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Controlled synthesis of 2D transition metal dichalcogenides: from vertical to planar MoS$_2$

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Abstract

Among post-graphene two dimensional (2D) materials, transition metal dichalcogenides (TMDs, such as MoS$_2$) have attracted significant attention due to their superior properties for potential electronic, optoelectronic and energy applications. Scalable and controllable powder vapor transport (PVT) methods have been developed to synthesize 2D MoS$_2$ with controllable morphologies (i.e. horizontal and vertical), yet the growth mechanism for the transition from horizontal to vertical orientation is not clearly understood. Here, we combined experimental and numerical modeling studies to investigate the key growth parameters that govern the morphology of 2D materials. The transition from vertical to horizontal growth is achieved by controlling the magnitude and distribution of the precursor concentration by placing the substrate at different orientations and locations relative to the source. We have also shown that the density of as-grown nanostructures can be controlled by the local precursor-containing gas flow rate. This study demonstrates the possibility for engineering the morphology of 2D materials by controlling the concentration of precursors and flow profiles, and provides a new path for controllable growth of 2D TMDs for various applications.

Introduction

Transition metal dichalcogenides, such as MoS$_2$, emerging as post-graphene 2D materials, are outstanding candidates for electronic and optoelectronic devices [1] as well as low cost catalysts for energy generation [2, 3]. The TMDs are sandwich structures with an atomic layer of transition metal in between two layers of chalcogen atoms. They are identified as van der Waals (vdW) solids with interlayer weak vdW forces and strong covalent in-plane bonds. It is appealing that most of atomically thin TMDs show exotic properties with respect to their bulk counterparts [1, 4, 5] benefiting from the nature of the anisotropic bonding [6, 7]. Mechanical and chemical exfoliation processes [8] have been developed and widely used to separate individual 2D layers from their bulk crystals at the lab scale. However, it is imperative to develop synthesis methods [9, 10] allowing uniform, scalable 2D films as well as precise control of morphology for applications. Numerous vapor phase growth methods, such as chemical vapor deposition (the precursors in CVD are typically outside of the reactor tube and at least involving one gas phase precursors, and thermally decompose to deposit the film) and PVT (no gas precursors), are successfully developed to grow horizontally stacked 2D MoS$_2$ monolayers [9, 11] and multilayers [12]. Such vdW structures are ideal candidates in optoelectronic devices [13] due to their indirect to direct bandgap transition as a function of thickness as well as in transistors [14] due to their high on/off current ratios ($>10^5$) [15, 16]. Vertically grown 2D TMDs, with exposed metastable edge sites and high surface energy, have also been investigated [17, 18] and show promise in catalysis and hydrogen evolution reaction [17, 19, 20].

Although significant progress has been made in the synthesis of 2D crystals and their heterostructures, little progress has been done to fundamentally address the underlying nucleation and growth mechanisms that control the morphology resulting from synthesis. This
understanding is important since material properties are strong functions of crystallographic orientation and morphology. Despite the extensive study of these structures, the key controlling mechanisms behind the resulting morphology in these crystals are yet to be understood.

As an example, in the family of 2D crystal TMDs, atoms on the basal plane of 2D TMDs do not have dangling bonds and thus are not chemically reactive, while atoms at the edges of the basal plane have higher free energy as preferred nucleation sites. Thus, during the synthesis, sheets tend to grow laterally into monolayer structures [17]. It is also reported that holding a constant low Mo precursor partial pressure ($P_{\text{Mo}}$) is beneficial to grow uniform monolayer thin film over a large area [21, 22]. There are also cases showing that quick sulfurization of metal-seeded substrates will lead to growth of vertically standing MoS$_2$ nanosheets [17, 23], which is driven by reduction in the elastic strain energy that forms during the horizontal growth of MoS$_2$ nanosheets on the substrate. None of those studies point out the critical parameters dictating the horizontal-to-vertical orientation transition during MoS$_2$ growth. This understanding is necessary before we can design new growth mechanisms to facilitate the development of new functionalized devices with novel applications.

