Strain-Driven and Layer-Number-Dependent Crossover of Growth Mode in van der Waals Heterostructures: 2D/2D Layer-By-Layer Horizontal Epitaxy to 2D/3D Vertical Reorientation

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Heterogeneously integrated 2D van der Waals (vdW) solids composed of compositionally distinct atomic layers are envisioned to exhibit exotic electrical/optical properties unattainable with their monocomponent counterparts. However, the underlying principle for their morphology-controlled chemical vapor deposition (CVD) growth and its associated growth variables have not been clarified, leaving their projected technological opportunities far from being realized. Herein, by employing tungsten trioxide (WO$_3$) nanowires as a model system that uniquely enables the detailed atomic-scale inspections of 2D/2D interfaces, the CVD growth mechanism of 2D molybdenum/tungsten disulfide vdW vertical stacks is studied. By employing extensive transmission electron microscopy (TEM) characterization, an intriguing growth mode transition is identified in these materials, i.e., 2D/2D layer-by-layer horizontal epitaxy to 2D/3D vertical layer reorientation, and it is confirmed that it is driven by varying 2D layer numbers. Corroborating molecular dynamics simulations clarify that the internal strain accumulated during the course of 2D layers growth dictates the final growth mode, further supported by TEM strain map analysis. This study not only sheds a new insight on better understanding the growth principles for 2D vdW heterostructures but also offers important technical guidance on tailoring their functionalities toward exploring 2D/2D heterojunction devices.
demanded in conventional heterojunction growths.[18–23] A large family of 2D vdW heterostructures has recently been developed through various chemical routes,[24–26] and one of the most explored material systems is 2D molybdenum/tungsten disulfides (MoS2/WS2) in vertical stacks.[23,27–31] In order to leverage their desired functionalities, it is essential to tailor the morphological variables of 2D layers during their growth stages, which would only be possible once their underlying growth mechanism is clarified. A large set of parameters that govern the thermodynamic and crystallographic conditions for 2D vdW heterostructure growths remains unclear,[42] leaving following questions to be answered: “How do the subsequent 2D layers grow on top of pre-existing 2D layers, and would it be possible to engineer their crystallographic orientations? If possible, what are the driving factors that determine their growth characteristics, and what would the atomistic structure of the resulting 2D/2D interfaces be?” Experimentally addressing these questions, thereby, clarifying the atomistic growth mechanism of 2D vdW vertical heterostructures is technically challenging for multiple reasons. From the material growth perspective, controlled integration of secondary 2D layers on top of pre-existing 2D layers is challenging in conventional approaches. For example, despite some successful demonstrations,[33,34] chemical vapor deposition (CVD) employing the simultaneous co-reactions of multiple precursors often results in the growth of distinct 2D layers either in a vertically stacked or in a horizontal stitching manner even under identical growth conditions,[35–37] making it difficult to establish a unified growth principle. Growth via a sequential CVD of one 2D material after the other have alternatively been explored,[7,9,16,28,38–41] which inevitably requires nontrivial microscopy investigations to visualize the atomistic 2D/2D vdW interfaces. For example, conventional cross-sectional transmission electron microscopy (TEM) has relied on the physical/chemical milling of 2D/2D vdW interfaces down to the thickness suitable for electron transmission, which is highly sophisticated/demanding and often results in a low success yield. Accordingly, investigating statistically a large number of 2D/2D vdW interfaces in their pristine forms is difficult, thus clarifying the associated 2D growth mechanism and its governing factors remains challenging.

