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Bottom-up synthesis of vertically oriented two-dimensional materials

R A Vilá1,2, K Momeni1,3, Q Wang4, B M Bersch1,2, N Lu1, M J Kim1, L Q Chen1 and J A Robinson1,2

1 Department of Materials Science and Engineering, The Pennsylvania State University, University Park, PA 16802, USA
2 The Center for 2-Dimensional and Layered Materials, The Pennsylvania State University, University Park, PA 16802, USA
3 Department of Mechanical Engineering, Louisiana Tech University, Ruston, LA 71272, USA
4 Department of Materials Science and Engineering, The University of Texas at Dallas, Richardson, TX 75080, USA

E-mail: jrobinson@psu.edu

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Abstract
Understanding nucleation and growth of two-dimensional (2D) and layered materials is a challenging topic due to the complex van der Waals interactions between layers and substrate. The morphology of 2D materials is known to vary depending on experimental conditions. For the case of MoS2, the morphology has been shown to vary from rounded (molybdenum rich) domains to equilateral triangular (sulfur rich) domains. These different morphologies can result in drastically different properties, which can be exploited for applications in catalytic reactions, digital electronics, optoelectronics, and energy storage. Powder vaporization (PV) synthesis of molybdenum disulfide (MoS2) can yield vertical domains, however, these domains are often ignored when the morphology evolution of MoS2 is discussed, thereby completely omitting a major part of the impact of the Mo:S ratio to the growth mode of MoS2 during PV. Combining experimental and numerical simulation methods, we reveal a vertical-to-horizontal growth mode transition for MoS2 that occurs in the presence of a molybdenum oxide partial pressure gradient. Transmission electron microscopy reveals that the growth of vertical MoS2 results from initial seeding of single crystalline molybdenum dioxide, followed by sulfurization from the substrate upward to form vertically oriented MoS2 domains.

Introduction
Semiconducting two-dimensional (2D) materials such as molybdenum disulfide (MoS2) are of interest for their potential applications in digital electronics, catalytic reactions, optoelectronics, and energy storage [1–4]. The ‘traditional’ route to synthesizing such materials is powder vaporization (PV) (often referred to as chemical vapor deposition) [4–9], where the equilibrium morphology is a strong function of the metal:chalcogen ratio (Mo:S for MoS2) [9, 10]. PV synthesis of MoS2 can yield vertical MoS2 structures [11, 12], however, these structures are often ignored when the morphology evolution of MoS2 is discussed [9, 10], thereby completely omitting a major part of the Mo:S ratio impact on morphology in this deposition technique. Vertically grown MoS2 exhibits enhanced catalytic activity at exposed edge sites [13–19]; therefore, understanding and controlling the synthesis of vertical MoS2 is crucial. Furthermore, a fundamental understanding of the thermodynamics and kinetics governing the reaction, nucleation, and growth of MoS2 from horizontal to vertical is vital for engineering layered material systems for the entire spectrum of applications. In this article, we elucidate the nucleation and growth mechanism of MoS2 from vertical to horizontal using experimental techniques and numerical simulations. We reveal that the partial pressure ratio of molybdenum oxide to sulfur, and its distribution, governs the growth mode of MoS2 between vertical and horizontal configurations.
Experimental

Synthesis
Prior to deposition, substrates are cleaned by sonication in acetone and isopropanol alcohol for 10 min each, then rinsed with deionized (DI) water. Substrates are then immersed in a heated piranha solution at 80 °C for 20 min and rinsed again with DI water. Preparation of the graphene substrate was completed by high-pressure silicon sublimation of 6H–SiC, as explained in detail elsewhere [20]. PV deposition of MoO3 was completed by placing a single substrate facedown in an alumina crucible 8.5 mm from a 1 mg MoO3 source (99.8%, Sigma-Aldrich). The crucible is placed at the center of a custom tube furnace within the primary hot zone. A fused quartz crucible with 250 mg of sulfur powder (99.995%, Alfa Aesar) was placed upstream from the crucible in a secondary hot zone to independently control the rate of vaporization and sublimation of the precursors. The furnace was then evacuated to remove impurities and filled with argon gas (99.99%) with a mass flow rate of 450 sccm, the pressure of the tube furnace was maintained at 710 Torr throughout deposition. The primary hot zone was heated to 750 °C at a rate of 50 °C min⁻¹ and the secondary hot zone was rapidly heated to 250 °C to vaporize the sulfur. Argon gas carries the sulfur vapor to the MoO3 source and substrate, allowing for reaction of the precursors and adsorption onto the substrate. After 10 min at 750 °C, the furnace was cooled at a rate of 30 °C min⁻¹ to room temperature. The same procedure is followed for the synthesis of MoO2 films, however, the sulfur precursor is precluded. Sulfurization of MoO2 films also was completed using the same experimental procedure above, however, the MoO3 precursor was removed to prevent further deposition of MoO2.

