Limiting Domain Size of MoS_2: Effects of Stoichiometry and Oxygen

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Supporting Information

S1. TEM Post-processing Details

TEM micrographs were processed using a custom MATLAB algorithm to identify the locations and orientations of the MoS_2 crystals with the challenge of being able to distinguish their particular scattering intensity from the background of the contrast caused by the crystalline metal grains from the substrate film. The key was using the particular intensity contrast of a single MoS_2 sheet which is relatively dark for the sulfur, brighter for molybdenum, and then dark again for sulfur when viewed edge-on. Stacks of MoS_2 have this intensity repeated for each layer. Image analysis was performed with a series of steps. First the background is removed by subtracting an image created by opening the raw image data with a 15 pixel radius disk. This reduces a portion of the contrast gradient across the image caused by things like sample thickness or metal grain orientation. Then

a successive convolution routine is run. A kernel image is created that has the correct shape and intensity profile to match the TEM contrast for a sheet of MoS_2. A loop convolves the background-corrected TEM data with the kernel as it is rotated in one degree increments. At every pixel the value kept is the maximum convolution value for any of the 180 orientations of the kernel at that point. The idea is that regions without any likeness to a MoS_2 sheet will have a relatively low and constant (as a function of kernel angle) convolution value. Regions with the sheet will show a maximum value for the kernel angle that is best aligned to that particular crystal orientation. This entire convolution routine is run a second time on the output image from the first routine. The second step further sharpens the image created and makes it easier to threshold the output image into a binary image that has values of one wherever there is a MoS_2 sheet and zero everywhere else. That binary image is then analyzed with a MATLAB built-in routine that locates and identifies all consolidated objects. This generates a list of every individual MoS_2 sheet along with the location of the object centroid and the angle the object (assuming an elliptical shape) is rotated relative to the orthogonal frame of the image. The final step of identifying which sheets belonged to the same crystal uses the same centroid location and rotation angle information. A routine was written that compared that information for all individual sheets. Sheets were clustered with the same crystal if they met two criteria: (1) the orthogonal spacing between them had to be less than a distance set to be slightly larger than the interplanar spacing of MoS_2; and (2) there had to be almost the same angle of rotation for each sheet. The output from these processing steps was a list of groups of sheets in the same crystal. From there the analysis could be run to answer what were the average number of layers per crystal and how large were the crystals on average in order to compare those values to the modeling results.

S2. Drag Calculation

Domain growth is slowed by solute-induced drag f and is described by the rate-controlling growth model:[1,2]

$$\frac{dD}{dt} = \frac{A}{D(t)} - f \tag{S1}$$

where $D(t)$ is the time-dependent average domain size, A is the mobility parameter and t is time. Then, assuming a constant drag, $f = A/D_{max}$ where D_{max} is the limiting domain size, and integrating the equation above, we get:

$$\frac{A}{D_{max}^2} \times t = \frac{D(t)}{D_{max}} + \ln \frac{D_{max}}{D_{max} - D(t)} \tag{S2}$$

where the initial domain size is set to zero. This formulation is fit to the average domain size data from simulations to calculate the mobility A for each case, as shown in Fig. S1. The resultant mobility parameters for each case are reported in Table S1. Finally, the constant drag for each case is calculated from $f = A/D_{max}$.

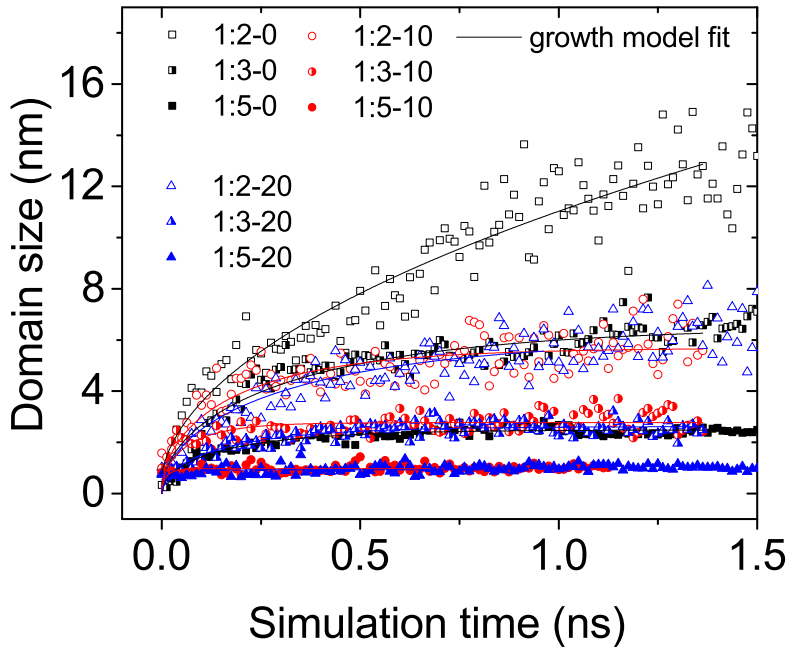

Figure S1: The average domain size as a function of time from simulation (symbols) fit (lines) to calculate mobility and drag.

