doi:10.1017/S1431927618008322
Microsc. Microanal. 24 (Suppl 1), 2018

Atomistic Insights into Thermolysis and Growth of Two-Dimensional MoS_2 Using *In situ* Electron Microscopy

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Understanding growth mechanisms at atomic resolution is critical for the tailored synthesis of two-dimensional (2D) materials. While the formation of 2D transition metal dichalcogenides (TMDs) through the thermal decomposition (thermolysis) of chemical precursors has been reported in the literature [1-3], *in situ* observation of the of the processes associated with the decomposition and growth at atomic level has not yet been attained. The potential to synthesize large area, 2D TMDs using spin coating and thermal annealing requires greater understanding of how heating parameters, the growth substrate, and precursor morphologies influence the resulting grain size, average layer number, and defect type and concentration of the 2D TMDs formed from thermolysis.

Here, *in situ* transmission electron microscopy (TEM) and *in situ* scanning transmission electron microscopy (STEM) were used to directly observe the dynamic processes involved in forming 2D MoS_2 at atomic resolution during thermolysis from an ammonium thiomolybdate $(NH_4)_2MoS_4$ precursor at elevated temperature. A Nion UltraSTEM 100 operated at 100 kV was used for the *in situ* experiments, which was equipped with a Protochips Fusion heating holder. A 0.1% wt. $(NH_4)_2MoS_4$ solution in dimethylformamide was drop-cast onto the Protochips heating chips and dried. The as-deposited precursor displayed different morphologies, such as thin clusters (Fig. 1a) or large, thick plates (Fig. 1b). Heating to 300 °C led to thermal decomposition of the precursor and formation of monolayer MoS_2 flakes. Depending on the initial precursor morphology, the resulting MoS_2 grains showed drastically different shapes. Isolated islands formed on the carbon substrate from areas with a thin layer of precursor (Fig. 1c). A comparison between the contrast of the atoms within the islands and single Mo atoms confirmed that the islands were monolayer MoS_2 flakes. On the other hand, for thicker precursor regions, large monolayer flakes formed along the edges of the thick precursor plate. The Mo and S atoms are expected to diffuse off those edges on the carbon substrate, leading to a morphology similar to diffusion limited dendritic growth. It was observed that the grain size increased as the heating temperature increased. At 600°C, merging of grains was captured during *in situ* TEM as shown in Fig. 2, where the grain indicated by the white arrow moved toward the two grains indicated by cyan arrows. *In situ* microscopy provided atomic-level insights on the growth mechanism during thermolysis to form 2D MoS_2. The influence of the initial precursor morphology, the growth substrate, and temperature will be presented [4].

References:

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[4] Research supported by Oak Ridge National Laboratory's Center for Nanophase Materials Sciences (CNMS), a U.S. Department of Energy Office of Science User Facility. The synthesis science was supported by Materials Sciences and Engineering Division, Office of Basic Energy Sciences, U.S. Department of Energy.