This study combines experimental research with theoretical and computational simulations to better understand the underlying physics and chemistry that governs nucleation and growth mechanisms in 2D vdW...
2D MoS$_2$ nanostructures are directly grown on Si substrates by transporting and sulfurizing the metal oxide powder. A shift is observed from vertical to horizontal growth as a result of altering the concentration and concentration gradient of Mo precursor through altering the flow of carrier gas and placing the substrate at different locations with different orientations in the furnace. This fundamental understanding can lead to a controllable growth of 2D TMD crystals with various morphologies suitable for a wide range of applications such as energy harvesting and nanoelectronics [21].

**Experimental synthesis and characterization, and numerical simulation results**

We used a conventional atmosphere pressure PVT technique with varied substrate positions to investigate the critical parameters controlling the growth morphology of 2D MoS$_2$. For the numerical simulations, the finite element method was employed to solve the coupled heat transfer, fluid flow, and diffusion problems involved in the powder vaporization process. Three different cases were considered: (i) substrate surface oriented normal to the flow stream in the hot-zone MoO$_3$ precursor crucible (figure 1(a)), (ii) substrate surface oriented parallel to the flow stream and located on top of the crucible and facing down (figure 3(a)), and (iii) substrate surface parallel to the flow stream positioned in downstream flow and facing up (figure 4(a)).

**Case I: vertical growth**

Facing toward the upstream (figures 1(a)–(b)), the vertically placed substrate shows a color change with a gradient darker on the top. The SEM images of the vertically-standing MoS$_2$ nanosheets grown on an Si/SiO$_2$ substrate are shown in figure 1(c), indicating higher density of MoS$_2$ nanofins at the top area (marked as 1).
The numerical simulation results for concentration of Mo precursor and flow in the PVT environment around the substrate are shown in figure 1 (d), which indicates a change in Mo concentration along the substrate and a Mo concentration gradient normal to it. Simulation results indicate significant reduction in the carrier gas velocity at the bottom of the substrate. This will reduce the mass flow of precursor, resulting in smaller number of nuclei and subsequently lower density of as grown nanofins. A lower concentration gradient is also observed near the bottom part of the substrate indicating a smaller thermodynamic driving force for the growth of nanofins, which can also reduce the density of vertical nanosheets. Figure 1(c) illustrates where the basal plane of MoS$_2$ is normal to the substrate with the growth orientation within the (0 0 2) plane that corresponds to TEM results. A typical as-synthesized MoS$_2$ nanofin with a lateral size of $\sim 1 \mu m$ is shown in figure 1(f), the edge of the nanosheet with five MoS$_2$ layers (figure 1(g)) with an interlayer spacing of $\sim 0.61 \pm 0.01 \text{ nm}$ indicating synthesis of thick nanosheets vertically standing on the substrate [17]. These results further demonstrate that the as-grown vertically standing nanosheets are single crystal multi-layer MoS$_2$.

The size of vertical MoS$_2$ structures can also be tuned by adjusting the concentration gradient as it determines the magnitude of thermodynamic driving force for the growth via the Mullins–Sekerka instability and the growth mechanism, which affects both the nucleation and growth rate. To demonstrate the feasibility of controlling the size of the vertical nanofins by concentration gradient, a set of experiments for the same configuration are performed with concentration of precursor changing by a factor of 2 (figures 2(a)–(c)) with other parameter fixed. Given that numerical simulations are performed for a normalized concentration, the results can be extended to this case (with only a different scaling factor). The vertical MoS$_2$ nanostructures are still considered as the dominant structures as we reduced the concentration of precursor, however they are smaller in size due to the smaller amount of precursor and concentration gradient in this case (from figures 2(a)–(c)). Large number of tiny nanostructures can be detected in between the large nanofins (figure 2(c)), indicating a dense packing of nuclei similar to the case with higher precursor concentration (figure 1(c)). However, only a limited number of these nuclei are grown to a fraction of height of the ones grown in figure 1(c), indicating the lack of sufficient concentration of precursors for the growth of these vertical nanostructures to a significant size.

