

## Supplementary information

### X-Ray photoelectron spectroscopy (XPS)

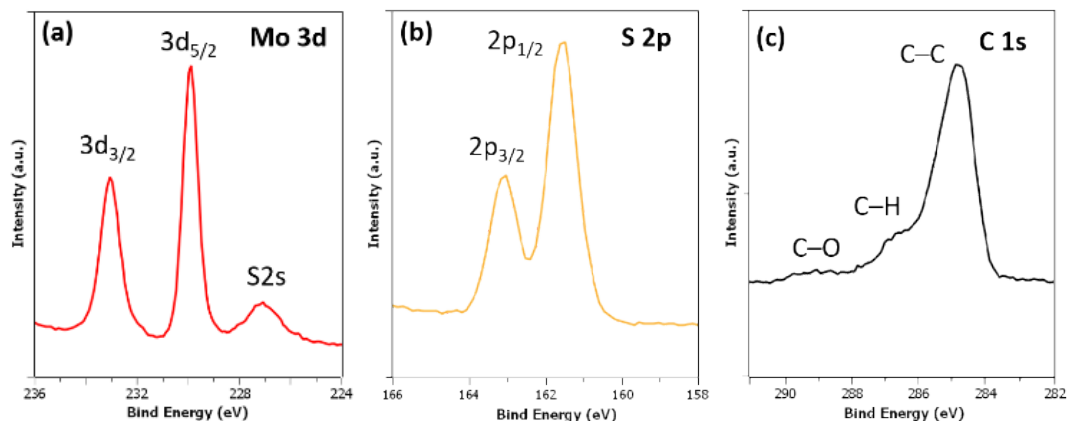


Figure S1: X-Ray photoelectron spectroscopy of a DLI-PP-MOCVD MoS<sub>2</sub> sample for (a) Mo 3d, (b) S 2p and (c) C 1s. Peak identifications are indicated.

Previous reports [1] revealed that MOCVD MoS<sub>2</sub> thin films could suffer from carbon contamination, or carbon deposition limiting the lateral growth of the grains and impacting general properties [2][3]. X-ray photoelectron spectroscopy (XPS) analysis was used to measure the binding energy of Mo, S and C to estimate the material composition and potential contamination of a sample deposited in the same conditions as S4. Figure S1a, S1b and S1c show the binding energy profiles for Mo 3d, S 2p, and C 1s, respectively. The peak positions are well in accord with reported values for MoS<sub>2</sub>, and quantitative analysis revealed that the deposited layers were nearly stoichiometric, with S/Mo in the range of 1.93 to 1.95 (Figure S1). It also showed that the carbon contamination of the film was limited, with levels between 10 and 14 at% (Figure S1c). It is likely that the amount of carbon still in the film originates from the partially-reacted Mo(CO)<sub>6</sub> and that using another precursor with the correct oxidation state could lower carbon contamination. Indeed, in MoS<sub>2</sub> the oxidation state of Mo is +4, while in Mo(CO)<sub>6</sub>, Mo is considered +0. It means that to generate MoS<sub>2</sub> from Mo(CO)<sub>6</sub>, the precursor molecules will have to undergo a number of redox reactions, hence reducing other species and generating even more disorder. The S/Mo molar ratio during deposition was kept minimal at only 20, as opposed to hundreds or even thousands [1]. It is believed that by limiting the molar flow of the molybdenum precursors and by separating the injections, the species on the surface were given enough time to react properly and to migrate to their preferred position [4], not leaving trapped species that could lead to sulfur vacancies.

### MC-050 reactor and temperature regulation

A schematic of the reactor is presented in Figure 2. As discussed in Methodology, the substrate is brought to deposition temperature through 6 infrared lamps, placed in a circle around the deposition chamber, and heating a susceptor in which it is placed. This means that the thermocouple, inserted in an opening in the susceptor (Figure S2), measures the temperature in the direct vicinity of the substrate, and that any condition change that could impact the surface temperature (injection of gas, pressure variations, ...) can be dealt with quickly and efficiently via a fast PID regulator. In 2D materials depositions, where the final thickness is around 1 nm, controlling the substrate's surface temperature is key. To do so, the PID can be finely tuned to respond instantly or with a delay to the perturbation, the former will counter any deviation in the temperature but may generate a larger overtemperature than a delayed response. This compares favorably with standard resistive heating where the perturbation is usually not seen. Thanks to the fast heating and cooling ramps, the reactor can also be used as a RTP tool for post-deposition crystallization, selenization or sulfurization if needed.

