

Supporting Information

Strain Engineering, Efficient Excitonic Photoluminescence, and Exciton Funnelling in Unmodified MoS₂ Nanosheets

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Methods

Fabrication of textured Si substrates. Fabrication of textured Si substrates required formation of a hard mask on the substrate surface, pattern transfer to the substrate *via* dry etching, and definition of the desired substrate texture *via* thermal oxidation.

The hard mask was defined by laser interference lithography (LIL), metal deposition, and lift-off. LIL began with applying an anti-reflective coating (ARC) on the substrate surface. Specifically, an ICON-7 ARC (Brewer Science) was spun at 3000 RPM and soft-baked on a hotplate at 200°C for 60 s. The process yielded a 70 nm-thick layer. After depositing the ARC, a negative photoresist (NR-7 500p-Futurrex, Inc.) was spun at 5000

RPM to obtain a thickness of ~ 300 nm. The photoresist was soft baked on a hot plate at 150°C for 60 s. The desired pattern (*i.e.*, a 2D array of circular trenches with pitch d) was transferred to the photoresist using a Nd:YAG laser with a wavelength of 355 nm. A Bragg grating was established *via* interference of the incident and the reflected laser beam. The reflected laser beam was created using a mirror placed perpendicularly to the sample. The period of the diffraction pattern was calculated from Bragg's law as $d = n\lambda / 2\sin\theta$, where n is the refractive index of air, d is the desired pitch or the distance between the periodic grating structures and θ is the angle of interference between the two laser beams. In our experiments the interference angle was varied between 33.15° and 12.34° to obtain patterns with pitch in the range of ~ 300 - 1000 nm. In order to obtain 2D arrays, the photoresist was exposed twice to the interference pattern. The sample was rotated by 90° between the two exposures. Following exposure, the photoresist was developed in MF-321 (Shipley) for 60 s. Upon development the photoresist was patterned in a 2D array of circular trenches. The ARC was removed from the bottom of the trenches by a 1 min oxygen plasma at 50 W. Circular Cr pads were obtained by a blanket deposition of ~ 40 nm-thick Cr layer followed by lift-off. Cr was e-beam evaporated. Reactive ion etching (RIE) in CF_4/O_2 was performed to obtain an array of Si posts. The Cr caps served as hard mask during dry etching. The power and the gas flow were kept constant at 100 W and 30 sccm, respectively. Various pressures in the range of 15-30 mTorr produced posts with different geometries. Posts of different amplitudes were obtained by tailoring the duration of the etching process between 10 and 20 minutes (Data not shown here). The Cr mask was removed by a commercially available Cr etchant (CR7-MicroChemicals GmbH). The Si substrates were thermally oxidized in O_2 at 950°C . Inverted Si funnels were achieved

after 10 h oxidation of Si posts with a diameter of ~ 300 nm. Different oxidation times yielded a variety of substrate textures (see two representative examples in Fig. S1). The thermal oxide was removed by wet chemical etching in a 49% hydrofluoric acid solution.

Transfer and strain engineering of MoS₂ nanosheets. Poly(methyl methacrylate) or PMMA (950A9-Microchem, Inc.) was spun on the receiving substrates at 3000 RPM for 30 seconds, yielding a thickness of ~ 1.5 μm . MoS₂ flakes were then extracted from a molybdenite crystal (2D semiconductors, Inc.) by mechanical exfoliation. MoS₂ sheets with thickness in the range of ~ 10 - 20 μm were transferred onto the PMMA-coated substrates. Exfoliation and transfer were mediated by a polydimethylsiloxane (PDMS) stamp. Afterwards, the MoS₂/PMMA/Si combination was soft-baked on a hot-plate at 90°C for 2 minutes. A clean PDMS stamp was brought in contact with the MoS₂ flakes to further thin them down by mechanical exfoliation of the topmost layers. MoS₂ nanosheets with an average thickness of 6 ± 2 nm and lateral dimensions of $\sim 50\times 50$ μm^2 were obtained using this process. Lateral dimensions of the MoS₂ flakes were estimated by optical microscopy. The thickness of the nanosheets was measured by atomic force microscopy and transmission electron microscopy. Average thickness was calculated over 5 measurements performed on 5 different MoS₂ flakes.