The density of the nanofins is also dependent on the change of the precursor flow rate. A set of experiments are performed as shown in Case I, with the flow rate of carrier gas (Nitrogen) varying from 50 sccm to 400 sccm with other factor fixed. The SEM images in figures 2(d)–(f) indicate that, as the flow rate increases, more precursor will be delivered onto the surface of the substrate. Therefore, the density of as-synthesized vertical nanofins increases and the flakes become thicker. It is noted that we have not seen obvious changes on the direction of the vertical MoS$_2$ nanosheets with respect to growth parameters in this case. The nanofins are observed as vertically grown with slight vertical angle misorientations and no particular epitaxy with respect to the substrate. We believe this is because of the poor crystallinity and roughness of the SiO$_2$ substrate surface which leads to randomly oriented nuclei leading to randomly oriented vertical nanofins. A set of experiments (figures 2(g)–(i)) of MoS$_2$ growth on different substrate surface is explored to show the effect of the substrate nature on the nucleation and growth. Mechanically exfoliated graphite surface owns a perfect crystallinity and atomically flat surface, from the SEM image of MoS$_2$ grown on graphite (figure 2(h)), several perfectly vertical nanosheets are observed on the substrate besides few randomly oriented MoS$_2$ islands which suggests the role of the substrate surface on the nucleation and growth. Also graphite and SiO$_2$ have different chemistries which can significantly affect the nucleation of MoS$_2$ on the substrate. As a comparison, c-plane sapphire with (0001) direction is also used as the growth substrate for vertical MoS$_2$ nanosheets. These experiments indicate perfectly vertical nanosheets on the substrate as the growth on graphite. In addition, we observed a certain epitaxial growth of the vertical nanofins on the substrate with all the nanofins following a specific orientation with respect to the substrate. This clearly demonstrate the substrate chemical and atomic structure nature play a crucial role on the nucleation, growth and orientation of vertical MoS$_2$ nanofins.

**Case II: planar triangle growth**

Planar triangular-shaped MoS$_2$ was synthesized by placing the substrate facing down on top of the crucible and leaving a small gap at the end of the crucible (figure 3(a)) to ensure the transport of carrier gas. Deposition on the substrate after growth is shown in figure 3(b), where the concentration of the Mo precursor in the central area of the substrate is too high to achieve 2D crystals because the substrate is very close to the MoO$_3$ source. However, the pressure of Mo reaches proper values to form 2D MoS$_2$ equilateral triangles along a parabolic curve on the substrate (figure 3(b)). Isolated MoS$_2$ islands with a side length of $\sim 5 \mu m$ are observed along the parabolic curve (figure 3(c) and schematic image in figure 3(e)). Two regions can be detected in the area where the SEM images were collected (figure 3(c)): (i) the area closer to the precursor source with many small MoS$_2$ triangles, and (ii) the area with larger yet fewer MoS$_2$ triangles. A large number of tiny MoS$_2$ nuclei are also observed in this area. The numerical simulations (figure 3(d)) show the concentration and flow of MoO$_3$ around the substrate in this setup. These simulations show a small change in the Mo concentration along the substrate and almost no concentration gradient normal to the substrate. The Raman spectrum (figure 3(f)) shows two
characteristic peaks corresponding to two vibrational modes in MoS$_2$, the $E_{2g}^1$ mode and $A_{1g}$ mode related to the in- and out-of-plane vibrations of molybdenum and sulfur atoms, respectively. The frequency difference between these two modes $\Delta k \sim 19$ cm$^{-1}$, indicating the number of MoS$_2$ layers matching well with reported CVD-synthesized monolayer MoS$_2$ [24]. The as-grown monolayer MoS$_2$ triangles show a strong photoluminescence (PL) peak (figure 3(g)) at 1.88 eV, which is close to the direct band gap of freestanding exfoliated single layer MoS$_2$ (1.90 eV) [25]. The full width at half-maximum (FWHM) of the PL peak is $\sim 65$ meV, which is also close to freestanding exfoliated MoS$_2$ (50–60 meV) [4]. These results indicate the high quality of as synthesized MoS$_2$ monolayer triangles.