Herein, we study the CVD growth mechanism of vertically stacked 2D MoS2/WS2 layers and unveil the fundamental factors that dictate the vdW assembly of 2D MoS2 layers on the basal planes of 2D WS2 layers. We employ single-crystalline-faceted tungsten trioxide (WO3) nanowires as a model system that offers distinct advantages over conventional approaches; 1) 2D WS2 layers are self-assembled from the single-crystalline WO3 nanowire surface via controlled sulfurization, yielding atomically flat 2D WS2 basal planes with precisely controlled 2D layer numbers. These morphology-controlled 2D WS2 layers serve as the growth template for subsequent 2D MoS2 layers growth. 2) This nanowire-assisted growth scheme enables the direct TEM visualizations of the atomic structures of 2D MoS2/WS2 vdW interfaces. Moreover, it circumvents the complicated cross-sectional TEM sample preparation and its associated operation demanded in conventional approaches, thus enables the inspection of a statistically large number of samples. Benefiting from these advantages, we unveil a unique transition of the growth characteristics in these materials, i.e., a transition from the layer-by-layer epitaxy of horizontally oriented 2D MoS2 layers to their vertical reorientation akin to the conventional Stranaski–Krstanov (SK) thin film growths, which is driven by varying 2D layer numbers. Corroborating molecular dynamics (MD) simulation studies identify that the internal strain accumulated during 2D layers’ growth plays a critical role in determining the growth mode, rendering excellent agreement with TEM observations, and strain map analysis.

Figure 1a illustrates the growth experiments. Highly single-crystalline hexagonal WO3 nanowires with faceted surfaces are prepared following a previously developed method.[42] 2D MoS2/WS2 vdW vertical heterostructure layers are subsequently grown on the nanowire surfaces in the following sequences. The nanowires are sulfurized by reacting with vaporized sulfur (S), yielding high-crystalline 2D WS2 layers with well-resolved 2D layers on the nanowire surface. Mo seed films of controlled thickness are subsequently deposited/sulfurized on the grown 2D WS2 layers, achieving 2D MoS2/WS2 vdW vertical stacks. Distinguishable morphologies are observed in the 2D MoS2/WS2 vdW vertical stacks with varying 2D MoS2 layer numbers. Figure 1b–g shows the morphologies of the 2D WS2 layers grown on WO3 nanowires obtained prior to the secondary deposition/sulfurization step in Figure 1a. The scanning electron microscopy image (Figure 1b) of as-prepared 2D WS2/WO3 nanowires reveals well-faceted surfaces whose crystalline structures were identified by extensive TEM characterization. Figure 1c shows a low-magnification bright-field (BF) TEM image of an isolated 2D WS2/WO3 nanowire. Figure 1d is the higher magnification view of the red box in Figure 1c, revealing the presence of 2D WS2 layers on the nanowire surface. The 2D WS2 layers exhibit excellent crystallinity indicated by the well-defined layer number (5 in this case) without any broken layers throughout the entire length (~7 μm). The layer number of the 2D WS2 converted from WO3 is highly controllable by adjusting the sulfurization conditions (Figure S1, Supporting Information). The crystallinity of the 2D WS2 layers and their interfaces were further characterized by annular dark-field (ADF) scanning TEM (STEM). Figure 1e shows a plane-view ADF STEM image of 2D WS2 layers on WO3 (different from Figure 1c,d), revealing an atomically sharp 2D WS2/WO3 interface and evenly spaced 2D layers. Figure 1f shows an ADF STEM image of a 2D WS2/WO3 nanowire cross-sectional view focused ion beam, revealing its faceted and smooth surface covered by 2D WS2 layers throughout its entire periphery. Figure 1g shows a high-resolution ADF STEM image corresponding to the red box in Figure 1f, revealing uniform 2D WS2 layers with an abrupt interface across the WO3 surface. The image also indicates that the nanowire is oriented along the [001] axis of hexagonal WO3.[43] All these TEM characterizations confirm that the 2D WS2 layers self-assembled from the single-crystalline WO3 present excellent crystallinity in their vertical layer stacking, which is desirable for the subsequent growth of 2D MoS2 layers on their basal planes. Details for the fabrication of WO3 nanowires and 2D layer growths are provided in the Experimental Section in the Supporting Information.