After obtaining the thin flakes, samples were annealed in a custom-built vacuum tube furnace to achieve selective sublimation of PMMA and dry release in place of MoS₂ nanosheets on the textured substrate. Annealing was performed at 300°C in a 5 sccm Ar flow. The pressure in the tube was maintained at 3 mTorr by a turbo-pump. Samples were placed horizontally in the tube furnace. The duration of the annealing process ranged from 5 h to 12 h depending on the lateral size of the MoS₂ flakes.

Atomic force microscopy. Atomic force microscopy (AFM) was used to characterize surface topography and measure the thickness of the MoS₂ nanosheets on flat substrates. Measurements were performed in tapping mode on an Asylum MFP3D atomic force microscope operated under tapping mode using a Si cantilever tip (NSC16) with a force constant of 40 N/m and a frequency of 160KHz. Data were analyzed using Gwyddion as software.

Scanning electron microscopy and preparation of lamellae for transmission electron microscopy. Scanning electron microscopy was performed on a FEI Quanta 3DTM instrument at an acceleration voltage of 20 kV and a filament current of 45 pA. Off-axis images were obtained by tilting the samples at an angle of 80°.

The FEI Quanta 3DTM was also used to prepare lamellas for transmission electron microscopy (TEM). For this purpose samples were coated with Pt sauce using a combination of e-beam and ion-beam deposition to prevent any damage to the surface of the MoS₂ layers. A cross-section of the sample was then obtained and thinned down to ~60 nm by milling with a focused beam of Ga ions. The lamella was then transferred to a TEM grid and welded to it using Pt deposition. Transfer of the lamella and Pt deposition were accomplished by a micromanipulator equipped with a gas injection source (GIS) needle.

Transmission electron microscopy. TEM was performed on a JEOL 2010F HRTEM/STEM system at an accelerating voltage of 200 kV and an electron gun source set at 110 pA.

Raman and photoluminescence spectroscopy. We performed micro-Raman and micro-photoluminescence (PL) spectroscopy in backscattering geometry on a LabRam HR[®] Evolution Raman microscope (Horiba). A He-Cd excitation laser (Kimmon Koha) with a wavelength of 442 nm was focused to a ~800 nm spot onto the sample by 100x objective with N.A.=0.5 (Olympus). The excitation power was ~60 μW. Micro-Raman and micro-PL spectra were both

acquired using a grating of 1800 gr/mm yielding a spectral resolution of 0.1 cm^{-1} . The results discussed in the manuscript were obtained from multiple point spectra (i.e., between 3 and 5). Raman and PL spectra were analyzed using Origin 9.0. The average positions of the A exciton peak as well as the center wavenumber of the E_{2g}^1 and A_{1g} vibrational modes, are reported in Table I.

Table I

	Relaxed MoS_2	Strained MoS_2
A exciton peak (nm)	677.49 \pm 1.49	696.82 \pm 5.33
E_{2g}^1 Raman peak (cm^{-1})	382.47 \pm 0.60	381.95 \pm 0.63
A_{1g} Raman peak (cm^{-1})	406.69 \pm 0.58	407.73 \pm 0.80

Tunability of the substrate texture.

A variety of textured substrates were obtained by tuning one or more of the following parameters: (i) interference angle during laser interference lithography, (ii) duration of the reactive ion etching, (iii) oxidation time. Si substrates textured with 6 different patterns are shown in Fig. S1).