Table S1: The mobility parameter A extracted from the growth model fitted to simulation data at different conditions. The mobility parameters are reported in nm^2/ns.

	1:2	1:3	1:5
0%	63.9 ± 4.1	35.8 ± 1.6	30.2 ± 1.5
10%	52.2 ± 5.3	35.8 ± 5.5	24.7 ± 13.6
20%	34.4 ± 3.5	13.7 ± 1.1	8.4 ± 2.8

S3. Effective Mo:S ratio with O-containing models

In oxygen-containing systems, some Mo atoms in the amorphous material form oxides or oxysulfides and so are not available to contribute to domain growth. To capture this, an effective Mo:S ratio was calculated by excluding the Mo/S atoms that were part of oxides or oxysulfides in the solute at the steady state. These effective Mo:S ratios are reported in the second column of Table S2, where the error reflects the standard deviation of the effective Mo:S ratio during the last 0.1 ns of the simulation. Next, the no-oxygen cases were used to determine the slope and intercept of a simple linear approximation of the relationship between Mo:S ratio and limiting domain size, as shown in Fig. S2. Finally, the error-weighted, best-fit line from the no-oxygen cases was used to predict the domain size for the oxygen-containing cases based on their effective Mo:S ratio. The simulation data for the no-oxygen cases with their linear fit and the predicted limiting domain sizes for the oxygen-containing cases are shown in Fig. S2. The actual and predicted limiting domain sizes for the oxygen-containing cases are shown in the right two columns of Table S2. The error for the predicted domain sizes was calculated from the error of the simulation domain size of no-oxygen cases.

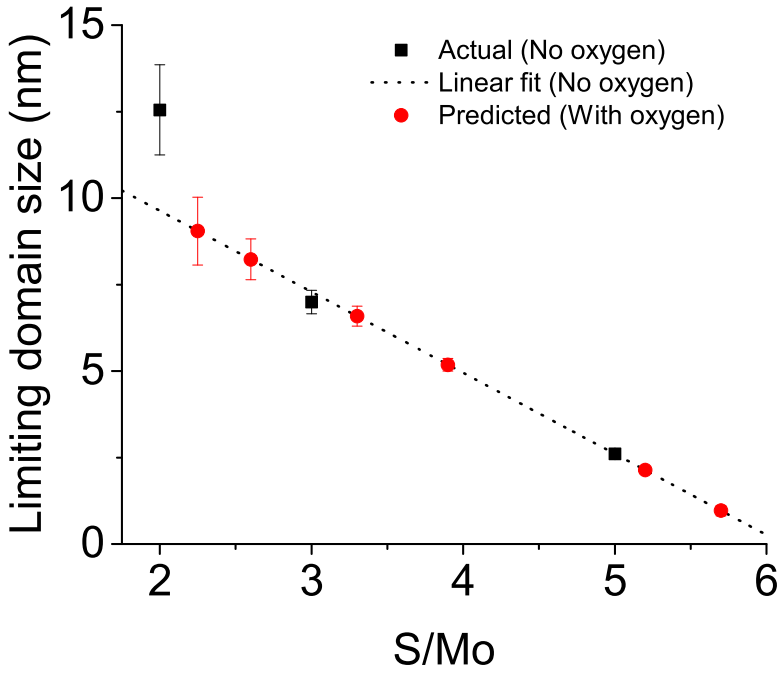

Figure S2: The limiting domain size for the no-oxygen cases (black squares) and their linear fit (dashed black line) and the predicted limiting domain size of the oxygen-containing cases calculated from the effective Mo:S ratio and the linear fit to the no-oxygen data. Note that the no-oxygen data fitting process was error-weighted so the limiting domain size at S/Mo=2 with the largest error affected the fit least.

Table S2: Effective Mo:S ratio for oxygen-containing cases and the limiting domain size (nm) obtained from the simulation and predicted using linear interpolation of the no-oxygen cases.

Initial Mo:S-O%	Effective Mo:S ratio	Simulation domain size	Predicted domain size
1:2-10%	1:2.25 $\pm$ 0.07	5.9 $\pm$ 0.9	9.0 $\pm$ 1.0
1:2-20%	1:2.6 $\pm$ 0.12	6.5 $\pm$ 0.8	8.2 $\pm$ 0.6
1:3-10%	1:3.3 $\pm$ 0.13	2.9 $\pm$ 0.4	6.6 $\pm$ 0.3
1:3-20%	1:3.9 $\pm$ 0.13	2.6 $\pm$ 0.2	5.2 $\pm$ 0.2
1:5-10%	1:5.2 $\pm$ 0.09	1.0 $\pm$ 0.2	2.1 $\pm$ 0.1
1:5-20%	1:5.7 $\pm$ 0.08	1.0 $\pm$ 0.2	1.0 $\pm$ 0.1

References

(1) Burke, J. E. Some factors affecting the rate of grain growth in metals. *Trans. AIME* **1949**, *180*, 73–91.

(2) Michels, A.; Krill, C.; Ehrhardt, H.; Birringer, R.; Wu, D. Modelling the influence of grain-size-dependent solute drag on the kinetics of grain growth in nanocrystalline materials. *Acta Mater.* **1999**, *47*, 2143–2152.