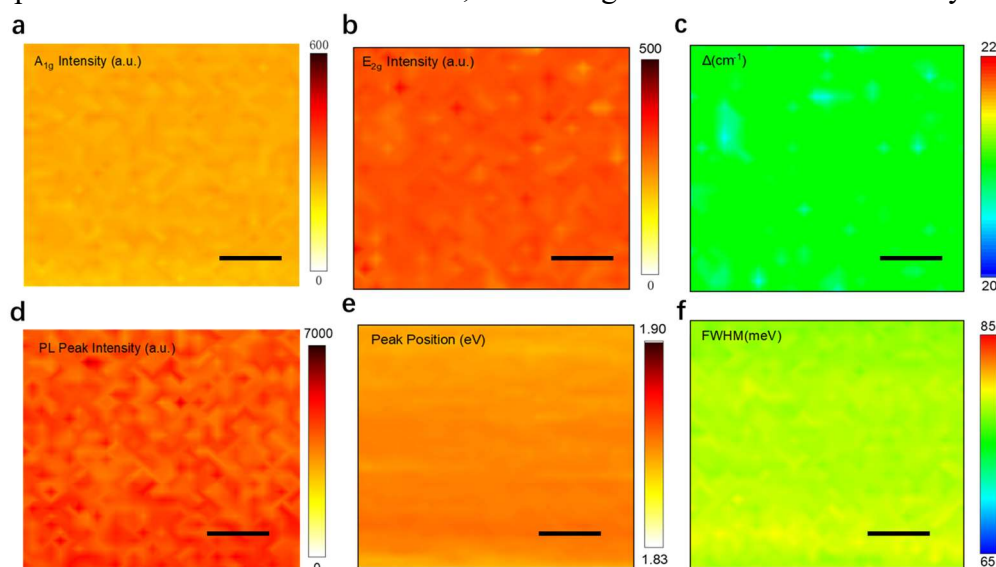
LEED diffraction are more uniform for continuous films with a mixture of two orientation domains (Supplementary Fig. 18b).



Supplementary Figure S18. The LEED patterns of single oriented MoS₂ films taken at the electron energy of 95eV (a) and the LEED patterns of multiple oriented MoS₂ films taken at the electron energy of 85eV (b).

Supplementary Note 13. High resolution PL and Raman mapping of MoS₂ single-crystal films

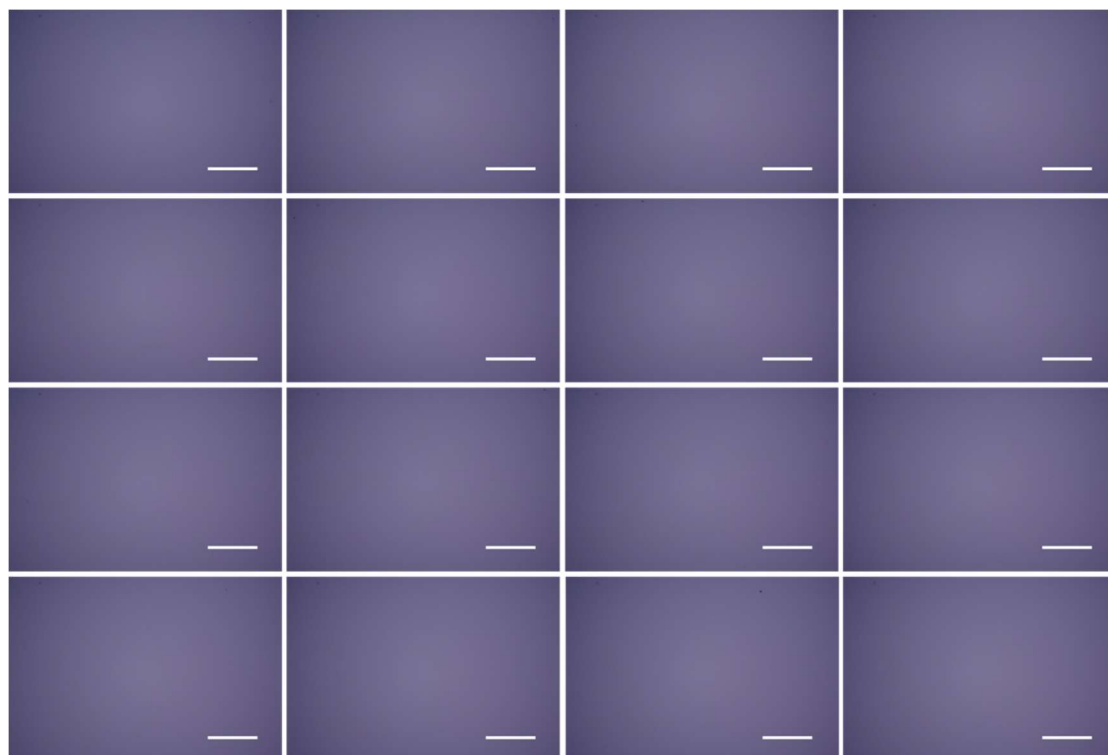
We perform high resolution PL and Raman mapping on MoS₂ wafers. Supplementary Figure 19 shows the PL and Raman mapping of MoS₂ single-crystal films: A_{1g} intensity (Supplementary Fig. 19a), E_{2g}^l intensity (Supplementary Fig. 19b) and the peak difference Δ between E_{2g}^l and A_{1g} (Supplementary Fig. 19c), PL peak intensity (Supplementary Fig. 19d), PL peak position (Supplementary Fig. 19e) and FWHM (Supplementary Fig. 19f). According to the statistics analysis, the average peak distance between the Raman peaks E_{2g}^l and A_{1g} of MoS₂ is about $20.5 \pm 0.5 \text{ cm}^{-1}$, and the average PL peak position is $1.86 \text{ eV} \pm 3 \text{ meV}$, and the average PL peak width at half height is $77 \text{ meV} \pm 2 \text{ meV}$. No apparent changes in the peak position and linewidth of both phonons and excitons are observed, illustrating the wafer-scale uniformity.