Figure 2 compares the morphologies of the 2D MoS2/WS2 vdW vertical stacks grown on WO3 by employing the secondary sulfurization of Mo (various thicknesses) shown in Figure 1. Figure 2a–e shows the characterization of
2D MoS$_2$/WS$_2$ vdW vertical stacks achieved with the sulfurization of $\approx$3 nm thick Mo. The Raman spectroscopy profile (Figure 2a) of as-prepared 2D MoS$_2$/WS$_2$ on WO$_3$ nanowires confirms the typical in-plane ($E_{12g}$) and out-of-plane ($A_{1g}$) vibration modes of 2D WS$_2$ and 2D MoS$_2$, indicating the formation of compositionally and structurally well-defined 2D MoS$_2$/WS$_2$ layers.[44] Figure 2b shows an ADF STEM image of a WO$_3$ nanowire with 2D MoS$_2$/WS$_2$ vdW vertical stacks on its surface. The magnified image of the red box reveals distinguishable image contrasts, indicating that the newly grown material (presumably, 2D MoS$_2$) on 2D WS$_2$ layers is composed of lighter atomic elements. Figure 2c shows the high-resolution ADF STEM image corresponding to the blue box in Figure 2b, revealing the vertical stack of 2D MoS$_2$/WS$_2$ layers on the WO$_3$ surface. Figure 2d,e characterizes the detailed morphologies of the 2D MoS$_2$/WS$_2$ and the 2D WS$_2$/WO$_3$ interfaces, distinguished by atomic number (Z) contrast. 2D MoS$_2$ layers grown on the basal plane of 2D WS$_2$ layers present a highly uniform interlayer spacing of $\approx$0.62 nm, which well matches the hexagonal [002] planes of MoS$_2$.[46] Moreover, the sequence of the individual Mo=S=W atomic bonds (Figure 2e) reveals that both the 2D MoS$_2$ and 2D WS$_2$ preserve semiconducting 2H phases across the 2D/2D interface. The localized distribution of constituent elements in each 2D MoS$_2$ and 2D WS$_2$ was also confirmed by energy dispersive X-ray spectroscopy in STEM mode (Figure S2, Supporting Information). The high crystalline quality of the 2D MoS$_2$ layers and their atomically sharp interfaces across 2D WS$_2$ layers are indicative of the vdW epitaxial growth on the basal planes of 2D WS$_2$ layers$^{[21,22]}$ with relaxed lattice constraints$^{[47-49]}$ and detailed growth mechanisms will be discussed below.

2D MoS$_2$/WS$_2$ vdW vertical stacks achieved by sulfurizing $\approx$12 nm thick Mo seeds exhibit contrasting growth characteristics (Figure 2f–i). Figure 2f shows an ADF STEM image of 2D MoS$_2$/WS$_2$ vdW vertical stacks grown on WO$_3$, which reveals that 2D MoS$_2$ layers readjust their layer orientations with respect to those of the underlying 2D WS$_2$ layers. The magnified view of the red box in Figure 2f exhibits the vertically slanted 2D MoS$_2$ layers on the basal planes of 2D WS$_2$ layers exposing their 2D edge sites on the nanowire surface. Interestingly, such vertically reoriented 2D MoS$_2$ layers are often observed on the horizontally oriented 2D MoS$_2$ layers (yellow lines in Figure 2f) grown on the basal planes of 2D WS$_2$ layers. This observation indicates that 2D MoS$_2$ layers grow from the interface of the Mo–WS$_2$ basal plane in a “bottom-to-top” manner under our growth conditions, and detailed growth mechanisms will be discussed in the later section. Figure 2g shows a high-resolution BF TEM image obtained from the nanowire surface, revealing the plane view of 2D MoS$_2$ vertical layers with exposed 2D edges.$^{[50]}$ Figure 2h,i shows representative TEM images, revealing a large number of 2D MoS$_2$ layers redirect their orientations as interfered by other layers impeaching from the opposite sides (blue and red arrows). This growth impediment of horizontal 2D MoS$_2$ layers and their vertical reorientation were consistently observed with 2D MoS$_2$/WS$_2$ vertical stacks obtained by the sulfurization of thick (typically, $\geq$8 nm) Mo. It is worth mentioning that identifying this unique 2D growth characteristic benefits from our nanowire-based...
Figure 2. a) Raman spectroscopy profile obtained from 2D MoS$_2$/WS$_2$-grown nanowires. b–e) TEM characterization of 2D MoS$_2$/WS$_2$ vdW vertical stacks obtained by sulfurizing ≈3 nm Mo. b) ADF STEM image of an isolated nanowire. c) Magnified view of the blue box in (b), revealing 2D MoS$_2$/WS$_2$ vertical stacks. d) ADF STEM image of a 2D MoS$_2$/WS$_2$/WO$_3$ interface. e) Detailed crystalline structure of the 2D MoS$_2$/WS$_2$ interface. f–i) TEM characterization of 2D MoS$_2$/WS$_2$ vdW vertical heterostructures obtained by sulfurizing ≈12 nm Mo. f) ADF STEM image of an isolated nanowire, revealing vertically reoriented 2D MoS$_2$ layers. g) Top-down plane-view HRTEM image revealing the edges of vertical 2D MoS$_2$ layers. h,i) Redirection of horizontal 2D MoS$_2$ layer orientation interfered by impeaching layers.

