Vapour phase growth and grain boundary structure of molybdenum disulphide atomic layers

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This supplementary information includes:
Figs. S1 to S16
References
MoO$_3$ ribbon preparation
As the precursor to MoS$_2$, MoO$_3$ films were prepared by the filtration or dispersion of their highly crystalline nanoribbons, which were produced hydrothermally through a process widely used for synthesis of this type of single-crystalline material $^1$. Sodium molybdate (Na$_2$MoO$_4$) or heptamolybdate tetrahydrate (NH$_4$)$_6$Mo$_7$O$_{24}$·4H$_2$O were used to synthesize MoO$_3$ nanoribbons. We dissolved 1.2 grams of these agents in nitric acid and transferred the solution to a Teflon container, which was heated at 170$^\circ$C for 1-2 hours. These MoO$_3$ nanoribbons have a high aspect ratio, roughly 20 microns in length, 1-2 microns in width, and a thickness in the range of 10-40 nanometers (Fig. S1a).

CVD growth process
The ribbons were then filtered or dispersed and large-area films were formed, cut into pieces, and placed on silicon substrates. This MoO$_3$-covered silicon substrate, along with several bare substrates designated for the growth of MoS$_2$ were placed close to each other at the center of the furnace vented with nitrogen at 200 sccm (Figs. S1b & S1c). At the opening of the furnace, a container with 0.8 - 1.2 grams of sublimated sulfur was placed at a location reaching an approximate maximum temperature of 600$^\circ$C. The center of the furnace was gradually heated from room temperature to 550$^\circ$C in 30min at a rate of approximately 20$^\circ$C/min. As the temperature approached 550$^\circ$C, the sulfur slowly evaporated; the chamber was then heated to 850$^\circ$C at a slower pace of ~5$^\circ$C/min. After 10-15 minutes at this temperature, the furnace was naturally cooled back to room temperature.

**Figure. S1** Precursors and CVD setup. (a) Scanning electron microscopy image of MoO$_3$
nanoribbons prepared through a standard hydrothermal method and used as precursors in varied densities or condensed films. These ribbons provide a robust method for dispersion, allowing for the examination of the different stages involved in the growth process. The scale bar is 4 μm. (b) The configuration used in our experiments for MoS\(_2\) film preparation. In this configuration, the MoO\(_3\) precursors are dispersed on SiO\(_2\)/Si substrates and placed in the center of the quartz container, and several bare or patterned clean substrates, designated for MoS\(_2\) growth, are positioned on the sides. The sublimated sulfur is placed close to the opening of the furnace, where it evaporates as the temperature at the center of the furnace approaches 550°C. Nitrogen is continuously streamed through the chamber with a flow rate of 200 sccm. (c) Schematic of the CVD growth of MoS\(_2\) highlighting the vapor phase reaction between MoO\(_{3-x}\) species and sulfur and the deposition of MoS\(_2\) on a designated substrate.

**Proposed MoS\(_2\) growth dynamics, effect of sulfur concentration and pressure on the growth process**

Although the full extent of the reaction between sulfur and MoO\(_3\) has not been explored, some information can be extrapolated from the extensively-studied interaction between MoO\(_3\) and H\(_2\)S\(^2-3\). It is known that this reaction includes a transition to the MoO\(_{3-x}\) species and the subsequent formation of oxisulfides\(^2\). At a suitable temperature range (200 - 400°C) and given sufficient reaction time, this reaction proceeds, and a complete conversion to MoS\(_2\) occurs\(^2,3\). It is postulated that similar stepwise transitions in vapor phase are involved in our experiments, in which H\(_2\)S is substituted with sulfur as reactant. When the intermediate oxides form, they diffuse across the bare substrates and, as a result of sulfurization, initially form the triangular MoS\(_2\) domains and further grow into continuous films (Fig S1c). The temperature dependent studies reveal the ideal temperature for the high-quality formation of these triangular flakes is in the range of 800 - 850°C, in agreement with the previously reported experiments\(^3\). The sulfur concentration in this process at a given time of the experiment depends on the position of its container relative to the center of the furnace, the outgoing flow of gases from the chamber, and the initial loading of the sulfur. The experiments demonstrate that, in the case of an insufficient sulfur supply, oxisulfide rectangular domains nucleate and grow, instead of MoS\(_2\) triangles and films (Fig S2a & b). As the sulfur concentration is increased to 0.5-0.7 grams, hexagonal MoS\(_2\) domains nucleate, and at >1 grams of sulfur, triangular domains dominate (Fig S2c & d).