Case III: thin film growth

The substrate is placed facing up next to the MoO$_3$ source. After deposition, we can observe a uniform color change on the whole substrate (figure 4(b)), indicating a uniform planar thin film growth (figure 4(c) and schematic image in figure 4(e)) on the substrate. The numerical simulations (figure 4(d)) for concentration of Mo precursor and flow around the substrate indicates smaller concentration along the substrate compared to the setup for growth of planar triangular MoS$_2$ (figure 3) and almost no concentration gradient normal to substrate. The dark-field TEM (DF-TEM) image in figure 4(f) shows that the average grain size is $\sim 50$ nm. There are small portions of MoS$_2$ monolayer grains merging with each other which can be observed in the fringes in DF-TEM image. It illustrates
the spatial homogeneity and continuity of the as-synthesized MoS₂ film. Figure 4(g) shows the selected area diffraction pattern of as-grown MoS₂ monolayer film with [0 0 2] zone axis. The polycrystalline nature of the film is clearly identified by the diffraction rings and the corresponding d spacing is associated with the (1 0 0), (1 1 0) and (2 0 0) planes [9].

The formation of MoS₂ planar thin film is also dependent on the change of the precursor flow rate, a set of experiments for the same configuration is performed as shown in Case III with the flow rate of carrier gas (Nitrogen) changing from 50 sccm, 200 sccm to 400 sccm. When the flow rate is low (the SEM image in figure 5(a)), the lateral growth of the TMD nuclei will be limited since the precursor supply is not sufficient. As the flow rate increases, it can increase the precursor supply. When the flow rate increases, the first layer is fully formed by Frank-van der Merve growth mechanism (figure 5(b)), and further growth is followed by a layer-by-layer growth mode. By further increase in the flow rate, we believe the growth mechanism transforms from planar thin film to vertical growth is by Stranski–Krastanov growth mode with MoS₂ small islands on top of the underlying films tend to vertical growth (figure 5(c)). This transformation is believed to be due to the changes in the interfacial energy between the film and vapor during growth by strain.

Growth mechanism
The 2D MoS₂ can grow either in type-I (vertical) and type-II (horizontal) texture [26], considering its crystallographic nature. Vertically grown MoS₂ fins are standing upright on the substrate by exposing their edge sites, while horizontal growth of MoS₂ displays...
their basal planes parallel to the substrate and may either form isolated islands or polycrystalline thin films (optical images of as-grown 2D MoS2 crystals are shown in supporting information figure S1 (stacks.iop.org/TDM/4/025029/mmedia)). Our theoretical and experimental observations indicate a kinetically-driven growth mechanism, where the growth mode (vertical versus horizontal) is determined by the concentration gradient of the precursor at the substrate, while the density of as-grown 2D TMDs is controlled by local flow rate.

During our experiments we changed the position of substrate (figures 1, 3 and 4), while keeping the same other growth conditions, temperature, concentration of precursors, flow rate, and growth time. The temperatures of the sulfur source, substrate, and MoO3 source are controlled and kept constant. The temperature of the sulfur source was ~230 °C, while in the hot-zone area Mo precursor and substrate was maintained at a temperature of 700 °C for all the three cases. The temperature profile of the furnace obtained from experimental measurements (figure S2) indicates that the temperature gradient over the substrate is negligible, which also matches with the numerical simulations. Proper partial pressure ratio Mo to S ($P_{Mo}/P_{S}$) is crucial to create a desirable sulfurizing environment considering the phase diagram of the Mo–O–S system [27]. $P_{Mo}/P_{S}$ can affect the edge energy of as-synthesized MoS2 and also dictates the conversion of MoO3 to suboxides [28, 29], which leads to the inhibition of MoS2 growth or formation of sp³-bonded clusters. Because of the long distance between the S source and substrate, as well as a small flow pressure gradient across the quartz tube, the sulfur vapor gradient on the substrate is negligible. In contrast, positioning the substrate in close vicinity of the MoO3 source crucible, implies a large gradient in the $P_{Mo}$ (equivalent to $\nabla c$) which is in accordance with numerical simulations in figure 6.