growth scheme as it allows for the direct visualization of 2D/2D interfaces with a large number of samples even without tedious TEM cross-section sample preparations. Detailed TEM characterization is provided in the Experimental Section of the Supporting Information and additional TEM images of nanowires with vertical 2D MoS$_2$ layers are presented in Figure S3 (Supporting Information).

Figure 3 illustrates an overview of the distinguishable growth characteristics observed in our 2D MoS$_2$/WS$_2$ vdW vertical stacks. Figure 3a,b depicts the initial growth stage of 2D MoS$_2$ layers forming on the basal planes of 2D WS$_2$ layers irrespective of Mo thickness. Upon reaching the growth temperature, the deposited Mo forms a droplet (presumably, solid (S) phase given its high melting temperature) on the surface of the solidus 2D WS$_2$ layers while vaporized (V) sulfur is being supplied. Accordingly, S–S (WS$_2$–Mo) and V–S (S–Mo) interfaces are newly formed and their energetics determine the growth preference of 2D MoS$_2$ layers (Figure 3a). Although the exact interfacial energy values are presently unavailable in this particular case, it has been theoretically/experimentally confirmed that S–S interfaces present higher interfacial energies over V–S interfaces providing preferred thermodynamic conditions for heterogeneous nucleation, well established in the studies of VS nanowire growths.[51–53] As a result, 2D MoS$_2$ layers are initiated to grow from the WS$_2$–Mo interfaces (black line in Figure 3a) in a horizontal manner, which is driven to minimize the total system energy by exposing their basal planes of low surface energies. Upon their continued growth consuming the deposited Mo, additional interfaces of MoS$_2$–Mo (black line in Figure 3b) are exposed offering preferred nucleation sites for subsequent growth. As a result, horizontal layer-by-layer growths of 2D MoS$_2$ are initially observed on top of 2D WS$_2$ layers irrespective of Mo thickness (Figure 2c–e and Figure 2f,i,g), indicative of the “bottom-to-top” growth manner. Figure 3c,d illustrates the horizontal-to-vertical cross-over of 2D layer growth characteristics determined by varying Mo thickness. Figure 3c describes the growth situation when thin (typically, ≤3 nm) Mo is sulfurized on the basal planes of 2D WS$_2$ layers. Mo films of such a small thickness consist of randomly disjointed tiny Mo nanoparticles with a high density of free volume in between them (inset TEM images). Throughout sulfurization, 2D MoS$_2$ layers grow in the layer-by-layer manner accompanying a substantive volumetric expansion, i.e., conversion of Mo to MoS$_2$, which is efficiently accommodated due
Figure 3. a,b) Schematics for the initial growth stage of 2D MoS<sub>2</sub> layers on 2D WS<sub>2</sub> layers. a) Mo nanoparticles exposing the S–S (Mo–WS<sub>2</sub> basal plane) interface, which provides preferred nucleation sites. b) Growth of a 2D MoS<sub>2</sub> layer on the interface, exposing another S–S interface for subsequent layer-by-layer growth. c,d) Schematics for the distinguishable growth characteristics obtained by sulfurizing Mo of different thickness. c) Layer-by-layer growth of horizontal 2D MoS<sub>2</sub> layers on 2D WS<sub>2</sub> layers achieved by sulfurizing thin Mo. The insets are representative ADF STEM (top) and TEM (bottom) images to show disconnected nanoparticles on the surface of a 2D WS<sub>2</sub>/WO<sub>3</sub> nanowire in a top/side view, respectively. d) SK-like growth of vertically reoriented 2D MoS<sub>2</sub> layers on 2D WS<sub>2</sub> layers, achieved by sulfurizing thick Mo. The inset is a representative TEM image to show the side view of a continuous Mo (∼9 nm thickness) on the surface of a 2D WS<sub>2</sub>/WO<sub>3</sub> nanowire.