Another important parameter interrelated to the sulfur concentration is the pressure. As the sulfur evaporates the pressure increases. The outgoing flow can be adjusted to control the maximum pressure reached in the experiment, which also controls the amount of sulfur in the chamber. The maximum pressure is used in the following discussion as a measure for the pressure dependency of the MoS\(_2\) growth. The measured pressure is the difference between the reference atmospheric pressure and the maximum pressure reached in these experiments. It is evident that both single-crystalline growth and density of nucleation are affected by the pressure. As the pressure increases less MoO\(_3\) is evaporated, and its simultaneous solid state sulfurization slows down and ultimately stops the process.
Figure. S2| Effect of sulfur concentration on the growth process. (a) At low sulfur concentrations, < 0.5 grams, rectangular domains are nucleated. (b) The Raman signature of these domains corresponds to oxisulfide (MoOS₂). The orthorhombic crystal structure of MoO₃ justifies the rectangular shape of these domains. Further sulfurization of the rectangular domains at temperatures of 800-1000°C reveals a significant solid phase stability of the material. The results are in agreement with our hypothesis that the triangular MoS₂ domains are nucleated as the vapor phase sulfur reduction of MoO₃ is completed on the surface of the substrate. (c) Nucleation of MoS₂ begins at sulfur concentrations in the range of 0.5-0.7 grams; however, the domains construct a hexagonal geometry. (d) At higher sulfur concentrations, >0.7 grams, triangular domain nucleation dominates the process.

In Fig. S3, the changes in the growth process is demonstrated by showing the most commonly observed features. At close to atmospheric pressures (0.5-1KPa) the supply of sulfur is low but sufficient MoO₃ is evaporated and typically oxisulfides or hexagonal isolated islands form (Fig S2). Additionally at the same pressures granular and thick films may grow (Fig S3a). Increasing the pressure to 1-4 KPa, the growth of small triangles initiates (Fig S3b) and it extends to large area films in the pressures range of 4-10K (Fig S3c). At these pressures both supplies of MoO₃ and sulfur are sufficient for large area growth and coalescence of triangular domains. At slightly higher pressures, 10-
40KPa sulfur is plentiful but lower evaporation of MoO$_3$ slows down its supply and isolated but very large, 50-80 $\mu$m, triangular domains form (Fig 3d). At higher pressures, 40-80KPa, these isolated triangles shrink in size and their morphology begins to change (Fig 3e). At the maximum pressures that the CVD chamber can withhold, 80-120KPa, isolated star shaped islands grow (Fig 3f). In conclusion the sulfur concentration is the limiting factor that determines the morphology and the size of the single crystalline domains and MoO$_3$ controls the density of nucleation and large-area growth of MoS$_2$. 

Figure 3 | Effect of pressure on the growth processes. (a) Granular films at 0.5-1KPa. (b) High density nucleation of triangular domains at 1-4 KPa. (c) Formation of large area films at 4-10KPa. (d) Growth of large area triangular domains at 10-40KPa. (e)
Formation of isolated triangular domains with modified shapes at 40-80KPa. (f) Star shaped domains at 80-120KPa

Controlled Nucleation and Growth of MoS$_2$

Figure. S4| Common features observed in the direct synthesis of MoS$_2$ on substrates. (a) SEM image showing the nucleation sites formed across the bare substrate in a random manner, leading to the formation of triangular MoS$_2$. (b) SEM image demonstrating the affinity of nucleation to the edges and rough surfaces. As evident from this image, a higher density of nucleation is frequently observed on the cross-sectional surface and at substrate edges. (c) Induced nucleation of MoS$_2$ domains near artificially-made circular edges on SiO$_2$. Some of the nucleated domains diffuse from these edges to flat surfaces. The scale bars are 1, 10, and 50 µm for (a), (b), and (c), respectively.
Figure. S5| Nucleation controlled growth process. (a-d) SEM images showing the nucleation controlled growth process through the patterning of silicon substrates. These patterns are discernable by the obvious contrast resulting from dense nucleation. Film growth is initiated by the nucleation and growth of triangular single-crystalline MoS$_2$. A sufficient supply of MoO$_3$ results in further growth and coalescence of such triangles, and ultimately, continuous large-area films with high level of crystallinity form. The scale bars in (a-d) are 100, 50, 50, and 400 μm, respectively.

