

Supporting Information for:

Topochemistry of Bowtie- and Star-Shaped Metal Dichalcogenide Nanoisland Formation

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Full simulation videos of polycrystal formation

Movies S1 and **S2** show, respectively, full evolution of simulated systems for **Fig. 2f** (bowtie) and **Fig. 2g** (star). In each movie, initial $t = 10$ time units are first shown in slower time and zoomed-in to show island nucleation and collision events in detail, followed by full videos of the entire simulation domain to show the large-scale structure evolution.

Phase field method details

The multi-component phase-field (MPF) model developed by Steinbach and Pezzola³³ served as the backbone in our simulations. Since the original MPF model does not consider the evolution of feedstock for epitaxial growth, here we advance a composite MPF model by augmenting it with the feedstock factor from a phase-field model by Karma and Rappel⁴⁸ where the effects of adsorption and desorption are considered.

The multicomponent phase field model is specified as follows. It starts from a general free energy functional,

$$G = \sum_{\alpha,\beta=1\dots N, \alpha>\beta} \frac{4\sigma_{\alpha\beta}}{\pi^2} \left(-\eta \nabla \phi_\alpha \cdot \nabla \phi_\beta + \frac{\pi^2}{\eta} \phi_\alpha \phi_\beta \right) + \lambda \xi h(\phi_N),$$

where $\sigma_{\alpha\beta}$ is either the grain–grain or grain–substrate interface energy between two phases α and β (GB or edge tension, respectively); η is the interface thickness, and ϕ_α is the order parameter of the α -th phase, where $\alpha = 1\dots(N-1)$ means MX_2 grain and $\alpha = N$ denotes the bare substrate, and we ensure that $0 \leq \phi_\alpha \leq 1$. The interpolation function h takes form of $h(\phi) = 2/\pi(2\phi - 1)[\phi(1 - \phi)]^{1/2} + 1/\pi \arcsin(2\phi - 1)$. The dimensionless supersaturation $\xi = (c_N - c_{eq})/c_s$, where c_N is the feedstock concentration, c_{eq} is the equilibrium value of c_N , and c_s is the nominal concentration of precursor in solid 2D MX_2 , provides the driving force to the grain growth with a coupling constant λ . For example, in the case of MoS_2 grown via sulfurization of MoO_3 on SiO_2 , ξ corresponds to adsorbed MoO_3 , as it is the limiting step of the synthesis.⁶

In the simulation, each MX_2 phase ϕ_α is assigned with a specific grain orientation θ_α . The GB energy is then evaluated as $\sigma_{\alpha\beta} = \sigma_1 |\sin(n\theta_{\alpha\beta})| + \sigma_2 |\sin(n/2\theta_{\alpha\beta})|$ where $n = 3$ so that MX_2 has a 3-

fold symmetry, and $\theta_{\alpha\beta} = |\theta_\alpha - \theta_\beta|$ is the misorientation. With this formulation, $\sigma_{\alpha\beta}$ has a global minimum at $\theta_{\alpha\beta} = 0 + 2\pi m/3$, and a secondary local minimum at $\theta_{\alpha\beta} = \pi/3 + 2\pi m/3$ with m integer. The values of σ_1 and σ_2 are taken to fit the lower bounds of respective GB from DFT calculations²⁵. For grain edges, the interface tension is $\sigma_{aN} = \sigma_0[1 + \delta \cos n(\psi_a - \theta_a)]$ where $\delta = 0.1$, $\sigma_0 = 1$ eV/Å, and ψ_a is the orientation of the edge normal (gradient of φ_a). An extra constraint on the order parameters is that they sum to unity, $\sum_{\alpha=1\dots N} \varphi_\alpha = 1$.

The governing equation for order parameters satisfying the constraint is:³³

$$\dot{\varphi}_\alpha = - \sum_{\beta=1\dots \tilde{N}} \frac{2\pi^2}{8\eta} \cdot \frac{\mu_{\alpha\beta}}{\tilde{N}} \left(\frac{\delta G}{\delta \varphi_\alpha} - \frac{\delta G}{\delta \varphi_\beta} \right)$$

where \tilde{N} is the local number of coexisting phases, and $\mu_{\alpha\beta}$ is the interface mobility. For MoS₂ GBs we set $\mu_{\alpha\beta} = \mu_0(\varphi_N)^{1/2}$ with μ_0 a universal coefficient. This locks the shape of GB upon formation. At free edges the mobility is $\mu_{aN} = \mu_0[1 + 2.5|\cos n(\psi_a - \theta_a)/2|]$. This form is chosen so that kinematic Wulff construction produces an equilateral triangular shape.