to the free volume. Accordingly, they continue to grow filling in the free volume without readjusting layer orientations. Figure 3d describes the growth situation when thick (typically ≥8 nm) Mo is sulfurized on the basal planes of 2D WS<sub>2</sub> layers. Depositing Mo to such a thickness results in a dense film composed of Mo nanoparticles that are continuously connected (inset TEM image). The volumetric expansion through the conversion of Mo to MoS<sub>2</sub> accompanies a significant accumulation of internal strain imposed by adjacently growing/impeaching 2D MoS<sub>2</sub> layers due to the limited free volume in between Mo. Accordingly, continuously growing 2D layers are forced to redirect layer orientations in a way to release the strain once they go beyond the initial horizontal growth stage (Figure 3b). This 2D growth mode transition is qualitatively understood to result from the competition of interfacial energy and lattice mismatch (strain energy) between the growing material (2D MoS<sub>2</sub>) and its substrate (2D WS<sub>2</sub>). The 2D MoS<sub>2</sub>/WS<sub>2</sub> interface with horizontal 2D layers is expected to have a lower interfacial energy than that with vertical 2D layers owing to the very small lattice mismatch of ∼0.25% (in-plane lattice for MoS<sub>2</sub> is \(a = 0.3161\) nm and that for WS<sub>2</sub> is \(a = 0.3153\) nm).\(^{[54,55]}\) Moreover, the horizontal/horizontal interface coherency advantage is anticipated to be small due to the weak vdW bonding present across the interface and the clean basal plane of 2D WS<sub>2</sub> layers without significant dangling bonds. Accordingly, the 2D MoS<sub>2</sub>/WS<sub>2</sub> interface with horizontal 2D layers is thermodynamically favored over that with vertical 2D MoS<sub>2</sub> layers whose formation is driven by strain energy relaxation. With increasing physical confinement, the coherency of 2D MoS<sub>2</sub> layers with the epitaxial 2D WS<sub>2</sub> layer breaks down. The transition of the layer orientation in 2D MoS<sub>2</sub> is akin to the SK thin film growth mode in which strain energy dominates (owing to the epitaxial lattice misfit) for thicker layers.\(^{[56]}\) Accordingly, the relaxation of the strain energy built up during 2D layers growth guides their orientation and determines the growth mode, which is dictated by the thickness of Mo (thus, 2D MoS<sub>2</sub> layer number) as verified below. It is noteworthy that the vertical 2D MoS<sub>2</sub> layers exposing dangling bonds present larger surface energy than horizontal 2D MoS<sub>2</sub> layers, as demonstrated by density functional theory calculations.\(^{[57,58]}\) The horizontal-to-vertical transition of 2D layer orientations efficiently compensates for the increased surface energy by relaxing the generated strain energy, thus lowers the total system energy.