Supplementary Figure 19. Raman and PL mapping of MoS₂ single-crystal films. Raman spectra mapping in terms of A_{1g} intensity (a), E_{2g}^l intensity (b) and the peak difference Δ between E_{2g}^l and A_{1g} (c). (d,e,f). PL mapping of peak intensity (d), peak position (e) and FWHM (f), respectively. Scale bars, 5 μm .

Supplementary Note 14. Optical micrographs of single-crystal MoS₂ at different areas

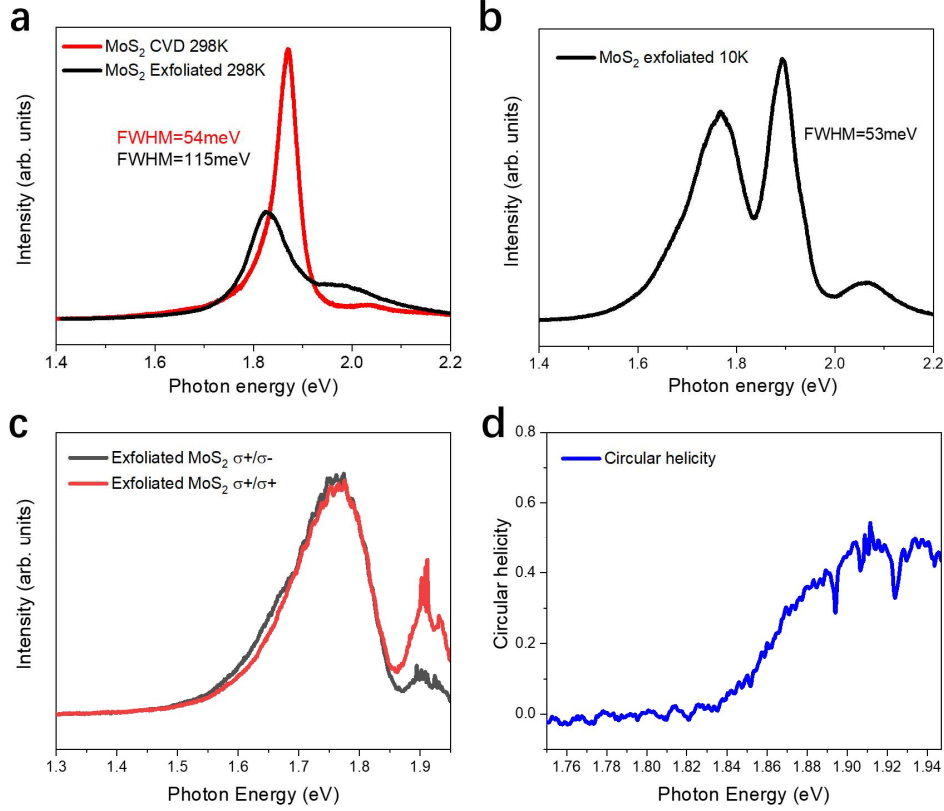
According to microscopy images taken at different locations across a 2-inch range (Supplementary Fig. 20), the excellent wafer-scale uniformity of the as-grown monolayer MoS₂ single crystal is scrutinized.



Supplementary Figure 20. Typical optical micrographs of MoS₂ grown on c-Al₂O₃ at different areas. Scale bar, 30 μm .

Supplementary Note 15. PL spectra of exfoliated monolayer MoS₂

Non-polarized PL spectra of exfoliated monolayer MoS₂ were performed and the full width at half maximum of the exfoliated monolayer MoS₂ is ~ 115 meV at 298K (Supplementary Fig. 21a) and ~ 53 meV at 10K (Supplementary Fig. 21b), which is about double of the values in our epitaxial monolayer MoS₂. The helicity-resolved PL spectra of the exfoliated monolayer MoS₂ was also performed at 10 K, excited by σ^+ radiation on resonance with the A exciton at 633 nm (1.96 eV) (Supplementary Fig. 21c), and the degree of exciton valley polarization is about 50% (Supplementary Fig. 21d).



Supplementary Figure 21. Optical characterization of exfoliated MoS₂. (a) Typical room-temperature PL spectra of exfoliated MoS₂ and CVD-grown MoS₂. (b) Typical PL spectra of exfoliated MoS₂ at 10K. (c) Circularly polarized photoluminescence spectra of exfoliated MoS₂ at 10K. (d) Circular polarization calculated from the PL spectra in c.

Supplementary Note 16. The transfer characteristics of h-BN encapsulated devices

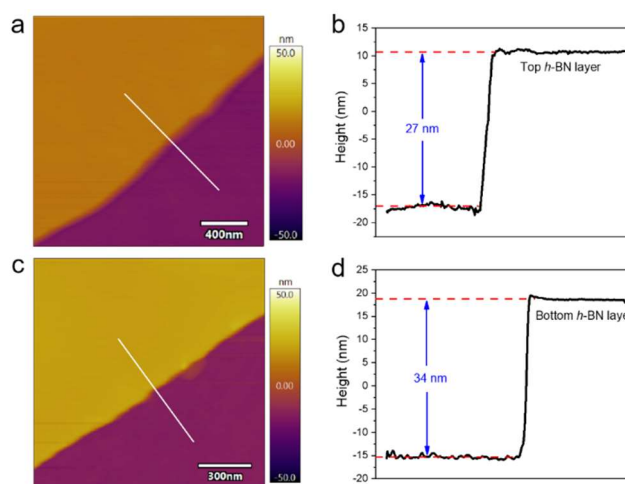
Supplementary Figure 22a (22c) shows the atomic force microscopy (AFM) image of the top (bottom) *h*-BN layer for *h*-BN encapsulated device in the main text. The corresponding height profiles (Supplementary Figs. 22b and 22d) indicate that the thickness of top and bottom *h*-BN layers is ~27 nm and ~34 nm, respectively.