The sulfur concentration and pressure controls provide the means to maximize the size of the single-crystalline domains, before they merge. Our experiments at lower MoO$_3$ concentrations, which allows for resolving the grains before they coalesce, show that a maximum triangular domain sizes in the order of 20-25 μm should be expected. This is in agreement with the results described for the pressure dependency of the MoS$_2$ growth, which illustrates the correlation between the maximum domain sizes and large area growth of the MoS$_2$ films. The existence of a maximum achievable grain size imposes restrictions on the pattern base strategy and control of crystallinity in the large area films. In Fig. S6a, where 20 μm$^2$ rectangular patterns with the spacing of 20 μm are used, although most triangular domains have not reached their maximum size (~20 μm), they
have already made contact with triangles nucleated from other sites and, as more precursor is provided, over-layers grow (Fig. S6b). However, for slightly larger patterns, 40 μm² rectangles with spacing of 40 μm, many triangles in the maximum size range are observed and they meet other domains at relatively larger sizes (Figs. S6c and d). Our experiments show that further pattern size increase results in insufficient nucleation and deters the large area growth. These results exemplify a general control mechanism in the pattern base growth for control of film size and crystal quality.

Figure. S6| Method for control of crystallinity in MoS₂ films through pattern-size variation. (a) MoS₂ synthesis at low densities of MoO₃ on 20 μm × 20 μm rectangular patterns located 20 μm apart shows that triangles with sizes ~10 μm have already made contact with triangles nucleated from other sites, suggesting an average grain size in the order of <10 μm for the films made on this type of patterns. (b) A further supply of MoO₃ results in the formation of films with high possibility of over-layer nucleation and over-layer growth. (c) MoS₂ synthesis using 40 μm × 40 μm rectangular patterns located 40 μm apart at low source supply. Triangular domains within the size range of 20 μm are commonly observed. (d) In these patterns, sufficient source supply allows domains of relatively larger sizes to merge into more continuous and high-crystalline films.
Figure. S7] Variation in patterns for the controlled nucleation and growth process. (A-D) The application of circular patterns demonstrates a similar nucleation and growth process. However, since growth in multiple directions from the initial nucleation sites at the edge of the circles is possible, overlapped and multi-layer growth is more prominent. (E-F) Growth using patterns with long rectangular bars where the nucleation is clearly affiliated to these bars; however, smaller surface area results in less surface nucleation, and therefore results in slower formation of the films. An incomplete and scattered formation of ~100 μm films results from the diffusion-limited nature of the synthetic process. The scale bars in all images are 40 μm.

Optical examination, Raman measurements, XPS and EELS
The optical images of the films and the triangular domains provide a qualitative measure of the samples’ thickness and uniformity (Fig. S8a). We further evaluate their thickness and surface roughness using Raman spectroscopy. It has been shown that the two vibrational modes of MoS2 tend to approach each other down to ~18 – 20 cm⁻¹ in single-layered samples, providing a robust thickness characterization tool for samples up to and including 4 layers 4. The measured differences between the characteristic Raman peak positions, E_{12g} and A_{1g} – acquired from areas presented in Fig. S8a – are 19.5 and 22.2 cm⁻¹, corresponding to the thicknesses of one and two layers (Fig. S8b). Our thickness
analyses across these samples indicate that these films are mostly single-layered, with occasional two- or few-layered regions. Raman intensity mapping has been proposed as a method for the investigation of grain boundaries in graphene. These studies showed that the D-band intensity in graphene could be utilized to detect nucleation sites and grain boundaries. In the present study, the Raman intensity mapping for characteristic band positions of single-layered samples, $E_{12g}$ (385 cm$^{-1}$) and $A_{1g}$ (405 cm$^{-1}$), from the merged triangles are collected. These results reiterate the thickness uniformity of the samples (Fig. S8c and d). In these maps, the nucleation sites are clearly discernable; however, no clear indications of changes in the vibrational properties are observed at likely grain boundaries. XPS measurements at every stage of the growth process, from the triangular domains to continuous films, provide strong evidence for the high-quality formation of MoS$_2$, as presented in Figs S9a and b. The information acquired from the position and intensity of the Mo 3$d$ and S 2$p$ bands on dispersed triangles, discontinuous films, and completed films demonstrate that the bonds in MoS$_2$ samples at every stage are fully formed. In these samples, the single molybdenum doublet Mo 3$d_{3/2}$ and Mo 3$d_{5/2}$ appear at binding energies of 233.9 eV and 230.9 eV, and the sulfur doublets S 2$p_{1/2}$ and S 2$p_{3/2}$ at 162.9 eV and 161.8 eV, respectively. These measurements match the characteristic band positions of fully-transformed MoS$_2$ during the sulfurization of MoO$_3$, validating its complete conversion during the growth process. Moreover, electron energy-loss spectroscopy (EELS) obtained from clean regions in the MoS$_2$ domains shows only the characteristic peaks of Mo (M-edge) and S (L-edge) without impurities (Fig. S9c), which further confirms these findings.
Figure. S8 | Thickness and chemical characterization of as-synthesized MoS$_2$ samples. (a) Optical image of MoS$_2$ films with optical contrast resembling single layered samples; the scale bar is 40 µm. (b) Raman measurements from the two points marked on (a) by red and black filled circles demonstrating the thickness variations in these samples. (c) The in-plane E$_{12g}$ and (d) out-of-plane A$_{1g}$ modes of vibration positioned at 385 and 405 cm$^{-1}$, respectively, corresponding to single-layered MoS$_2$. These maps demonstrate the thickness consistency in these triangles; it is evident that these triangles consist of nucleation centers made of MoS$_2$ particles with larger thickness. Grain boundaries are not clearly detected based on the Raman measurements.