Characterization
Scanning electron microscopy (SEM) images were recorded on a Merlin (Carl Zeiss, Oberkochen, Germany) field-emission SEM utilizing the in-lens secondary electron detection mode with a 10 kV accelerating voltage. Raman spectroscopy was performed on a LabRAM HR Evolution (Horiba, Kyoto, Japan) operated at room temperature with a 488 nm excitation wavelength. In order to preserve the as-grown morphology of vertical fins during focused ion beam (FIB) milling, a 100 nm conformal coating of hafnium oxide (HfO2) and/or alumina (Al2O3) was deposited by atomic layer deposition using a 150 LE (Kurt J Lesker, Pennsylvania, USA) heated to 250 °C. To prevent charging during FIB milling, a conductive 10/50 nm titanium and gold layer was deposited by electron-beam evaporation in a Lab-18 (Kurt J Lesker, Pennsylvania, USA). Cross-sectional transmission electron microscopy (TEM) specimens were prepared with a Nova 200 DualBeam (FEI, Oregon, USA) FIB-SEM equipped with an OmniProbe manipulator (Oxford Instruments, Abingdon, United Kingdom). Upside-down transfer and milling technique has been applied to avoid the curtain effect. Cross-sectional samples were thinned to 100 nm with a 30 kV Ga ion beam and then to 70 nm with a 5 kV Ga ion beam to remove surface damage caused by 30 kV ion beam. High angle annular dark field (HAADF)-STEM and annular bright field (ABF)-STEM images were recorded with a JEM-ARM200F (JEOL, Tokyo, Japan) aberration-corrected electron microscope. In all the experiments, the microscope was operated in STEM mode at 200 kV and the convergence semi-angle of the incident electron beam was set to be 24 mrad with a probe size of approximately 0.1 nm in diameter.

Modeling
The coupled set of heat transfer (equation (S1), see supporting information), diffusion (equation (S2)), and Navier–Stokes (equation (S3)) equations are solved simultaneously for the reaction chamber, encompassing the source, substrate, and crucible. We have used commercial finite element software package COMSOL with free tetrahedral mesh elements, PARADOISO direct solver, and backward Euler method to solve the time-dependent equations [21]. Different mesh densities are considered to ensure a mesh-independent solution. Constant temperature boundary condition is utilized along the walls of CVD furnace, which follows the experimentally measured temperature profile. Argon is the carrier gas (450 sccm inflow), an Al2O3 crucible, and a diffusion coefficient of \(8 \times 10^{-4} \text{ m}^2\text{s}^{-1}\) is considered with vanishing outflow of pressure.

Results and discussion
Synthesis of MoS2 was accomplished via simultaneous sublimation and vaporization of molybdenum trioxide (MoO3) and sulfur (S2) respectively [5], the experimental set-up is illustrated in figure 1(a). Considering the complex nature of the vaporization process and various controlling parameters affecting the growth of the MoS2, which are not experimentally accessible, we have modeled the sublimation and transport of MoO3 to understand the growth process (figure S1, see supporting information). The coupled system of equations governing the heat transfer, gas flow, and diffusion of MoO3 are numerically solved using the finite element modeling technique (equations (S1)–(S3)) [21]. This simulation demonstrates the presence of a large concentration gradient of MoO3 near the substrate, indicating a decrease in the partial pressure of MoO3 as the distance from the MoO3 source increases. Alternatively, the long distance between the sulfur source and substrate yields a uniform partial pressure of S2 over the substrate surface. Furthermore, we note that MoO3 likely
reduces to MoO$_2$ in the vapor phase due to the relative stability of MoO$_2$ compared to MoO$_3$ [22], which results in a mixture of various molybdenum oxides in the gas phase (represented as 'MoO$_x$' in this work). Growth kinetics is also affected by the rate of flow of precursor material, which is determined by the carrier gas flow pattern. Considering a no-slip condition on the substrate and walls of the crucible, we expect less precursor to reach the areas close to the walls, which subsequently inhibits the growth rate. This is consistent with both experimental results and numerical simulations.