Supplementary Figures 23a and 23b show a metal/*h*-BN/metal structure for capacitance measurement. The effective area between top and bottom metal electrodes is $20 \times 33 + 5 \times 3 \mu\text{m}^2$; the thickness of *h*-BN is ~54 nm (Supplementary Fig. 23c). The measured capacitance is $\sim 382 \times 10^{-15} \text{F}$. Then we can extract the dielectric constant of *h*-BN $\epsilon_r = \frac{C \cdot d}{\epsilon_0 \cdot S} = \frac{382 \times 10^{-15} \text{F} \times 54 \text{nm}}{8.854 \times 10^{-12} \text{F/m} \times (20 \times 33 + 5 \times 3) \mu\text{m}^2} = 3.452$, which is in good agree with previous results^{6,7}. Based on the measured dielectric constant of *h*-BN, we can

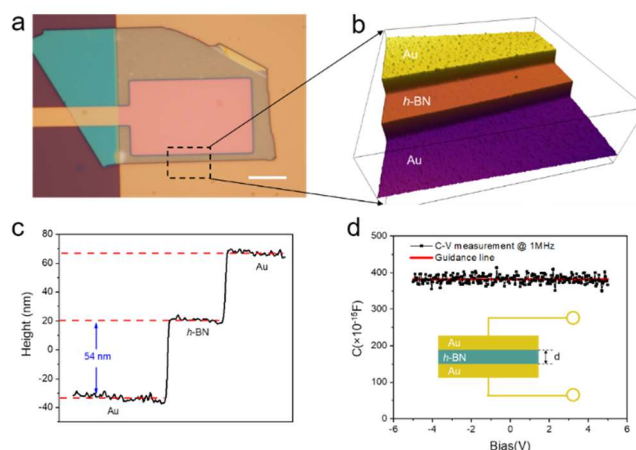
obtain the capacitance per unit area for top gate ($C_i = \frac{\epsilon_0 \cdot \epsilon_r}{d} = \frac{8.85 \times 10^{-12} \text{F/m} \times 3.45}{27 \times 10^{-9} \text{m}} = 1.131 \times 10^{-7} \text{F/cm}^2$) and bottom gate ($C_i = \frac{8.85 \times 10^{-12} \text{F/m} \times 3.45}{34 \times 10^{-9} \text{m}} = 0.872 \times 10^{-7} \text{F/cm}^2$).

The *h*-BN encapsulated devices with different channel length fabricated utilizing the pick-up technique (see method). Photograph of the *h*-BN encapsulated devices is

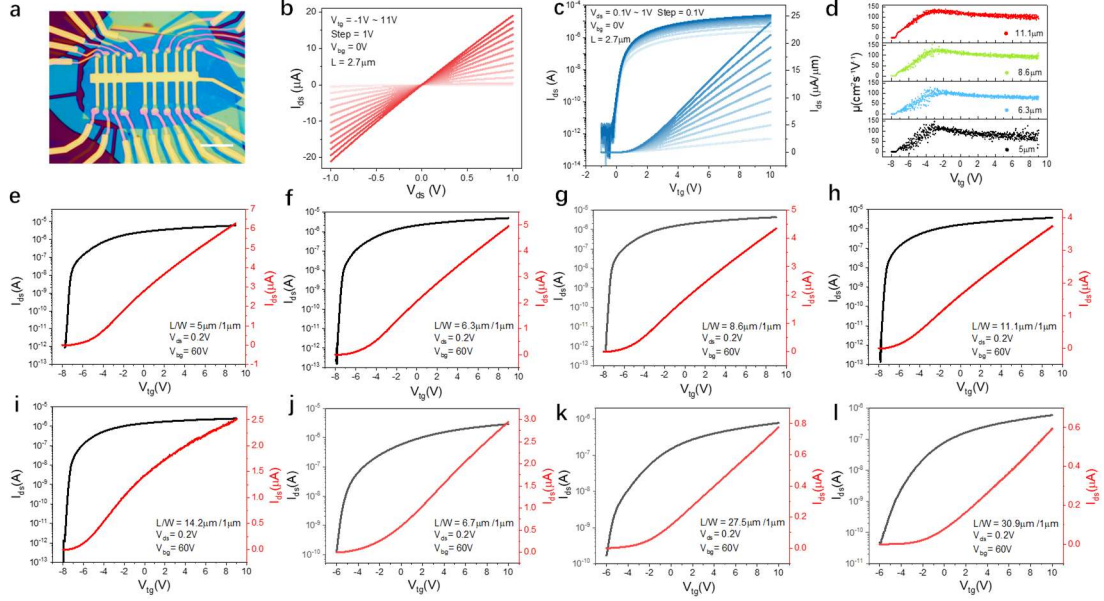
shown in Supplementary Fig. 24a. Supplementary Figures 24b and c show the room-temperature output (Supplementary Fig. 24a) and transfer (Supplementary Fig. 24a) characteristics of a *h*-BN encapsulated device with channel length of 2.7 μm and channel width of 1 μm . We calculated the variation of device mobility with top gate voltage for different channel lengths (Supplementary Fig. 24d), and the extracted field-effect mobility can reach $\sim 140 \text{ cm}^2\text{s}^{-1}\text{V}^{-1}$. Supplementary Figure 24e-l show the transfer curves of MoS₂ device with different channel length: 5 μm (Supplementary Fig. 24e), 6.3 μm (Supplementary Fig. 24f), 8.6 μm (Supplementary Fig. 24g), 11.1 μm (Supplementary Fig. 21h), 14.2 μm (Supplementary Fig. 24i), 6.7 μm (Supplementary Fig. 24j), 27.5 μm (Supplementary Fig. 24k), 30.9 μm (Supplementary Fig. 24l).



Supplementary Figure 22. (a,b) The AFM image of the top *h*-BN layer (a) and its corresponding height profiles (b). (c,d) The AFM image of the bottom *h*-BN layer (c) and its corresponding height profiles (d).