Experimental observation of vertical growth of 2D MoS2, Case I, is shown in figure 1. Numerical simulations of the growth (figures 1(d) and 6(a)) reveal an obvious concentration gradient of the Mo precursor normal to the substrate. It is worth noting that the arrows are pointing to the direction along which concentration of precursor increases that is opposite to the direction of diffusive flux. At the beginning of the growth, nucleus of an MoS2 flake is formed on the substrate resulting in a concentration gradient between the top and bottom of the nucleus. A higher concentration on the top of the nucleus results in a self-amplifying concentration gradient that provides a driving force for the growth of MoS2 normal to the substrate, i.e. the Mullins–Sekerka instability and growth [18] (similar to the concentration gradient leading to dendrite growth).

Changes in the interface energy also plays a crucial role during the growth of 2D nanomaterials. Here the substrate/vapor interface will be substituted by substrate/MoS2 interface and vapor/MoS2 interface, which itself is a function of precursor concentration. For vertical growth of MoS2 fins, more vapor/MoS2 interface and edge sites are created rather than the substrate/vapor interface, which means the change in interface energy should be positive (Volmer–Weber growth mechanism). Besides the main effect introduced by precursor concentration and its gradient, carrier gas flow rate also has a non-trivial effect on the final morphology. For each case, we fixed the N2 flow rate at 200 sccm for Mass Flow Controller. Numerical simulations demonstrate the flow rate at different sections of the PVT furnace (specified by density of stream lines and their coloring in the figures 1, 3 and 4). For the standing substrate, as illustrated in figures 1(d) and 6(a), there is an increase in the local flow rate where the substrate is located. This increase can be seen in the background color of the schematic showing a decrease in the concentration as we move from the top to the bottom of the substrate surface. The role of kinetics will be enhanced under high flow rates, where higher mass transfer leads to a faster crystal growth rate [18]. This describes our experimental observations in figures 1(b) and (c), with the top side of the vertical substrate with higher flow rate showing denser vertical MoS2 fins as opposed to the bottom.

For planar monolayer triangle growth in Case II, numerical simulations (figures 3(d) and 6(b)) display negligible concentration gradient normal to the substrate. As we mentioned above, the change in the interface energy is a function of precursor concentration ($P_{Mo}$ and $P_{S}$) which is not positive consider-
The monolayer structure of the as grown triangles (Frank-van der Merve growth mechanism). If the change in interface energy was positive, we would have seen multilayers instead of a monolayer MoS\(_2\) (Volmer–Weber growth mechanism). Thus the flakes tend to spread laterally, forming planar single layer triangles with a crystallography direction of (0 0 2) to minimize the overall surface energy. The traditional sulfurization of metal or metal compounds during the PVT process for an upside down substrate setup only leads to the formation of triangular-shaped MoS\(_2\) \cite{28} that is similar to Case II. The numerical simulation of the growth process for Case II (figures 3(d) and 6(b)) indicate that moving from area (i) to area (ii) on the substrate, concentration of the precursor, \(c\), and magnitude of its gradient, \(|\nabla c|\), reduce. The lesser concentration, \(c\), results in fewer nucleation sites and the smaller \(|\nabla c|\), results in lower thermodynamic driving force, which subsequently is in effect of fewer super critical nuclei. In area (i) the many supercritical MoS\(_2\) triangles formed, start to grow, depleting the MoS\(_2\) concentration in the surrounding gas phase, which further lim-