The MoO$_x$:S$_2$ partial pressure ratio, and its gradient, plays a critical role in the observed morphology evolution. This is evident in SEM images of the resulting PV deposition on a silicon carbide (6H–SiC) substrate (figures 1(b)–(d)) as a function of distance from the MoO$_3$ precursor. Regions on the substrate near the MoO$_3$ source yield vertically oriented domains (referred to as 'fins') (figure 1(b)) that evolve into a mixture of fins and lateral domains (figure 1(c)), and finally only lateral domains (figure 1(d)) as one moves away from the MoO$_3$ source. This behavior corresponds well to a high, intermediate, and low MoO$_x$:S$_2$ partial pressure ratio, respectively, and can be understood when considering surface and edge energy of MoS$_2$ are a function of gas composition and partial pressure of gas species [10]. Changes in the surface and edge energy ($\Delta E$) from a vapor/substrate system to a vapor/MoS$_2$/substrate system is a primary factor in determining the growth mode as layer-by-layer ($\Delta E < 0$, Frank–van der Merve) [23], island ($\Delta E \geq 0$, Volmer–Weber) [24], or layer-plus-island (initial $\Delta E < 0$ followed by $\Delta E \geq 0$, Stranski–Krastanov) [25]. Therefore, the MoO$_x$:S$_2$ partial pressure ratio modifies the surface and edge energy change and can indirectly affect the growth mode of MoS$_2$.

The vertical to horizontal morphology evolution is independent of the substrate. This becomes apparent when comparing the morphology evolution of MoS$_2$ grown on different substrates, including silicon dioxide on silicon (SiO$_2$/Si), sapphire (Al$_2$O$_3$), and epitaxial graphene (EG) (figure S2). Therefore, we hypothesize that the changes in the surface/edge energies are minor and morphology evolution is primarily a function of a MoO$_x$:S$_2$ partial pressure ratio gradient. PV deposition of MoS$_2$ on 6H–SiC and Al$_2$O$_3$ yields fins that only grow in specific orientations, while fins deposited on SiO$_2$/Si and EG are randomly oriented, indicating epitaxial growth of fins can occur on single crystalline substrates. Horizontal domains appear more randomly oriented due to the weak van der Waals interaction at between MoS$_2$ layers and the substrate. Considering the original wafer orientation of 6H–SiC, fins are identified to grow along the hexagonal symmetry related directions: [11\bar{2}0], [\bar{2}1\bar{1}0], [112\bar{1}], [\bar{2}1\bar{1}2], [1\bar{1}0\bar{0}], [1\bar{1}0\bar{1}].
and [1210] (figure S3). Further inspection of the fin morphology by imaging a cleaved cross-sectional sample under SEM reveals a faceted isosceles triangular morphology (figure 1(e)). The faceted morphology of fins indicates that the morphology is determined by the growth kinetics of crystallographic faces as related to the minimization of surface energy during growth. Raman spectroscopy reveals that lateral domains are 2H–MoS2 on the other hand, vertical fins are determined to be a mixture of 2H–MoS2 and monoclinic MoO2 (figure 1(f)). The presence of MoO2 and MoS2 in the fins suggests that multiple mechanisms could be responsible for the formation of vertical fins: (1) nucleation and growth of MoO2 fins followed by sulfurization to form partially sulfurized MoO2 fins; or (2) a growth competition between MoO2 and MoS2 leading to a multi-component fin.

To elucidate the fin growth mechanism, we eliminated sulfur during synthesis to compare the morphology and structure to those resulting from the co-flow process. Even without the presence of S2, the aligned fin morphology is still achieved close to the MoO3 source (figure 2(a)); however, the formation of lateral domains is precluded. Raman spectroscopy (figure 2(b)) confirms the composition of the fins as monoclinic MoO2 and spatially mapping the intensity of the Raman shift at 497 cm−1 (figure 2(c)) demonstrates that MoO2 is limited to the fin morphology. This suggests that the MoO2/6H–SiC interfacial energy is much higher than the MoO2/vapor interfacial energy, resulting in an island-like (Volmer–Weber) growth mode [24]. We also note that the MoO3 concentration gradient normal to the substrate can result in a self-amplifying concentration gradient (figure S4) described by the Mullins–Sekerka instability and growth [27], which can also promote vertical growth.