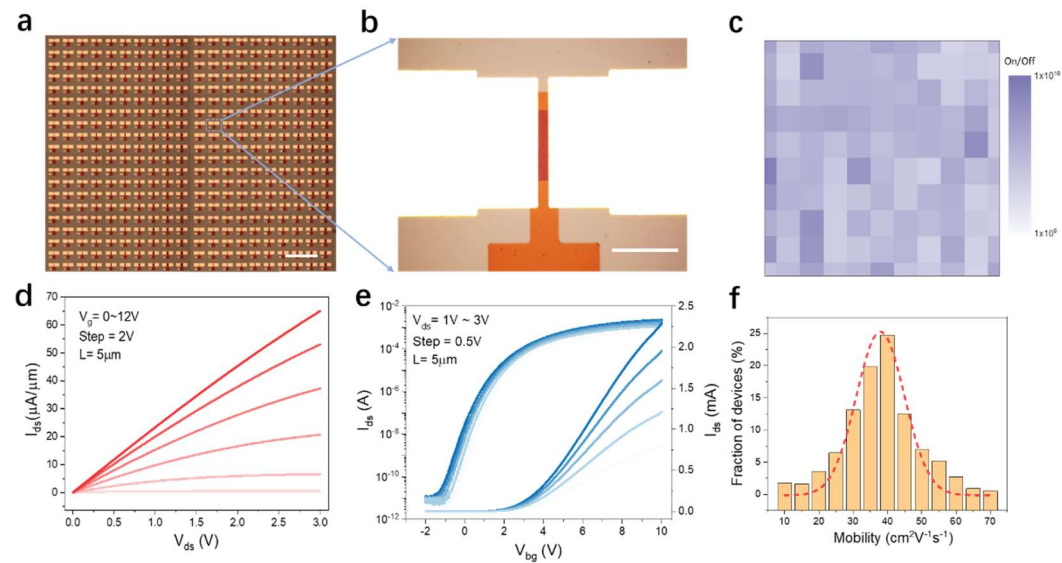
Supplementary Figure 23. (a) Optical image of a metal/*h*-BN/metal structure. The effective area between top and bottom metal electrodes is $20 \times 33 + 5 \times 3 \mu\text{m}^2$. (b,c) The thickness of *h*-BN is ~ 54 nm measured by AFM. (d) C-V curves. The measured capacity is 382 fF.



Supplementary Figure 24. FET performance of single MoS₂ devices. (a). Photograph of the single MoS₂ device. Scale bar, 10 μm. (b,c) Output and transfer curves of a *h*-BN encapsulated MoS₂ device with channel length/width (L/W) of 2.7/1 μm. $V_{bg} = 0V$. (d) The mobility with the change of V_{tg} at different channel lengths, $W = 1\mu m$, $V_{bg} = 60V$, $V_{ds} = 0.2V$. (e-l) Transfer curves of a *h*-BN encapsulated MoS₂ device with different channel.

Supplementary Note 17. Batch produced uncapsulated MoS₂ devices performance

Batch production of uncapsulated FET arrays over several centimeters is shown in Supplementary Fig. 25a. The 100 random FETs show an average on/off ratio $\sim 10^8$ (Supplementary Fig. 25c) and the statistical distribution of device mobility is shown in Supplementary Fig. 25f. Supplementary Figure 25d and 25e show the output (Supplementary Fig. 25d) and transfer (Supplementary Fig. 25e) curves of a typical device with channel length/width of 5/40 μm.

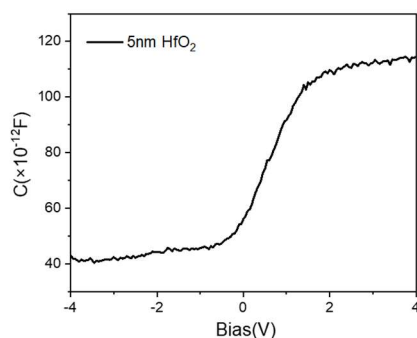


Supplementary Figure 25. FET performance of batch produced MoS₂ devices. (a) Photograph of a fabricated FET array. Scale bar, 1 mm. (b) Enlarged image of a unit cell, Scale bar, 45 μm. (c)

The on/off ratio of 100 random FETs. (d) Output and (e) transfer curves of a typical device with channel length/width of 5/40 μm . (f) The statistical distribution of device mobility.

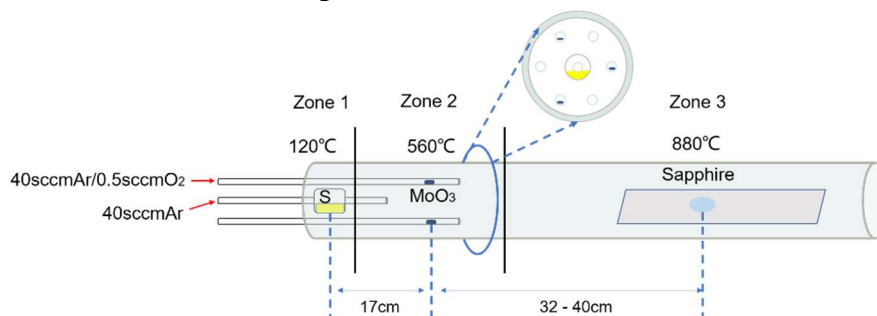
For our short-channel HfO_2 devices in the main text, the corresponding C-V curve with the measurement frequency of 1 kHz, and amplitude of 50 mV is shown Supplementary Fig. 26. The capacitance per unit area at $V=4$ V is $C_i =$

$$\frac{1.15 \times 10^{-1} \text{ F}}{100 \times 10^{-6} \times 100 \times 10^{-6} \text{ m}^2} = 1.15 \times 10^{-6} \text{ F/cm}^2.$$

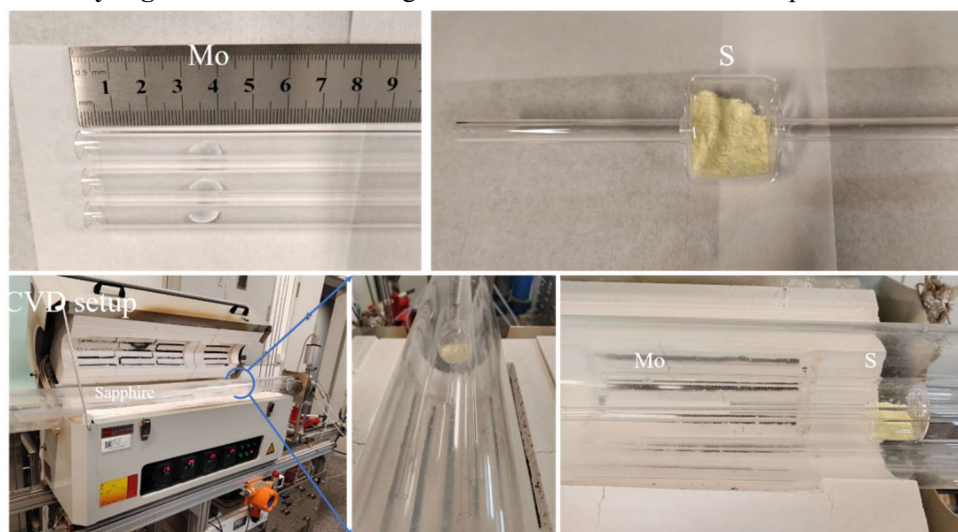


Supplementary Figure 26. The gate capacitances for the short-channel HfO_2 devices.

