

## Identifying and Engineering the Stacking Sequence in CVD Grown Few-layer MoS<sub>2</sub> via Aberration-corrected STEM

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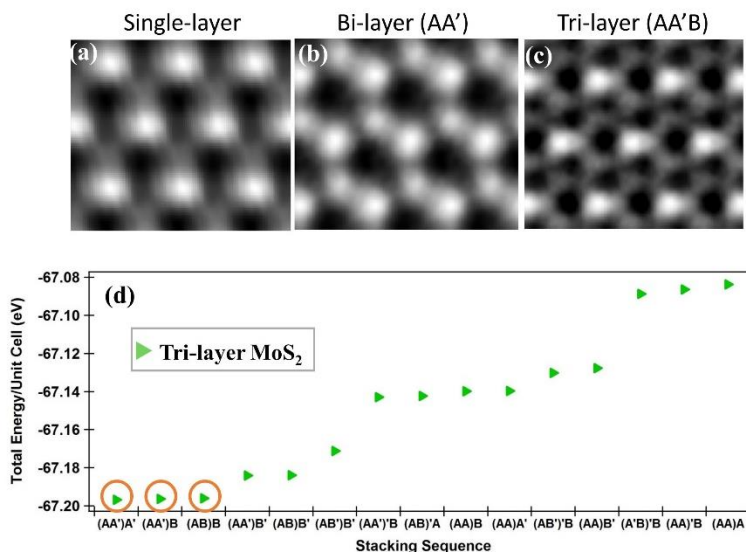
As a promising candidate for the next-generation electronics, large-scale single- and few-layer MoS<sub>2</sub> grown by chemical vapor deposition (CVD) method is an important advancement towards the technological implementation of this material [1][2]. However, compared to exfoliated MoS<sub>2</sub>, CVD grown few-layer MoS<sub>2</sub> often exhibits mixed stacking sequences. These different stacking sequences can significantly impact the electronic and optical properties of MoS<sub>2</sub>, and are presumably caused by the high-temperature growth condition of CVD method. Here, we report the preferred intrinsic stacking sequence in CVD grown few-layer MoS<sub>2</sub> identified by annular-dark-field (ADF) imaging in an aberration-corrected scanning transmission electron microscope (AC-STEM) operated at an ultra-low voltage—50 keV. We then use a combined *in-situ* AC-STEM setup to study the stacking sequence evolution of few-layer MoS<sub>2</sub> under synergistic thermal effect and electron irradiation to unravel the role of high temperature in the final stacking sequence.

To probe the intrinsic stacking sequence in CVD grown MoS<sub>2</sub>, low-voltage STEM imaging is an ideal tool. Considering the threshold for S vacancy formation in single-layer MoS<sub>2</sub>—80keV [3], the low operation voltage—50 keV enables the extensive imaging of atomically thin MoS<sub>2</sub> without introducing significant structural damage. Figures 1a-c show the experimentally obtained STEM ADF images of CVD grown 1-, 2-, and 3-layer MoS<sub>2</sub>. By comparing to simulated STEM ADF images based on known stacking sequences, we identify the structure for 1-layer MoS<sub>2</sub> is H phase, and the stacking sequence for 2-layer MoS<sub>2</sub> is AA', corresponding to 2H phase. We find 3-layer MoS<sub>2</sub> has a preferred stacking sequence of AA'B, which is a mixed phase of 2H and 3R. First-principles calculations reveal that the mixed phase is among the most stable stacking sequences in 3-layer MoS<sub>2</sub> (fig. 1d) [4].

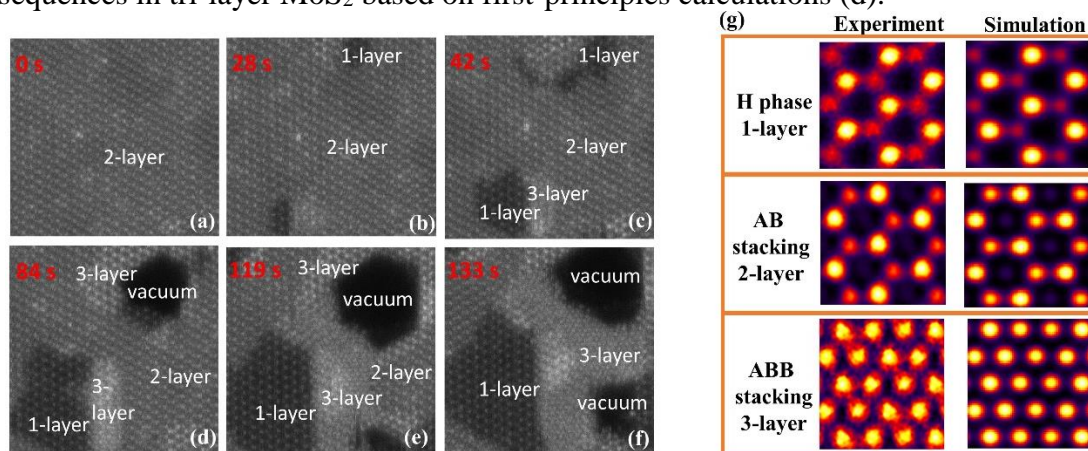
To understand how the growth temperature affects the final stacking sequence in CVD grown MoS<sub>2</sub>, we study the stacking sequence evolution in few-layer MoS<sub>2</sub> while it is *in-situ* heated at different temperatures and imaged by a higher-voltage electron beam (80keV). In this experiment, we start with AB stacked bilayer MoS<sub>2</sub>, the 80 keV electron beam knocks out one layer of MoS<sub>2</sub> atom-by-atom and leaves the H-phase single-layer MoS<sub>2</sub> behind. The evaporated Mo and S atoms redeposit onto the neighboring AB-stacked bilayer MoS<sub>2</sub> and form trilayer MoS<sub>2</sub> with different stacking sequences at different temperatures (Figs. 2 a-f). We find redeposited trilayer MoS<sub>2</sub> at 600°C shows a preferred stacking sequence ABB (corresponding to 3R phase, Fig. 2g), and a high-energy defective ABC' stacking at 700°C. Our study suggests that high temperature plays an important role in determining the stacking sequence in synthesized few-layer MoS<sub>2</sub>.

References:

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- [2] A. M. van der Zande *et al.*, Nat. Mater. **12** (2013), p.554.
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**Figure 1.** Experimental atomic-resolution STEM ADF images of single-layer (H phase), bi-layer (AA' stacking) and tri-layer (AA'B stacking) CVD grown MoS<sub>2</sub> (a-c, respectively), and stability of different stacking sequences in tri-layer MoS<sub>2</sub> based on first-principles calculations (d).



**Figure 2.** The evolution of stacking sequence in few-layer MoS<sub>2</sub> while *in-situ* heated at 600 °C inside STEM. (a)-(f), Time-series STEM ADF images of bilayer MoS<sub>2</sub> under the synergistic thermal effect and irradiation. Redeposited trilayer MoS<sub>2</sub> shows a preferred stacking sequence ABB, which corresponds to 3R phase. (g) identifying the stacking sequence in 1-, 2- and 3-layer MoS<sub>2</sub> by comparison between the experimental and simulated STEM ADF images.