To further investigate the exclusive role of the strain energy in determining 2D layer growth mode, we performed MD simulations using reactive force field (ReaxFF) potential, a general force field that can describe bond-breaking events\(^{[59]}\) and has been adopted to describe the various mechanical properties of 2D MoS<sub>2</sub> layers.\(^{[60,61]}\) Since it is technically challenging to directly simulate the growth event of 2D MoS<sub>2</sub> layers with identical experimental conditions, we performed nonequilibrium MD simulations by introducing protocols to mimic the strain imposed by the sulfurization of Mo. We first identified how pristine 2D MoS<sub>2</sub> in the form of single and multilayers rearrange
their layer orientations under lateral strain. Figure 4a–c compares the morphologies of 2D MoS₂ layers in pristine states (top panels) and under lateral strain (bottom panels). Consistent with previous experiments and calculations,[62,63] 2D MoS₂ layers can bear a large degree of mechanical flexibility/bendability under lateral strain, particularly, for the hexalayers (Figure 4c). This finding indicates that deformed 2D MoS₂ multilayers do not suffer from the weakening of vdW interaction across their basal planes once they are formed. Accordingly, they are not easily separable under externally exerted lateral strain, but rearrange their layer orientations. In addition, deformed 2D MoS₂ layers possess energy penalties of several hundred kcal per mole compared to the horizontal 2D layers in pristine states. This trend becomes more pronounced with increasing physical confinement against the rearrangement of 2D MoS₂ layers such as when they are grown from Mo nanoparticles of high densities. In Figure 4d, MD simulations were performed by exerting lateral strain to multiple 2D MoS₂ layers, which describes their initial growth stage in the physically confined environment (corresponding to Figure 3d). Upon increasing lateral strain, the 2D MoS₂ layers initially in a horizontal orientation start to readjust their layer orientations to relieve the exerted strain. Due to the intrinsically high flexibility (Figure 4a–c), they can easily bend while maintaining interlayer vdW bonds. Upon continued growth, the layers reach a certain curvature limit by being pushed together and rotate along the direction perpendicular to the initial strain orientation. As a result, initially, two separated quadlayers stick together to form one bundle of vertically reoriented octalayers. Figure 4e illustrates the MD simulation results performed for 2D MoS₂ layers of larger layer numbers, describing the structural rearrangement of initially horizontal 2D MoS₂ octalayers upon increasing strain. Although the layers do not completely rotate in the vertical orientation, they prefer to be realigned perpendicular to the direction of the exerted strain forming obliquely oriented layers, consistent with Figure 2i. To compare the growth characteristics of 2D MoS₂ layers with less physical confinement (corresponding to Figure 3c), we also simulated the structural configuration of isolated horizontal monolayers under lateral strain (Figure 4f). Once the initially separated two monolayers impinge upon each other, they become slightly deflected to relieve the strain accompanying the slip of one layer on the other rather than rotating layer orientations. Subsequently, they form horizontally oriented bi-layers and this event continuously happens on the numerous nucleation sites (Mo nanoparticles) filling the free volume in between them. As a result, horizontally oriented 2D MoS₂ multilayers are grown (corresponding to Figure 2b–e). Detailed simulation conditions are given in the Experimental Section in the Supporting Information.