Supplementary Note 18. Schematic diagram and photographs of our specially designed multisource CVD setup

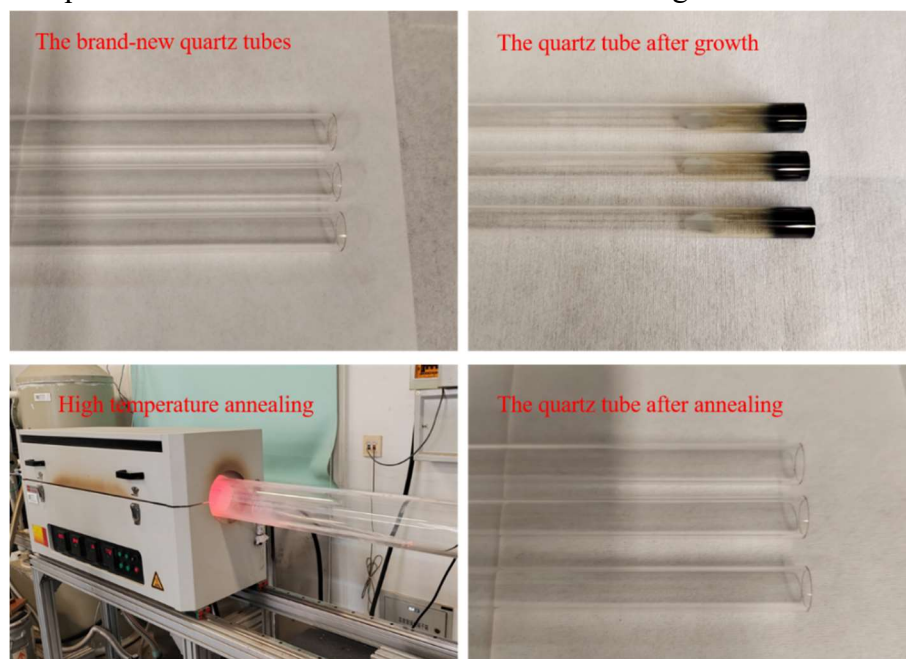


Supplementary Figure 27. Schematic diagram of the multisource CVD setup.



Supplementary Figure 28. Photographs of our three-temperature-zone CVD setup and the location of the solid-state sources and the substrate.

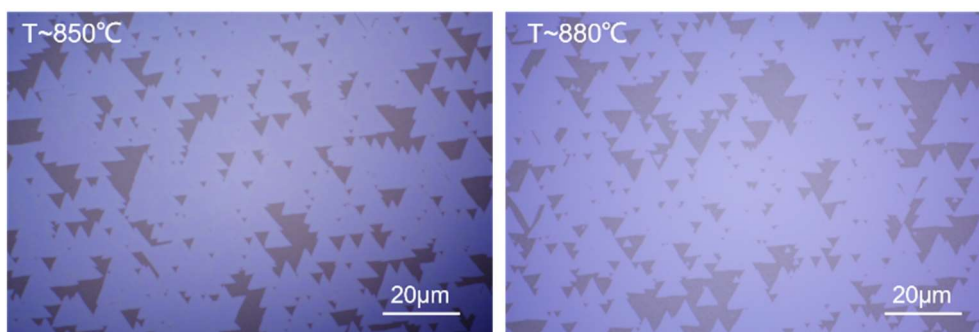
The quartz tube would develop a coating of Mo/MoO₃ after the growth, as shown in Supplementary Fig. 29. To eliminate this effect, we will anneal the used quartz tubes in an air atmosphere at a high temperature (>1000°C) for 1h after the growth, and at the same time extract the exhaust gases from the high temperature annealing (residual Mo source, S source) through negative pressure pump. As can be seen from Supplementary Fig. 29, the quartz tubes after high temperature annealing are as clean as brand-new quartz tubes and will not interfere with the next growth.



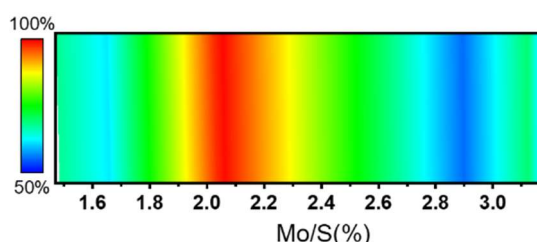
Supplementary Figure 29. The photographs of brand-new quartz tubes, the quartz tube after growth and the quartz tube after annealing (previously used one).

Supplementary Note 19. Unidirectional epitaxy at 850°C

In addition to the unidirectional epitaxy at 880°C in the main text, we also achieve the unidirectional growth at 850°C (Supplementary Fig. 30). However, at different growth temperatures, the corresponding S/MoO₃ precursor ratio is different. For example, Supplementary Figure 31 shows the degree of unidirectional alignment against the MoO₃/S precursor ratios at a growth temperature of 850°C. Clearly, the best MoO₃/S precursor ratio that show ~100% unidirectional alignment is ~2.1%. This is contrast to the best MoO₃/S precursor ratio of ~4.5% at a growth temperature of 880°C (Fig. 1c in the main text).



Supplementary Figure 30. Unidirectional growth of MoS₂ at different growth temperatures and different growth conditions.



Supplementary Figure 31. Proportional changes of the single oriented MoS₂ domains grown by varying the MoO₃/S ratio at a growth temperature of 850°C.