TEM confirms the vertical morphology and reveals the single crystalline nature of the MoO2 fins. Utilizing high-resolution scanning transmission electron microscopy (STEM) with a HAADF detector, one can identify the epitaxial growth of MoO2 on 6H–SiC (0001) (figures 2(d) and (e)), and verify the MoO2 spacing in the fins matches that of MoO2 along the [001] zone axis (figure 2(f)). STEM imaging of a MoO2 fin, collected with an ABF detector, reveals the position of oxygen atoms and overlaying the atomic projection of MoO2 as viewed down the [001] axis further confirms the composition and structure of fins (figure S5). From identification of the zone axis, the basal plane and sidewalls of MoO2 fins can be identified as (010) and (100), respectively. The observed isosceles triangular morphology of the (100) plane can be further explained by the (122) cleavage plane which sits 40.8° above the basal plane (figure S6), which is good agreement with the experimentally measured angle of vertical fins, the MoO2 fin morphology is schematically illustrated in figure 2(g).

The orientation of MoO2 fins on 6H–SiC (and other crystalline substrates) is heavily influenced by the strain at the MoO2/substrate interface. Constraining the MoO2 [001] axis to be parallel to the 6H–SiC [1120] direction, the structures of O-terminated MoO2 (010) and Si-terminated 6H–SiC (0001) can be directly overlaid. This leads to the formation of a Moiré pattern between the O from MoO2 and Si from 6H–SiC (figure 2(h)). As the MoO2 (010) plane is rotated with respect to the 6H–SiC [0001] axis, the local strain is
increased until a maximum is reached when the MoO$_2$ [001] axis is parallel to the 6H–SiC [1010] direction (30$^\circ$ from [1120]). Further rotation of the MoO$_2$ (010) reduces local strain until the MoO$_2$ [001] axis is parallel to 6H–SiC [2110] (60$^\circ$ from [1120]), reforming the original Moiré pattern (figure S6). This suggest that growth of MoO$_2$ parallel to the 6H–SiC [1120], [2110], and [1210] directions can minimize strain energy between the MoO$_2$ (010) and 6H–SiC (0001) surfaces. While total strain can differ due to various relaxation mechanisms, this result provides insight to the origin of oriented growth of MoO$_2$ fins on single crystalline 6H–SiC and Al$_2$O$_3$ substrates.

Elimination of sulfur during synthesis provides strong evidence that vertical domains formed during co-flow of sulfur and MoO$_2$ results from nucleation and growth of MoO$_2$ fins followed by sulfurization into MoS$_2$. From kinetic theory we directly relate the partial pressure ($P_i$) and molecular mass ($M_i$) of a gaseous species $i$, and temperature ($T$) to the impingement rate ($\Phi_i$) of the species $i$ (equation (1)) [28]:

$$\Phi_i = \frac{1}{\sqrt{2\pi k T}} \left( \frac{P_i}{\sqrt{M_i}} \right)$$

where $k$ is Boltzmann’s constant. For the case of a high $P_{MoS_2}$: $P_{S_2}$ ratio, the impingement rate of MoO$_2$ is much greater than the impingement rate of S$_2$ ($\Phi_{MoO_2} \gg \Phi_{S_2}$). Assuming sulfur readily sulfurizes MoO$_2$ into MoS$_2$ [5], one can approximate the MoO$_2$ growth rate ($\gamma_{MoS_2}$) as a function of difference between $\Phi_{MoO_2}$ and $\Phi_{S_2}$, i.e., $\gamma_{MoO_2} \approx \Phi_{MoO_2} - \Phi_{S_2}$ [28]. Using the same assumptions, the growth rate of MoS$_2$ can be approximated by the impingement of sulfur onto the substrate ($\gamma_{MoS_2}$) because $S_2$ is the rate limiting species when $P_{MoO_2} \gg P_{S_2}$.