The detailed formulation for the evolution of order parameters is given in Ref.⁴⁹ and omitted here for brevity. The evolution of the supersaturation required to solve it is given by:^{48,50,51}

$$\xi = \nabla(D\nabla\xi) - \frac{\dot{\xi}}{\tau_s} + F + \frac{\partial h(\phi_N)}{\partial t}$$

where F is the deposition flux, D is the diffusion coefficient of ξ , and τ_s is the desorption time. With constant F and τ_s the supersaturation at equilibrium will be $\xi_{eq} = F\tau_s$. The diffusion coefficient D is uniform across the substrate surface. Using units of characteristic length l , and time $\tau = l^2 \tilde{D}/D$, we can rewrite the equations with $\tilde{\tau}_s = \tau_s D / (l^2 \tilde{D})$, $\tilde{\mu} = \mu_0 \tilde{D} / D$, $\tilde{\sigma} = \sigma / \sigma_1$, and $\tilde{F} = \tilde{D} l^2 F / D$ as new parameters to obtain a dimensionless system. We solve it in *Matlab* by discretization with a time step of 0.01τ for the order parameters evolution, 0.0007τ for supersaturation evolution, and space grid resolution of l . The boundary conditions are periodic and fast Fourier transform is used as a highly effective way to get field variable derivatives. The initial supersaturation is set to be at equilibrium everywhere, accordingly $F = \xi_{eq} / \tau_s$. Each nucleus starts from a circle with a radius of either $3l$ or $5l$.

Aside from GB energies based on literature DFT values, simulation parameters were determined empirically by tuning to reproduce the features of single-crystalline island growth. Experiment shows that if feedstock concentration is low, nearly perfect triangles grow, while 3-point-stars appear at high concentrations,⁷ which is consistent with onset of diffusion instability. Although the pressure of the feeding gas in experiments can differ by 5 magnitude of order under experimental conditions, computational limitations allow us only to explore the high supersaturation regimes. Thus the equilibrium concentration ξ_{eq} was varied from 0.1 to 0.3 in the simulations. The coupling coefficient was held at a fixed value of $\lambda = 20$ so that only ξ_{eq} determines stability of growth shape. Other parameters are listed in **Table S1**. The results show that by varying ξ_{eq} from low to high, the island shape evolves from a triangle (**Fig. 2c**) to a nonconvex 3-point star (**Fig. 2d**), as seen in experiments.^{6,7}

Table S1. List of parameters for the phase-field simulation. Tildes are omitted for dimensionless parameters.

Parameter	Symbol	Value
<i>GB energy (C₆ term)</i>	σ_1	1 eV/Å
<i>GB energy (C₃ term)</i>	σ_2	0.5 eV/Å
<i>Characteristic length</i>	l	50 nm
<i>Interface thickness</i>	η	$7l$
<i>Coupling coefficient</i>	λ	20
<i>Desorption time</i>	$\tilde{\tau}_s$	2.5
<i>Diffusivity</i>	\tilde{D}	150
<i>Mobility</i>	μ_o	2

Analytical calculation of capillary torque

The result that torque acting upon colliding islands scales as inverse square of the angle can be obtained in the harmonic approximations, assuming that the unit cells of edges are connected one-to-one with finite-range harmonic springs (bonds):

$$\epsilon = \begin{cases} \frac{ky^2}{2}, & 0 \leq y < h \\ \frac{kh^2}{2}, & y \geq h \end{cases}$$

Here, y is the distance from a unit cell on one edge to its counterpart on the other and h is the maximum (breaking) bond length. Integrating ϵ over all such pairs along the edge (as indexed by coordinate x), we get the total energy:

$$E = \int_0^{h \cot(\alpha/2)} \frac{k}{2} \left(2x \sin \frac{\alpha}{2} \right)^2 dx = \frac{2}{3} h^3 k \left(\cos \frac{\alpha}{2} \right)^3 / \sin \frac{\alpha}{2} \approx \frac{4h^3 k}{3\alpha}$$

A similar result is obtained for the Morse potential, $\epsilon = D \left(1 - e^{-y\sqrt{k/2D}} \right)^2 - D$, and integrating in x to infinity:

$$E = \int_0^{+\infty} \left(D \left(1 - e^{-2x \sin \frac{\alpha}{2} \sqrt{k/2D}} \right)^2 - D \right) dx = \frac{3\sqrt{D}}{2\sqrt{2}k \sin \alpha/2} \approx \frac{3\sqrt{D}}{\sqrt{2}k\alpha}$$

In both cases $E \propto 1/\alpha$ and thus the torque $dE/d\alpha \propto 1/\alpha^2$.

The above derivation assumed an infinitely stiff crystal lattice. For very small values of α , local relaxation should create an upper bound on the torque determined by material elasticity.

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