Supplementary Note 20. General mechanism of the single-crystal TMD growth

Recently, some works have reported the growth of single-crystal TMDs on sapphire substrates^{1,8-10}. However, these works rely heavily on the surface step engineering (e.g., controlling the surface step orientation and height), which typically requires the specially-designed substrates such as deliberately engineered off-cut angles or annealing at harsh temperatures. Remarkably, we realize the epitaxial growth of wafer-scale single-crystal MoS₂ monolayers on industry-compatible of general *c*-plane sapphire substrates by simply controlling the S/MoO₃ precursor ratio, showing high novelty.

Regarding the general mechanism, a universal symmetry framework has been theoretically established to guide the growth of wafer-scale single-crystal 2D materials, i.e., the symmetry group of the substrate should be a subgroup of 2D material¹¹. In the light of such general guideline, *c*-plane sapphire with C_{3v} symmetry offers a possible industry-compatible substrate for the epitaxial growth of wafer-scale single-crystal MoS₂ with point group D_{3h} (C_{3v} plus a mirror-reflection symmetry σ_h). However, the adsorption energy of the most preferred domain orientation (i.e., 30°) is just slightly lower than that at 90° configuration. This usually results in two antiparallel grains and twin boundaries, as in the earlier results^{12,13}. Consequently, the key strategies to achieve the growth of wafer-scale single-crystal MoS₂ is to enlarge the binding energy difference between the most preferred domain orientation and its antiparallel domain. For previously reported wafer-scale growth of single-crystal TMDs via surface step engineering, it does follow the general guideline where the sapphire step edge-TMDs interaction breaks the symmetry of the antiparallel orientations. In our work, we enlarge the binding energy difference between the most preferred domain orientation and its

387 antiparallel domain to realize wafer-scale single-crystal MoS₂ by precisely controlling
388 the S/MoO₃ precursor ratio.

389 **Supplementary Table 1. Comparison of monolayer TMD electrical performance**

Synthetic way	Layer	Channel length	T _{ox} (nm)	I _{on} (uA/um)	Mobility cm ² V ⁻¹ s ⁻¹	On/off	Ref.
CVD	1L-MoS ₂	200nm	30nm HfO ₂	535	140	10 ⁹	This work
CVD	1L-MoS ₂	8.2nm	6nm HfO ₂	2.5	1.1	10 ⁶	[14]
CVD	1L-MoS ₂	15nm	10nm HfO ₂	5	\	10 ⁶	[15]
CVD	1L-MoS ₂	50nm	5nm HfO ₂	156	21.4	10 ⁶	[16]
CVD	1L-MoS ₂	2μm	300nm SiO ₂	18	122.6	\	[17]
CVD	1L-MoS ₂	72nm	30nm SiO ₂	320	35.7	\	[18]
CVD	1L-MoS ₂	8.3μm	270nm SiO ₂	6	43	\	[19]
CVD	1L-MoS ₂	20μm	300nm SiO ₂	0.14	7	10 ⁶	[20]
CVD	1L-MoS ₂	500nm	30nm Al ₂ O ₃	450	102.6	10 ⁹	[21]
CVD	1L-MoS ₂	10μm	35nm Al ₂ O ₃	6	75	10 ⁸	[22]
CVD	1L-MoS ₂	4μm	20nm Al ₂ O ₃	16.7	30	10 ¹⁰	[23]
CVD	1L-MoS ₂	1μm	15nm HfO ₂	55	54	\	[24]
MOCVD	1L-MoS ₂	1.6μm	285nm SiO ₂	10	30	10 ⁶	[25]
CVD	1L-MoS ₂	1μm	285nm SiO ₂	49	64	10 ⁷	[26]
CVD	1L-MoS ₂	100nm	285nm SiO ₂	62.5	13	\	[27]
CVD	1L-MoS ₂	10nm	5-6nm Al ₂ O ₃	426	30	\	[28]
CVD	1L-MoS ₂	80nm	6nm Al ₂ O ₃	20	\	10 ⁶	[29]
CVD	1L-MoS ₂	400nm	30nm SiO ₂	280	34	10 ⁶	[30]
CVD	1L-MoS ₂	450nm	30nm HfO ₂	65	55	\	[31]
Exfoliated	1L-MoS ₂	10nm	300nm SiO ₂	540	26.7	10 ⁷	[32]
Exfoliated	1L-MoS ₂	120nm	100nm SiNx	560	\	10 ⁷	[33]
Exfoliated	1L-MoS ₂	500nm	30nm HfO ₂	320	60(250K)	10 ⁸	[34]
Exfoliated	1L-MoS ₂	450nm	93nm SiO ₂	240	83	10 ⁸	[35]
Exfoliated	1L-MoS ₂	600nm	90nm SiO ₂	10	13.2	10 ⁶	[36]
Exfoliated	1L-MoS ₂	1.3μm	30nm HfO ₂	22	320	10 ⁶	[37]
Exfoliated	1L-MoS ₂	1.5μm	6nm HfO ₂	125	16	\	[38]
Exfoliated	1L-MoS ₂	2μm	72nm Al ₂ O ₃	20	11	10 ³	[39]
Exfoliated	1L-MoS ₂	1.9μm	15nm h-BN	22	\	10 ⁹	[40]
Exfoliated	1L-MoS ₂	2μm	300nm SiO ₂	5	27.6	10 ⁶	[41]
Exfoliated	1L-MoS ₂	1.2μm	100nm SiO ₂	85	48	10 ⁷	[42]
Exfoliated	1L-MoS ₂	2μm	30nm Al ₂ O ₃	450	41	10 ⁷	[43]
CVD	1L-MoSe ₂	5μm	300nm SiO ₂	\	1	10 ⁶	[44]
CVD	1L-MoSe ₂	3μm	300nm SiO ₂	\	30	10 ⁴	[45]
CVD	1L-WS ₂	30nm	5.5nm HfO ₂	322	\	\	[46]
CVD	1L-WS ₂	\	300nm SiO ₂	\	50	10 ⁷	[47]
CVD	1L-WS ₂	\	300nm SiO ₂	\	20	10 ⁸	[48]
CVD	1L-WS ₂	120nm	100nm SiNx	331	\	10 ⁷	[33]
CVD	1L-WSe ₂	6μm	300nm SiO ₂	\	150(holes)	10 ⁷	[49]
CVD	1L-WSe ₂	\	90nm SiO ₂	\	82(holes)	\	[50]
CVD	1L-WSe ₂	1.5μm	300nm SiO ₂	7.6	40	\	[51]