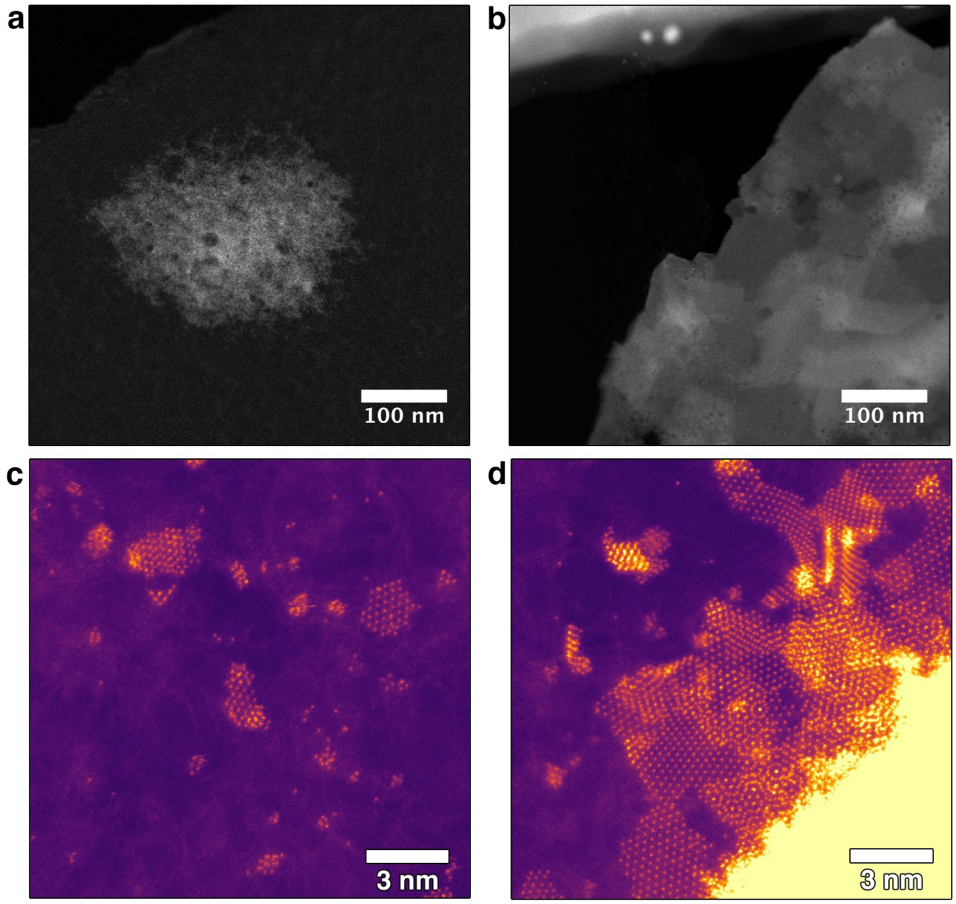

Figure 1. STEM images acquired from (a) thin 0.1% wt. $(NH_4)_2MoS_4$ precursor cluster on amorphous carbon substrate and (b) thick precursor plate on carbon substrate. (c) Faceted monolayer MoS_2 islands after heating at 300 °C from dilute precursor area. (d) Formation of 2D MoS_2 flakes along edge of thick precursor after heating at 300 °C.

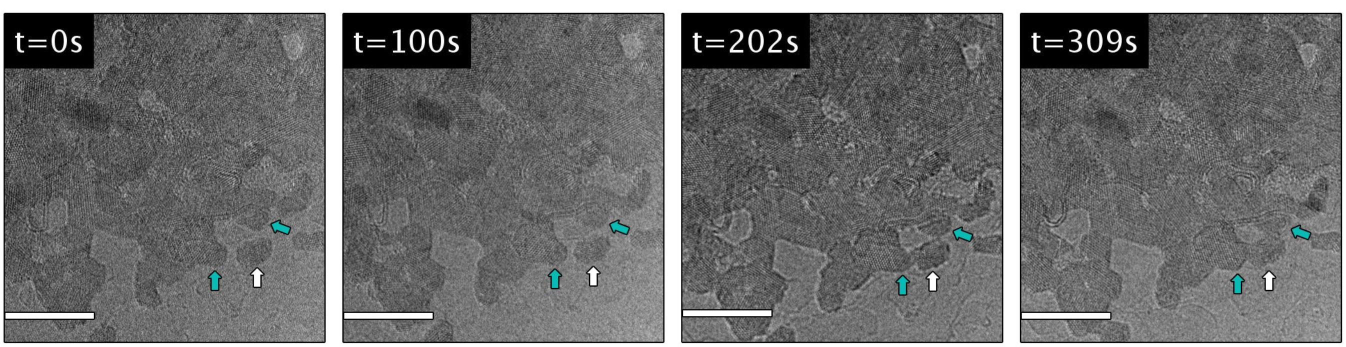

Figure 2. TEM images acquired from same area at different times showing grain growth of monolayer MoS_2. Grain indicated by white arrow gradually moves toward two grains indicated by cyan arrows. Scale bars are 10 nm.

https://doi.org/10.1017/S1431927618008322 Published online by Cambridge University Press