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**Figure 6.** Effect of Mo precursor concentration and its distribution in vicinity of the substrate on the growth mode. (a) Concentration gradient (background color) is plotted and direction of the gradient, i.e. is shown by the arrows, where the arrows are that are colored with the scale of \(|\nabla c|\) for Case I. Large concentration gradient normal to the substrate is found, which describes the growth of vertical Mo nanofins. Concentration of Mo precursor (background color) and its gradient (arrows) are higher for Case II (b) compared to Case III (c) in the vicinity of the substrate. Although direction of gradient is along the substrate in both cases, lower concentration gradient in Case III (c) leads to the formation of uniform monolayer multigrain films, in contrast to isolated MoS\(_2\) islands in Case II (b).
its the growth of MoS$_2$ triangles. In contrast, there are fewer supercritical MoS$_2$ triangles in the area (ii) and thus depletion of MoS$_2$ in the gas phase is not a limiting factor. This justifies the fewer yet larger MoS$_2$ triangles that are forming in the area (ii) compared to the area (i).

For the configuration where the substrate is laying down next to the crucible (Case III), the concentration of the Mo precursor is lower than Case II and only a small gradient exists along the substrate (figures 4d and 6c). Comparing to Case II, it is obvious that $P_{Mo}/P_s$ is lowered and thus the $P_{Mo}/P_s$ is relatively small. Comparing figures 3(c) and 4(c), the size of the triangular-shaped MoS$_2$ monolayers grown in Case II are in the order of a few microns while the size of individual grains in the monolayer thin film grown in Case III is of a few tens of nanometers. This indicates a smaller number of nucleation sites in Case II compared to Case III, which may be interpreted by the higher energy of the critical nucleus at the growth conditions of Case II compared to Case III. In this case, more detailed analysis needs to be performed using ab initio calculations to find the energy change during the formation of MoS$_2$ nuclei as a function of $P_{Mo}/P_s$ [30]. Simulation results presented for Case III (figure 4(d) and 6(c)) indicate the velocity of carrier gas flow over the substrate is larger in Case III compared to Case II, which is in effect of greater mass flow toward the substrate and higher nucleation rate in Case III. However, a smaller concentration of precursor and its gradient, $c$ and $\nabla c$, in the vicinity of the substrate is revealed in Case III compared to Case II, which lower the thermodynamic driving force for the nucleation and growth of layered MoS$_2$ nanostructures. Thus, in the Case III, although there are larger number of nuclei, the thermodynamic driving force for their growth is smaller compared to Case II. This results in a larger number of small monolayer MoS$_2$ grains that are grown to cover surface of the substrate, forming an atomic thin multi-grain film of MoS$_2$ (figure 4(f)), where the size of each individual grain is smaller than the size of individual MoS$_2$ triangles shown in figure 3(c) for Case II. Different grain shapes are observed in Case III due to the complex nature of interactions between different grains and the kinetics of growth. The setup presented in Case III is preferred to maximize the overall coverage of the monolayer by facilitating the lateral expansion of the flakes. It is thus critical to maintain a low and constant $P_{Mo}$ as well as the proper carrier gas flow rate over the substrate to obtain a uniform monolayer thin film.

This study further demonstrates that the density of as-grown nanostructures can also be controlled by the precursor flow rate during synthesis. This provides a new mechanism for controllable growth of 2D MoS$_2$ with different orientations and morphologies for applications in energy, catalysis, electronic devices and ultrathin integrated circuits.

**Method**

**Powder vapor transport synthesis of 2D MoS$_2$ crystals**

Silicon substrates with 300 nm of SiO$_2$ were used as growth substrates. These substrates were cleaned as follow: first sonicated in acetone and isopropyl alcohol for 10 min each and then cleaned with deionized water, followed by immersion in Piranha solution (3:1 mixture of H$_2$SO$_4$ and H$_2$O$_2$) for 30 min, afterwards, they were sonicated and rinsed with deionized water again and dried with pure nitrogen.

Molybdenum disulfide (MoS$_2$) is synthesized via oxide powder vaporization by three configurations. The setup of vertical MoS$_2$ growth is shown in figure 1(a). In all cases, ~1 mg MoO$_3$ (99.99% Sigma Aldrich) is placed in the crucible in the hot zone of the furnace (~700 °C). Sulfur powder (~150 mg, 99.5% Alfa Aesar) is put in another crucible, which is placed 15 cm upstream away from the center crucible, the temperature for sulfur is ~230 °C. High purity nitrogen is introduced into the furnace as carrier gas for the whole process.