Exfoliated	1L-WS ₂	\	10nm Al ₂ O ₃ /300nm SiO ₂	\	83	10 ⁸	[52]
Exfoliated	1L-WSe ₂	1.2μm	72nm Al ₂ O ₃	210	142	10 ⁶	[53]
Exfoliated	1L-WSe ₂	9.4μm	17.5 nm ZrO ₂	\	250(holes)	10 ⁶	[54]
Exfoliated	1L-WSe ₂	2.4μm	300nm SiO ₂	34	180	\	[55]

Supplementary References

- 1 Fu, J.-H. *et al.* Oriented lateral growth of two-dimensional materials on c-plane sapphire. *Nat. Nanotechnol.*, **18**, 1289-1294 (2023).
- 2 Aljarb, A. *et al.* Interfacial Reconstructed Layer Controls the Orientation of Monolayer Transition-Metal Dichalcogenides. *ACS Nano* **17**, 10010-10018 (2023).
- 3 Kresse, G. & Furthmüller, J. Efficient iterative schemes for ab initio total-energy calculations using a plane-wave basis set. *Phys. Rev. B* **54**, 11169-11186 (1996).
- 4 Blöchl, P. E. Projector augmented-wave method. *Phys. Rev. B* **50**, 17953-17979 (1994).
- 5 Tkatchenko, A. & Scheffler, M. Accurate Molecular Van Der Waals Interactions from Ground-State Electron Density and Free-Atom Reference Data. *Phys. Rev. Lett.* **102**, 073005 (2009).
- 6 Tang, J. *et al.* Vertical Integration of 2D Building Blocks for All-2D Electronics. *Adv. Electron. Mater.* **6**, 2000550 (2020).
- 7 Laturia, A., Van de Put, M. L. & Vandenberghe, W. G. Dielectric properties of hexagonal boron nitride and transition metal dichalcogenides: from monolayer to bulk. *npj 2D Mater. Appl.* **2**, 6 (2018).
- 8 Li, T. *et al.* Epitaxial growth of wafer-scale molybdenum disulfide semiconductor single crystals on sapphire. *Nat. Nanotechnol.* **16**, 1201-1207 (2021).
- 9 Wang, J. *et al.* Dual-coupling-guided epitaxial growth of wafer-scale single-crystal WS₂ monolayer on vicinal a-plane sapphire. *Nat. Nanotechnol.* **17**, 33-38 (2022).
- 10 Zhu, H. *et al.* Step engineering for nucleation and domain orientation control in WSe₂ epitaxy on c-plane sapphire. *Nat. Nanotechnol.*, **18**, 1295–1302 (2023).
- 11 Dong, J., Zhang, L., Dai, X. & Ding, F. The epitaxy of 2D materials growth. *Nat. Commun.* **11**, 5862 (2020).
- 12 Yu, H. *et al.* Wafer-Scale Growth and Transfer of Highly-Oriented Monolayer MoS₂ Continuous Films. *ACS Nano* **11**, 12001-12007 (2017).
- 13 Aljarb, A. *et al.* Substrate Lattice-Guided Seed Formation Controls the Orientation of 2D Transition-Metal Dichalcogenides. *ACS Nano* **11**, 9215-9222 (2017).
- 14 Xu, K. *et al.* Sub-10 nm Nanopattern Architecture for 2D Material Field-Effect Transistors. *Nano Lett.* **17**, 1065-1070 (2017).
- 15 Nourbakhsh, A. *et al.* in *2015 Symposium on VLSI Technology (VLSI Technology)*. T28-T29.
- 16 Zhu, Y. *et al.* Monolayer Molybdenum Disulfide Transistors with Single-Atom-Thick Gates. *Nano Lett.* **18**, 3807-3813 (2018).
- 17 Wang, Y. *et al.* Van der Waals contacts between three-dimensional metals and two-dimensional semiconductors. *Nature* **568**, 70-74 (2019).
- 18 Smithe, K. K. H., English, C. D., Suryavanshi, S. V. & Pop, E. High-Field Transport and Velocity Saturation in Synthetic Monolayer MoS₂. *Nano Lett.* **18**, 4516-4522 (2018).
- 19 Dumcenco, D. *et al.* Large-Area Epitaxial Monolayer MoS₂. *ACS Nano* **9**, 4611 (2015).

430 20 Zhang, J. *et al.* Scalable Growth of High-Quality Polycrystalline MoS₂ Monolayers on SiO₂
431 with Tunable Grain Sizes. *ACS Nano* **8**, 6024 (2014).

432 21 Li, T. *et al.* Epitaxial growth of wafer-scale molybdenum disulfide semiconductor single
433 crystals on sapphire. *Nat. Nanotechnol.* **16**, 1201-1207 (2021).

434 22 Li, N. *et al.* Atomic Layer Deposition of Al₂O₃ Directly on 2D Materials for High-
435 Performance Electronics. *Adv. Mater. Interfaces* **6**, 1802055 (2019).

436 23 Yu, L. *et al.* in *2015 IEEE International Electron Devices Meeting (IEDM)*. 32.33.31-
437 32.33.34.

438 24 Meng, W. *et al.* Three-dimensional monolithic micro-LED display driven by atomically
439 thin transistor matrix. *Nat. Nanotechnol.* **16**, 1231-1236 (2021).

440 25 Kang, K. *et al.* High-mobility three-atom-thick semiconducting films with wafer-scale
441 homogeneity. *Nature* **520**, 656-660 (2015).

442 26 Sun, L. *et al.* Concurrent Synthesis of High-Performance Monolayer Transition Metal
443 Disulfides. *Adv. Fun. Mater.* **27**, 1605896 (2017).