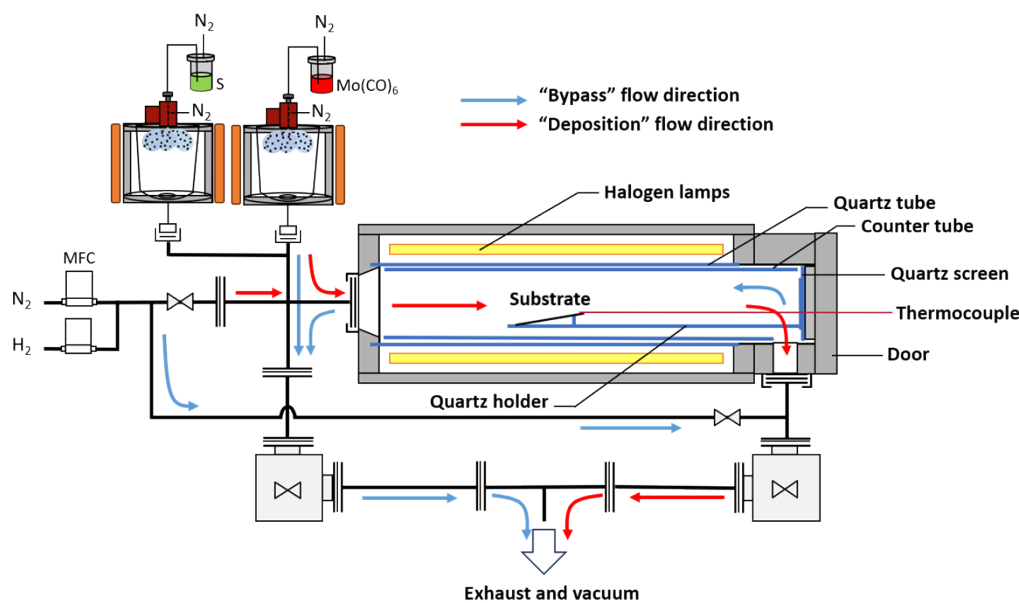


Figure S2: Schematic representation of the MC-050 reactor. Gas stream directions in the case of deposition (in red) and preparation (in blue) are presented.

## DLI deposition processes

The 12x11 mm Si/SiO<sub>2</sub> (96 nm) substrates were cleaned in acetone (C<sub>3</sub>H<sub>6</sub>O, technical, Acros Organics), isopropanol (C<sub>3</sub>H<sub>7</sub>OH, 99.8%, Höfer Chemie gmbh) and deionized water (H<sub>2</sub>O, Acros Organics) under ultrasonic agitation for 10 minutes each, before being blown dry with nitrogen. They were then immediately loaded on the susceptor of the reaction chamber for deposition. The process is as follows: following sample installation, the chamber is closed and brought to about 0.02 mbar. For monolayer depositions, it is imperative that the substrate be thoroughly cleaned and free of adsorbates, therefore, to ensure complete desorption of remaining contaminants, the samples were kept for 30 minutes under vacuum at room temperature inside the deposition chamber. For the first part of the process, the pumping direction is reversed so that all species are pumped from the deposition chamber to the back of the reactor. DLI-CVD and DLI-ALD processes differ from this point forward.

## DLI-CVD / DLI-PP-CVD

Nitrogen (800 sccm) is flowed through the chamber (200 sccm through the gas line, and 300 sccm through both injection heads); the pressure is set to 5 mbar and the susceptor holding the samples is brought to the deposition temperature of 750°C at a rate of 2°C/s. Infrared heating allows for much faster temperature ramps but was set to 2°C/S to accommodate multiple substrates and heterostructures. The reactor is kept in this state for 5 minutes for homogenization purposes. While still in reverse direction pumping, 0.3 g/min of both precursors are injected and vaporized to prepare the evaporation system for deposition. The Mo(CO)<sub>6</sub> source is then cut, hydrogen is brought inside the gas mix (40 sccm) and the pumping direction is switched back to the deposition direction so that all species are brought in contact with the substrates. For 60 seconds, only S is injected to clean any remaining contaminants, and prepare the surface of the substrate for MoS<sub>2</sub> deposition. In the standard DLI-CVD, both precursor solutions are brought in at a flowrate of 0.3 g/min for 45 seconds. In the PP-CVD process, the deposition works in cycles. During one cycle, one pulse of 6 ms of Mo(CO)<sub>6</sub> is injected while the S injection is set to 0.3 g/min for 20 seconds. This 20-second cycle is repeated 100 times to achieve full-coverage MoS<sub>2</sub> monolayer deposition. At the end of the last cycle, the pumping flow direction is switched to cut any more addition to the deposited film, H<sub>2</sub> is stopped, infrared lamps are shut down and the substrates are allowed to cool naturally to 200°C at 5 mbar under 800 sccm of N<sub>2</sub>. After reaching 200°C, nitrogen injection through both injector heads are cut and the samples are brought to about 0.6 mbar under 200 sccm N<sub>2</sub> until 100°C. Upon reaching 100°C, the chamber is purged and pumped two times to remove any remaining potentially harmful gas from the environment. At 40°C, the samples are unloaded from the reactor.

DLI-MOCVD-grown monolayers were highly crystalline but consisted of nanometric grains and incorporated medium amounts of carbon.