In regions where the $P_{MoO_2} \gg P_{S_2}$, the growth rate of MoO$_2$ is much greater than MoS$_2$ ($\gamma_{MoO_2} \gg \gamma_{MoS_2}$). Consequently, the rate of nucleation and growth of MoO$_2$ fins is greater than its sulfurization rate, precluding lateral MoS$_2$: experimentally this growth regime is observed near the MoO$_3$ source as shown in figure 1(b), and schematically it is illustrated in figure S8. Reducing $P_{MoO_3}$ to an intermediate MoO$_3$:S$_2$ partial pressure ratio leads to reduction of $\gamma_{MoO_2}$ while $\gamma_{MoS_2}$ remains unchanged (sulfur limited). As $\gamma_{MoO_2}$ is reduced, there is a transition to a mixture of MoO$_2$ fins and MoS$_2$ lateral domains (figure 1(c)). Further reduction of $P_{MoO_3}$ below some critical value ultimately reduces $\gamma_{MoO_2}$ to a point where MoO$_2$ nuclei cannot reach a critical radius for stabilization prior to sulfurization. In the regime where $P_{MoO_3} \ll P_{S_2}$, the rate limiting species becomes MoO$_3$, resulting in complete sulfurization of MoO$_3$ species. Experimentally this growth regime is observed farthest from the MoO$_3$ source (figure 1(e)), and is schematically it is illustrated in figure S9.

Examining fins at various points during sulfurization (figures 3(a)–(d)) reveals the MoO$_2$ transformation into MoS$_2$ begins at the MoO$_2$ sidewalls, resulting in a core–shell MoO$_2$/MoS$_2$ fin (figure 3(b)). Evident from the minimal transformation of the MoO$_2$ fin sidewall into MoS$_2$ (0001), sulfurization of the MoO$_2$ sidewall kinetically limits diffusion of sulfur through the newly formed MoS$_2$ (0001) plane [29]. Only considering sulfur diffusion from the surface-inward, it would be expected that sulfurization of MoO$_2$ fins would be self-limiting. However, continued sulfurization reveals that the oxide-to-sulfide transformation rate is greatest at the MoO$_2$/substrate interface (figure 3(c)). This is likely due to strain, disorder, and defects that ultimately increase the diffusion mobility of sulfur at the MoO$_2$/substrate interface, which in turn provides a pathway for sulfur diffusion and oxide-to-sulfide transformation. Furthermore, the van der Waals gap between newly formed layers of MoS$_2$ creates a vertical pathway for sulfur diffusion,

![Figure 3](image-url)
leading to a MoS$_2$/MoO$_2$ transformation front (figure 3(c)) that enables complete transformation of MoO$_2$ into MoS$_2$ (figure 3(d)). The sulfurization process and transformation of MoO$_2$ fins into MoS$_2$ is schematically illustrated in figure 3(e).

MoS$_2$ layers within the fully sulfurized fin (figure 3(d)) share a common [0001] axis, however, MoS$_2$ layers are observed to take various orientations (figure S10). We hypothesize that the different orientations are related to differences in the rate of sulfurization of MoO$_2$ at the surface, interface, and bulk. We note that MoS$_2$ (31.63 cm$^3$ mol$^{-1}$) has a molar volume 60% larger than MoO$_2$ (19.77 cm$^3$ mol$^{-1}$), and complete sulfurization of the MoO$_2$ fin should result in a 60% increase in volume. However, the volume of fins typically decreases after sulfurization suggesting that the transformation of MoO$_2$ into MoS$_2$ is an inefficient process whereby Mo, MoO$_x$, and O desorb from the fin during sulfurization.

**Conclusion**

The growth mechanism of vertical MoS$_2$ fins and lateral MoS$_2$ domains synthesized via PV has been investigated by deliberate introduction of a MoO$_2$ partial pressure gradient. The MoO$_2$/S$_2$ partial pressure ratio and its distribution are found to be the primary parameters controlling the morphology of MoS$_2$ between lateral domains and vertical fins when metal-oxide precursors are utilized. Furthermore, through removal of the sulfur precursor during synthesis we elucidate that MoS$_2$ fins are formed through a two-step process: Volmer–Weber MoO$_2$ fin growth, followed by sulfurization. In the case where synthesis occurs on crystalline substrates, strain minimization at the MoO$_2$ (010)/6H–SiC (0001) interface leads to preferable orientation of MoO$_2$ [001] to 6H–SiC [1120], [2110], and [1210] directions. Subsequently, we find that sulfurization of MoO$_2$ fins is not simply a ‘surface-inward’ transformation, but rather occurs primarily at the interface between MoO$_2$ fins and the substrate and migrates upward as MoS$_2$/MoO$_2$ transformation fronts. The work presented here clearly demonstrates that tuning the metal-oxide to chalcogenide precursor partial pressures not only controls the lateral morphology of 2D materials, but is key to realizing vertically oriented 2D structures.

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**References**

[23] Frank F C and van der Merwe J H 1949 Proc. R. Soc. A 198 205