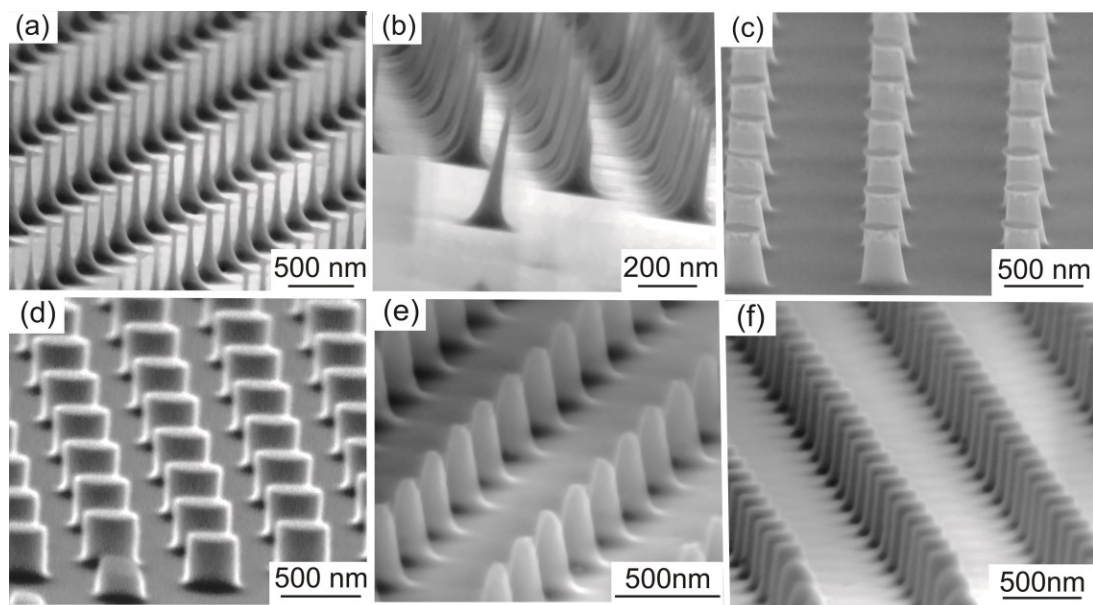


Figure S1. Off-axis scanning electron micrographs (SEMs) of textured Si substrates with various patterns. 2D arrays of ultra-sharp tips with a 330 nm pitch (a) and a ~ 600 nm pitch (b) 2D arrays of truncated cones (c) and cylinders (d) 2D array of rounded tips (e)-(f).

Atomic force microscopy of MoS₂ nanosheets.

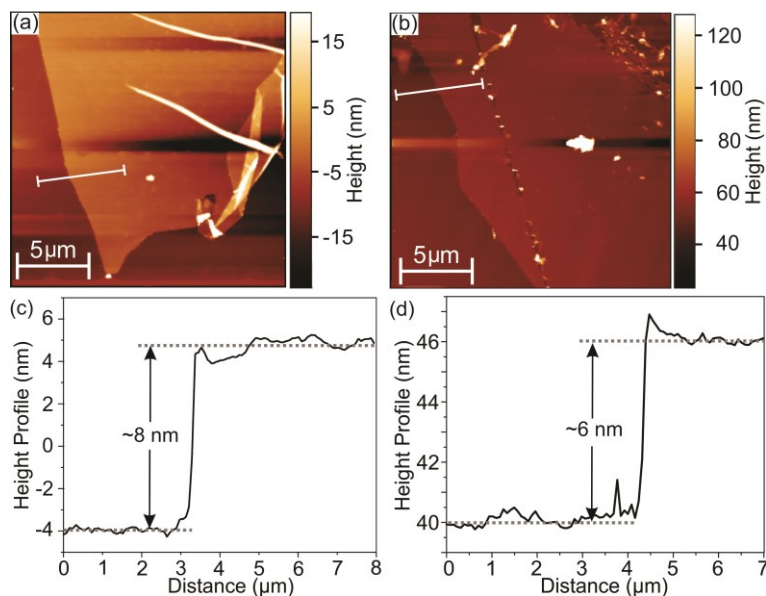


Figure S2. (a)-(b) Surface topography of selected regions of two typical MoS₂ flakes on SiO₂/Si. The flakes have been transferred by dry release in place during Ar annealing. (c)-(d) Height profiles taken across the lines in (a) and (b), respectively. The thickness of MoS₂ nanosheets as measured by atomic force microscopy was consistently in the range of 4-8 nm for the characterized flakes.

Out-of-plane vibrational mode of bulk and few-layer MoS₂ at various stages of the process