## DLI-ALD / DLI-RTALD

Nitrogen (800 sccm) is flowed through the chamber (200 sccm through the gas line, and 300 sccm through each injection heads) and the substrates are brought to 250°C at a ramp of 2°C/s. The reactor is kept in this state for 5 minutes for homogenization purposes. While still in reverse direction pumping, 0.3 g/min of both precursors are injected and vaporized to prepare the evaporation system for deposition. Then all injections (gas and liquid) through the injection heads are stopped, lowering the total flow of nitrogen to 200 sccm and the pumping direction is switched back to the deposition direction. The ALD process is a ABAB-cycle type where A is 1 pulse of 30 ms of the S 0.005 M solution followed by a 10 s purge time, and B is 1 pulse of 30 ms of the Mo(CO)<sub>6</sub> 0.005 M solution followed by a 10 s purge time. After 150 cycles, the pumping flow direction is switched to cut any more addition to the deposited film, infrared lamps are shut down and the substrates are allowed to cool naturally until 100°C. Upon reaching 100°C, the chamber is purged and pumped two times to remove any remaining potentially harmful gas from the environment. At 40°C, the samples are unloaded from the reactor.

DLI-ALD-grown layers were poorly crystallized and contained significant amounts of carbon. Even so, they can be used in applications where small grain size and high contamination levels are acceptable, in catalytic applications for example. To crystallize the layers and be able to compare the properties with MOCVD, few samples were produced and annealed directly after the deposition, by Rapid Thermal Annealing (RTA) in the same tool (DLI-RTALD). The annealing consisted in a rapid heating to 750°C (5°C/s) at 10 mbar of nitrogen (150 sccm) and under a continuous injection of the sulfur precursor solution (0.3 g/min) to counter sulfur evaporation.

## Standard CVD process

MoS<sub>2</sub> was grown by CVD on SiO<sub>2</sub>/Si plates using MoO<sub>3</sub> (Sigma-Aldrich, 25 mg) and sulfur (Sigma-Aldrich, 250 mg) powders as solid precursors using a 1-inch quartz tube furnace. MoO<sub>3</sub> powder was placed in the center of the heating zone of the furnace, while sulfur was placed upstream at the furnace inlet. Prior to growth, air was evacuated by flowing Ar (ultra-high purity, Linde) for 15 minutes at 200 sccm, after which the tube was heated to 200 °C for 10 minutes. The temperature was then increased to 750 °C under Ar (100 sccm) and it was held at this value for 15 minutes before cooling naturally to room temperature.

## Ultra-low frequency Raman spectra of DLI-PP-MOCVD MoS<sub>2</sub> samples

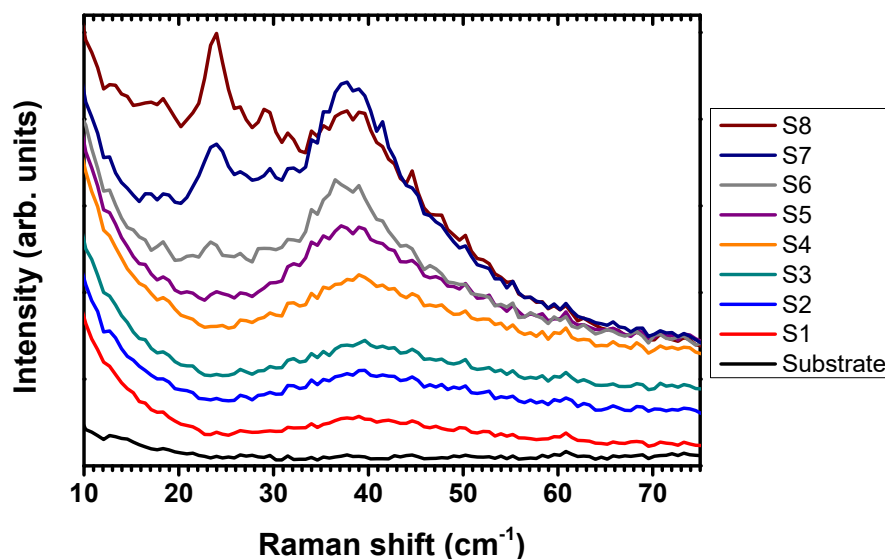


Figure S3: Ultra-low frequency Raman spectra of DLI MoS<sub>2</sub> samples S1 to S8 and of corresponding SiO<sub>2</sub>/Si bare substrate. Presented spectra are the average extracted from 121 points Raman maps.

1. McCreary, Kathleen M., et al. "Synthesis of High-Quality Monolayer MoS<sub>2</sub> by Direct Liquid Injection." *ACS applied materials & interfaces* 12.8 (2020): 9580-9588.
2. Gali, Sai Manoj, et al. "Electronic and transport properties in defective MoS<sub>2</sub>: impact of sulfur vacancies." *The Journal of Physical Chemistry C* 124.28 (2020): 15076-15084.
3. Zhang, Xixia, et al. "Unravelling the effect of sulfur vacancies on the electronic structure of the MoS<sub>2</sub> crystal." *Physical Chemistry Chemical Physics* 22.38 (2020): 21776-21783.
4. Kajikawa, Yuya, and Suguru Noda. "Growth mode during initial stage of chemical vapor deposition." *Applied surface science* 245.1-4 (2005): 281-289.