Figure. S9 | Chemical analysis of MoS$_2$ single triangular domains and films. (a-b) The XPS measurements revealing the complete formation of MoS$_2$ at every stage of the growth process, i.e. from the nucleation of small triangles to continuous films. (c) EELS spectrum acquired from the defect-free MoS$_2$ monolayer film, showing the S L-edge and Mo M-edge.

Figure. S10 | BF and DF TEM images of MoS$_2$ films. (a) BF TEM image of the MoS$_2$ film. (b) DF TEM image of the same region showing a large MoS$_2$ grain across the whole film. The DF image shown in (b) was obtained by stitching 507 different DF images, acquired with a spacing of 3 µm under the same microscope conditions. (c) An individual DF image acquired from the square area shown in (b).
Figure. S11| Two modes of boundary formation. Grains with different orientations are indicated by red and blue lines. (a) Tradition grain boundaries involve the formation of chemical bonds between the two in-plane grains at the boundaries. The growth process can further extend through the nucleation of a new layer with crystal orientation similar or different from one of the original in-plane grains. (b) Overlapped grain junctions are a mode of boundary formation, in which no chemical bonds between the two in-plane grains form and the two grains may grow on top of each other. This mode can be distinguished from the traditional grain boundaries in (a) through high-resolution electron microscopy imaging, where a discontinuity in the lattice structure of conventional grain boundaries is noticeable (see Fig. 4 in the main text).
Figure. S12 | STEM-ADF images of the second MoS2 layer grown along the grain boundaries. (a) Low magnification ADF image showing the formation of second layer along the grain boundary (highlighted). (b) Atomic resolution ADF image showing the grain boundary covered by a second layer. (c) Fourier filtered image of (b) showing the position of one grain in the first layer. (d) Fourier filtered image of (b) showing the position of the other grain in the first layer and the second layer with the same orientation. The grain boundary is highlighted by the yellow dashed lines.
Figure. S13] Burgers vector analysis of the MoS$_2$ grain boundaries. (a) A negative-contrast STEM-ADF image of a 21° MoS$_2$ grain boundary. (b) False-color image of (a), with Mo atoms highlighted. Burgers vectors are shown as black arrows, and are calculated by drawing Burgers circuits (shown as red and green lines) and by recording the vectors that would complete the circuits. Following the same notation for Burgers vector in graphene with hexagonal lattice, all dislocations have the shortest Burgers vector (1, 0) with the smallest energy, and with a magnitude proportional to its squared Burgers vector. The result strongly suggests that dislocations can be constructed by inserting or removing a semi-infinite stripe of atoms along the armchair direction in the Mo-oriented lattice.
Figure. S14 | STEM-ADF imaging of an overlapped junction between two monolayer MoS$_2$ grains with 17° rotation. (a) Low-pass filtered ADF image. (b) FFT of the image showing two sets of MoS$_2$ diffraction spots with 17° rotation. (c) FFT-filtered image using one set of diffraction spots highlighted in cyan in (b). (d) FFT-filtered image using one set of diffraction spots highlighted in yellow in (b). Note that there is no discontinuity in the lattice structure within each grain at the junction point, confirming that the two
layers continue to grow on top of each other without forming in-plane chemical bonds. (e) False-color FFT-filtered image constructed from (c) and (d). (f) Magnified view of the highlighted region in (e) showing the distinct Moiré fringes generated from the overlapping of the two grains.