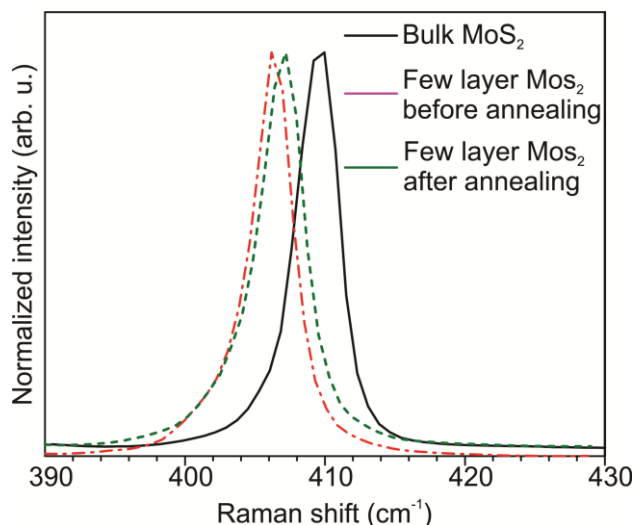


Figure S3. Comparison of A_{1g} Raman modes acquired from bulk MoS₂ (black solid line) and from few layer MoS₂ extracted from the bulk crystal *via* mechanical exfoliation. The out-of-plane vibrational modes were measured for few-layer MoS₂ upon transfer to a PMMA-coated planar substrate (red dash-dotted line), and after dry release in place on the new substrate surface (green dashed line). No significant change of the FWHM can be observed among the three the three Raman modes, which confirms that carrier concentration in few layer MoS₂ stays unmodified after the annealing process. The estimated values of the FWHM for the A_{1g} Raman modes of bulk and few layered MoS₂ before and after release in place ranged from 3.2 cm⁻¹ to 3.6 cm⁻¹.

Partial progression of MoS₂ release in place.

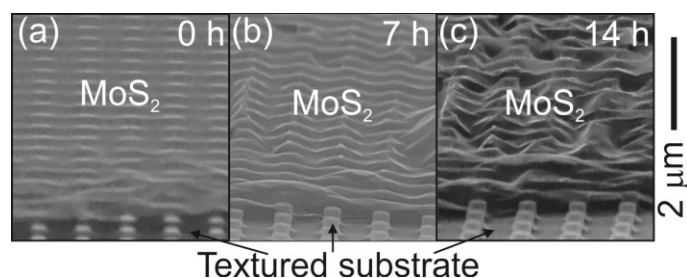


Figure S4. Off-axis scanning electron micrographs illustrating the progression of the PMMA pyrolysis and dry release in place of MoS₂ nanosheets onto a textured Si substrate. The Si substrate is textured with a 2D array of posts. Images are taken upon transfer of the nanosheet onto the PMMA coated Si (a), and after 7 h (b) and 14 h of vacuum annealing at 250° C. The substrate texture becomes increasingly visible as the PMMA sublimates. The MoS₂ nanosheet gradually conforms to the substrate as pyrolysis of the polymer progresses.

Direct comparison and thickness measurements of strain-engineered and relaxed MoS₂.

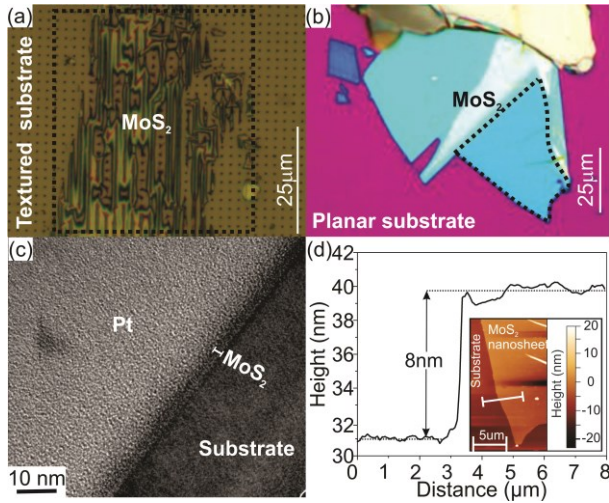


Figure S5. Direct comparison of a strain-engineered and a relaxed MoS₂ nanosheet undergone identical fabrication processes. Top-view optical micrographs of selected regions of few-layered MoS₂ on a textured (a) and on a planar substrate (b). Raman and PL spectroscopy are performed at multiple points within the areas enclosed by the dashed line. The uniform optical contrast between the MoS₂ flakes in the selected regions and the substrates suggests that nanosheets have a uniform thickness over the areas (c) Cross-sectional transmission electron micrograph of the MoS₂/substrate combination within the area enclosed by the dashed line. (d) Cross-sectional profile obtained by atomic force microscopy. The inset shows the surface topography of the MoS₂ nanosheet on a planar substrate. The cross-sectional profile is measured along the white line. (a), (b), and (d) have been previously reported and discussed throughout the manuscript.