Furthermore, we experimentally evidenced the presence of the local strain in 2D MoS₂ layers in a horizontal-to-vertical transition by applying TEM geometric phase analysis (GPA) map, a phase shift analysis of lattice fringes.[64] GPA quantifies and maps strain fields from high-resolution TEM/STEM images by describing how the lattice fringes of the images vary across their fields of view. Figure 4g,h presents the TEM GPA analysis and their methodological details are provided in the Experimental Section in the Supporting Information. Figure 4g shows a representative ADF STEM image used for the GPA mapping and Figure 4h presents the strain map corresponding to the red box in Figure 4g. The yellow dotted lines in both the images represent the 2D MoS₂/WS₂ interfaces and
the false colors in the image quantify the strain field (shear strain, $\varepsilon_{xy}$ in this case) with respect to a reference orientation. The strain map image clearly reveals that the 2D MoS$_2$ layers in a horizontal-to-vertical transition exert a significant amount of local strain, denoted by the varying colors. In contrast, the WO$_3$ and 2D WS$_2$ layer regimes exhibit uniform color distributions except for their interfaces, further rendering good agreement with the MD simulation analysis. The GPA strain maps for $\varepsilon_{xx}$ and $\varepsilon_{yy}$ corresponding to Figure 4g are presented in Figure S4 (Supporting Information) and those for the plane view of vertically aligned 2D MoS$_2$ layers are provided in Figure S5 (Supporting Information). While previous studies suggest a possibility of internal strain on influencing 2D layer growth characteristics,[10] we emphasize that the present study theoretically and experimentally clarifies and quantifies its exclusive role in dictating 2D layer orientation, which can be generalized to the growth of 2D vdW heterostructures as well.

Lastly, we provide a detailed discussion on the growth characteristics of vertically aligned 2D MoS$_2$ layers in vdW heterostructures. Although the “bottom-to-top” layer growth dominantly occurs (Figure 3d), we note that a more comprehensive picture of vertically aligned 2D layer growth can be obtained by considering two competing kinetic factors, i.e., sulfuration kinetics of deposited metals versus growth kinetics of 2D layers driven by the metal (Mo)-substrate interfacial energy. This consideration suggests that 2D layer growths can also initiate via the sulfuration of Mo films from their “top” surface as far as their thickness is large enough. In this case, the sulfuration kinetics on the film surface (V–S interface) locally dominates the growth kinetics on the growth substrate (S–S interface). In order to verify this hypothesis, we carefully examined the morphologies of vertically aligned 2D MoS$_2$ layers in vdW heterostructures, particularly by focusing on the 2D layers exposed on the top surface. We typically observe that the vertically aligned 2D MoS$_2$ layers of relatively small thickness exhibit the “open-end” 2D edges where their vertical alignment is well retained all the way to the top surface (Figure 5a, yellow box). This observation indicates the dominance of 2D layer growth kinetics over the sulfuration kinetics on the surface, confirming the “bottom-to-top” growth fashion. Meanwhile, the vertically aligned 2D MoS$_2$ layers of relatively large thickness (prepared from thick Mo) exhibit 2D layers of random orientations with respect to the vertical alignment, typically localized on the top surface (Figure 5b, yellow box). This observation indicates that 2D MoS$_2$ layers were additionally grown through the sulfuration initiating from the top surface. We further confirm the generality of this film-thickness-dependent distinguishable growth fashion by carrying out the growth and TEM cross-sectional characterizations of 2D MoS$_2$ layers vertically grown on SiO$_2$/Si substrates. The vertically aligned 2D MoS$_2$ layers of relatively small thickness exhibit the “open-end” 2D edges on the surface (Figure 5c, red box), confirming the dominance of the “bottom-to-top” layer growth. Meanwhile, the vertically aligned 2D layers of relatively large thickness contain randomly oriented 2D layers on the surface, suggesting the dominance of surface sulfuration (Figure 5d, red box).

In conclusion, by employing single-crystalline WO$_3$ nanowires as a model system, we investigated the CVD growth mechanism of 2D MoS$_2$/WS$_2$ vdW vertical stacks with controlled layer orientations. We identified that their growth characteristics transit from 2D/2D layer-by-layer horizontal epitaxy to 3D-like vertical SK mode, which strongly depends on the number of 2D MoS$_2$ layers. MD simulations combined with TEM strain map analysis reveal that the internal strain developed during 2D layers growth dictates the growth mode variation. This study greatly deepens our understanding on the growth principle of 2D vdW solids and has an important implication for their technological developments.

Supporting Information
Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest
The authors declare no conflict of interest.