444 27 Liu, H. *et al.* Statistical Study of Deep Submicron Dual-Gated Field-Effect Transistors on
445 Monolayer Chemical Vapor Deposition Molybdenum Disulfide Films. *Nano Lett.* **13**, 2640-
446 2646 (2013).

447 28 English, C. D., Smithe, K. K. H., Xu, R. L. & Pop, E. in *2016 IEEE International Electron*
448 *Devices Meeting (IEDM)*. 5.6.1-5.6.4.

449 29 Cao, W., Liu, W., Kang, J. & Banerjee, K. An Ultra-Short Channel Monolayer MoS₂ FET
450 Defined By the Curvature of a Thin Nanowire. *IEEE Electron Device Letters* **37**, 1497-
451 1500 (2016).

452 30 McClellan, C. J., Yalon, E., Smithe, K. K. H., Suryavanshi, S. V. & Pop, E. in *2017 75th*
453 *Annual Device Research Conference (DRC)*. 1-2.

454 31 Sanne, A. *et al.* Radio Frequency Transistors and Circuits Based on CVD MoS₂. *Nano Lett.*
455 **15**, 5039-5045 (2015).

456 32 Xie, L. *et al.* Graphene-Contacted Ultrashort Channel Monolayer MoS₂ Transistors. *Adv.*
457 *Mater.* **29**, 1702522 (2017).

458 33 Shen, P.-C. *et al.* Ultralow contact resistance between semimetal and monolayer
459 semiconductors. *Nature* **593**, 211-217 (2021).

460 34 Lembke, D. & Kis, A. Breakdown of High-Performance Monolayer MoS₂ Transistors. *ACS*
461 *Nano* **6**, 10070 (2012).

462 35 Rai, A. *et al.* Air Stable Doping and Intrinsic Mobility Enhancement in Monolayer
463 Molybdenum Disulfide by Amorphous Titanium Suboxide Encapsulation. *Nano Lett.* **15**,
464 4329-4336 (2015).

465 36 Liu, W. *et al.* in *2013 IEEE International Electron Devices Meeting*. 19.14.11-19.14.14.

466 37 Radisavljevic, B., Whitwick, M. B. & Kis, A. Integrated Circuits and Logic Operations
467 Based on Single-Layer MoS₂. *ACS Nano* **5**, 9934-9938 (2011).

468 38 Wang, J. *et al.* Integration of High-k Oxide on MoS₂ by Using Ozone Pretreatment for
469 High-Performance MoS₂ Top-Gated Transistor with Thickness-Dependent Carrier
470 Scattering Investigation. *Small* **11**, 5932-5938 (2015).

471 39 Kang, J., Liu, W. & Banerjee, K. High-performance MoS₂ transistors with low-resistance
472 molybdenum contacts. *Appl. Phys. Lett.* **104**, 093106 (2014).

473 40 Zheng, X. *et al.* Patterning metal contacts on monolayer MoS₂ with vanishing Schottky

474 barriers using thermal nanolithography. *Nat. Electron.* **2**, 17-25 (2019).

475 41 Xie, L. *et al.* A facile and efficient dry transfer technique for two-dimensional Van der Waals
476 heterostructure. *Chin. Phys. B* **26**, 087306 (2017).

477 42 Kappera, R. *et al.* Phase-engineered low-resistance contacts for ultrathin MoS₂ transistors.
478 *Nat. Mater.* **13**, 1128-1134 (2014).

479 43 Yu, Z. *et al.* in *2018 IEEE International Electron Devices Meeting (IEDM)*. 22.24.21-
480 22.24.24.

481 44 Li, J. *et al.* Chemical Vapor Deposition of 4 Inch Wafer-Scale Monolayer MoSe₂. *Small*
482 *Science*, **2**, 2200062 (2022).

483 45 Meng, Y. *et al.* Repairing atomic vacancies in single-layer MoSe₂ field-effect transistor and
484 its defect dynamics. *npj Quantum Materials* **2**, 16 (2017).

485 46 Sun, Z. *et al.* Statistical Assessment of High-Performance Scaled Double-Gate Transistors
486 from Monolayer WS₂. *ACS Nano* **16**, 14942-14950 (2022).

487 47 Aji, A. S., Solís-Fernández, P., Ji, H. G., Fukuda, K. & Ago, H. High Mobility WS₂
488 Transistors Realized by Multilayer Graphene Electrodes and Application to High
489 Responsivity Flexible Photodetectors. *Adv. Fun. Mater.* **27**, 1703448 (2017).

490 48 Yun, S. J. *et al.* Synthesis of Centimeter-Scale Monolayer Tungsten Disulfide Film on Gold
491 Foils. *ACS Nano* **9**, 5510-5519 (2015).

492 49 Stoeckel, M.-A. *et al.* Boosting and Balancing Electron and Hole Mobility in Single- and
493 Bilayer WSe₂ Devices via Tailored Molecular Functionalization. *ACS Nano* **13**, 11613-
494 11622 (2019).

495 50 Ji, H. G. *et al.* Chemically Tuned p- and n-Type WSe₂ Monolayers with High Carrier
496 Mobility for Advanced Electronics. *Adv. Mater.* **31**, 1903613 (2019).

497 51 Wang, Y. *et al.* P-type electrical contacts for 2D transition-metal dichalcogenides. *Nature*
498 **610**, 61-66 (2022).

499 52 Cui, Y. *et al.* High-Performance Monolayer WS₂ Field-Effect Transistors on High-κ
500 Dielectrics. *Adv. Mater.* **27**, 5230-5234 (2015).

501 53 Liu, W. *et al.* Role of Metal Contacts in Designing High-Performance Monolayer n-Type
502 WSe₂ Field Effect Transistors. *Nano Lett.* **13**, 1983-1990 (2013).

503 54 Fang, H. *et al.* High-Performance Single Layered WSe₂ p-FETs with Chemically Doped
504 Contacts. *Nano Lett.* **12**, 3788-3792 (2012).

505 55 Allain, A. & Kis, A. Electron and Hole Mobilities in Single-Layer WSe₂. *ACS Nano* **8**,
506 7180-7185 (2014).