Figure. S15 | STEM-ADF image of a grain boundary with 21° tilt angle. (a) Low-pass filtered image. (b) Image after low-pass filtering and partial filtering of the direct diffraction spot in the FFT, which aims to remove the contrast variation due to surface contamination. The light blue circles highlight the positions of Mo-oriented 5|7 dislocation cores at the grain boundary, and the orange circles highlight Mo-oriented 5|7 dislocation cores with an S₂ substitution.

Density functional calculations
The total energy first-principles calculations are performed using density functional theory (DFT) within the local density approximation (LDA) and the projector-augmented wave (PAW) method, as implemented in Vienna Ab-initio Simulation Package (VASP). The grain boundaries (GBs) are modeled with similar tilt angle (21°) as those in the experiment. The periodic models incorporate oppositely-aligned Mo-oriented 5|7 in a large supercell. The in-plane lattice parameters are roughly 34 Å and 11 Å in the perpendicular direction and along the GBs, respectively. Between the layers, a vacuum layer of 12 Å is introduced and in all structures, a plane-wave-based total energy minimization scheme with an energy cutoff of 280 eV – is applied until the force on each atom is less than 0.01 eV/Å.

Formation energies for S₂ substitution are defined by:

$$E_f = E_{S_2-sub} - E_{Mo-5|7} - \sum \Delta n_i \mu_i$$

Here, $E_{S_2-sub}$ and $E_{Mo-5|7}$ are the total energies of S₂-substituted and un-substituted Mo-oriented 5|7s within similarly-sized supercells, respectively; $\Delta n_i$ and $\mu_i$ are the change in
the number of atoms and the chemical potentials of species $i$, for Mo or S. In thermodynamic equilibrium with the MoS$_2$, $\mu_{\text{Mo}}$ and $\mu_{\text{S}}$ satisfy the equation $g_{\text{MoS}_2} = \mu_{\text{Mo}} + \mu_{\text{S}}$, where $g_{\text{MoS}_2}$ is the Gibbs free energy of an infinite MoS$_2$ sheet per unit molecule. The formation energies are calculated under the S-rich condition, taking chemical potential of the bulk-S as reference.

**Optical devices for opto-electrical characterization of MoS$_2$**

To demonstrate the optical properties and device performance of the MoS$_2$ films, photolithography was used to prepare electrodes on these samples for photocurrent measurements (Fig. S15b). We measured the voltage dependence of the devices’ photoelectric response and calculated an ON/OFF ratio of ~10 and ~3 for single- and multi-layered devices, respectively (Fig. S15c and S15d). These results highlight a significant enhancement in the photocurrent response and photosensitivity of the single-layered, as compared to the multi-layered samples. We also measured the wavelength dependence of the photo-current for wavelengths ranging from 750 nm down to 200 nm (Fig. S15.e). The experiments reveal photocurrent properties similar to those observed in single-layered and bulk samples $^{11,12}$. As shown in Fig. S15e, the photocurrent signal drastically increases as the wavelength decreases to around 700 nm, corresponding to the absorption energy edge (~1.8eV) of single-layered MoS$_2$. 

Figure. S16 | Phototransistors and Photocurrent measurements. (a) FET device arrays prepared using lithography process. (b) Phototransistors for photocurrent characterization. At a laser wavelength of 405 nm, the photocurrent response of the MoS$_2$ films is measured for (c) single-layered flakes and (d) few-layered samples. For single-layered flakes, an ON/OFF current ratio of ~10 is demonstrated; for few-layered samples, this ratio was measured to be ~3. These results reveal a significant enhancement in the ON/OFF current ratio for the single-layered devices. (e) Wavelength dependency of the photocurrent in single-layered samples reveals the broad absorption band in this material. The onset of the photocurrent at ~700nm, as indicated by the dotted line, is associated to the bandgap energy of single-layered samples ~ 1.8 eV.

References