The PVT growth is conducted at atmospheric pressure in a 15 mm (diameter) horizontal tube furnace (Mini-mite). The quartz tube is initially pumped down to $1 \times 10^{-4}$ mbar and purged with nitrogen gas repeatedly to remove air contamination. The growth conditions are as follows: (1) Sit for 20 min at 150 °C to remove water contamination; (2) Ramp to 400 °C in 15 min and hold at 400 °C for 10 min; (3) Ramp to 700 °C in 30 min; (4) Hold at 700 °C for 10 min and cool down to 560 °C; (5) Open furnace for rapid cooling. The whole process is at a flow rate of 200 sccm high purity nitrogen.

**Characterization**

Scanning electron microscopy (SEM) was carried out using a Leo 1530 FESEM. A Witec confocal Raman system with 532 nm laser was utilized for Raman/PL characterization with an operation power ~1 mW. Transmission electron microscopy (TEM) was used to examine the morphology and layer number of the MoS$_2$ nanosheets. Vertical growth of MoS$_2$ was transferred onto the TEM grid from the substrate by mechanical scratching, and sonication in IPA. A drop of the solution was further placed on the TEM grid for analysis. Monolayer MoS$_2$ film was transferred to the TEM grid by a PMMA method. FEI Talos S/TEM at 80 kV was used to study the atomic and chemical structure of as-grown MoS$_2$ in this study.
Numerical simulation

The 2D numerical model was developed using the commercial finite element software package COMSOL [31], where the coupled system of heat transfer, equation (1), diffusion, equation (2), and fluid flow, equation (3), are considered [32]. The partial pressure of Mo precursor, i.e. concentration of Mo, and its distribution is the key element in determining the growth mode: vertical versus lateral. The heat transfer equation is

\[ Q = ρC_p \frac{∂T}{∂t} + ρC_p \mathbf{u} \cdot \nabla T + \nabla \cdot q = -k \nabla T; \]  

where \( Q \) is the heat source (neglected in our simulations), \( ρ \) is density, \( C_p \) is the heat capacity (at constant pressure), \( T \) is the temperature, \( \mathbf{u} \) is the velocity of the carrier gas that is obtained by solving the Navier–Stokes equations (equation (3)), \( q \) is the heat flux vector, and \( k \) is the thermal conductivity coefficient. The diffusion equation is

\[ R = \frac{∂c}{∂t} + \nabla \cdot (-D \nabla c) + \mathbf{u} \cdot \nabla c; \quad N = -D \nabla c + \mathbf{u}; \]  

where \( c \) is the concentration of Mo precursor, \( D \) is the diffusion coefficient, and \( R \) is the source of Mo precursor. Finally, the Navier–Stokes equations that determine the fluid flow are

\[ \frac{∂\mathbf{u}}{∂t} + \rho(\mathbf{u} \cdot \nabla) \mathbf{u} = \nabla \cdot [-p \mathbf{I} + \mu(\nabla \mathbf{u} + (\nabla \mathbf{u})^T)] + \mathbf{F}; \]  

\[ \nabla \cdot \mathbf{u} = 0, \]  

where \( p \) is pressure, \( \mathbf{I} \) is the unit matrix, \( \mu \) is the dynamic viscosity, superscript \( T \) means matrix transpose, and \( \mathbf{F} \) is the volumetric applied force, such as gravity, which was neglected in our simulations. We also used experimental measurements to determine the temperature of the furnace, which is used later in our numerical simulations for calculating the heat transfer and temperature of the carrier gas inside the quartz tube (figure S1). The solution domain is discretized using general triangular meshes with refinement at the corners and interface of the carrier gas and solids. The carrier gas flow is modeled as incompressible flow and temperature dependent properties (density, dynamic viscosity, thermal conductivity, and heat capacity at constant pressure) of Argon are utilized.

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