Towards Scalable Epitaxy of Atomically Thin Gallium Selenide on Graphene: A Multiscale DFT-KMC Framework for Optimizing Growth Conditions

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Abstract

The precise engineering of atomically-thin (two-dimensional, 2D) semiconductors requires advanced manufacturing techniques and fundamental understanding of growth processes. Here, we present a multiscale computational study of epitaxy of 2D GaSe on graphene. Our approach combines density functional theory (DFT) calculations with kinetic Monte Carlo (KMC) simulations to explore the growth parameter space and establish quantitative links between atomistic processes and mesoscale growth evolution. DFT is used to determine the energetics governing adsorption, diffusion, nucleation, and interlayer interactions, while KMC simulations capture growth dynamics depending on substrate temperature, Ga and Se fluxes, and the flux ratio (Fig. 1a). This study provides a guide to optimization of experimental growth conditions, scale up, and manufacturing of 2D semiconductors.

For traditional epitaxy of semiconductors, such as silicon, the epitaxial layer interacts covalently with the substrate due to the presence of dangling bonds on its surface, which determine the orientation and atomic lattice of the grown layer. In contrast, van der Waals (vdW) epitaxy involves weak vdW interactions between the substrate and the vdW layer. It can be realized on substrates with passivated dangling bonds or on a vdW layer, like graphene, for growth of different materials without the constraints on lattice matching that applies to traditional epitaxy. Graphene provides an atomically smooth, hexagonal honeycomb lattice surface for growth of individual vdW GaSe layers (Fig. 1b-c).

Our integrated framework (Fig. 1a) for epitaxy of GaSe on graphene enables mapping the probability of growth rate, nucleation density, layer uniformity, and multilayer formation across experimentally relevant conditions, and it reveals the key trade-off features and dependencies between structural quality of the formed material and deposition rate. High temperatures and/or atomic fluxes generally accelerate growth kinetics but tend to degrade film uniformity, whereas more mild growth conditions improve layer control at the expense of throughput, thus highlighting the need for finding balanced growth conditions. By analyzing these competing effects, we identify regimes for high-quality atomically thin GaSe layers in agreement with the experiment (Fig. 1b-c). The KMC simulations identify an optimal parameter window for high-quality 2D GaSe growth on graphene, as required for exploitation of GaSe in nanoelectronics.

At low substrate temperature of 723 K, surface diffusion limited growth produces dendritic GaSe island morphologies. As temperature increases, enhanced surface and edge atom mobility promote the formation of compact triangular GaSe domains. At 1123 K (Fig. 2), high diffusion rates lead predominantly to compact, well-defined islands across a wide range of atomic fluxes. The specific Ga and Se fluxes, and their ratio further regulate the competition between growth rate and structural relaxation. High atomic fluxes increase surface coverage but reduce the effective annealing time, thus promoting dendritic features. Se-rich conditions, however, suppress Ga accumulation and stabilize the 2D growth. Thus, the optimal growth regime corresponds to elevated substrate temperatures combined with Se-rich conditions (Ga/Se < 0.1), as required to compensate for the high volatility of the Se-atoms.

KMC is used to investigate growth rates (Fig. 3), defects and nucleation as a function of the growth parameters. The model predictions are validated by experiments in the literature [2,3,4] and recent data of GaSe growth on scalable graphene by molecular beam epitaxy (Fig. 1b-c). The validated multiscale framework, therefore, provides a predictive and transferable strategy for guiding experimental growth, optimizing process conditions, and accelerating the scale up of 2D GaSe and related multi-layered structures.

References

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Figures

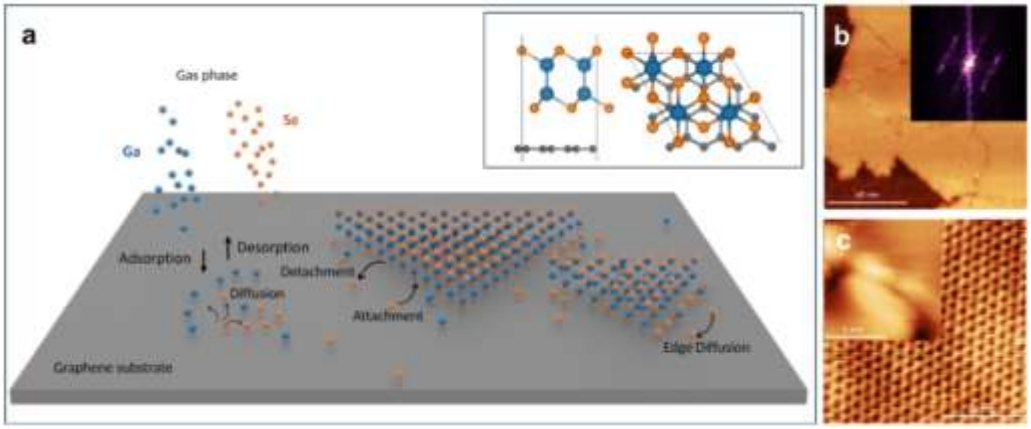

Figure 1. Crystal structure and growth kinetics of 2D GaSe on graphene. (a) Schematic of the kinetic Monte Carlo (KMC) simulation illustrating lattice events during growth, including adsorption, desorption, diffusion, attachment/detachment, and edge diffusion, together with the crystal structure of GaSe on graphene. (b) Scanning tunneling microscopy (STM) image of GaSe grown by molecular beam epitaxy (MBE) on graphene, with the corresponding reflection high-energy electron diffraction (RHEED) pattern shown in the inset. (c) High-resolution STM image revealing the atomic structure of the graphene substrate (main panel) and GaSe (inset).

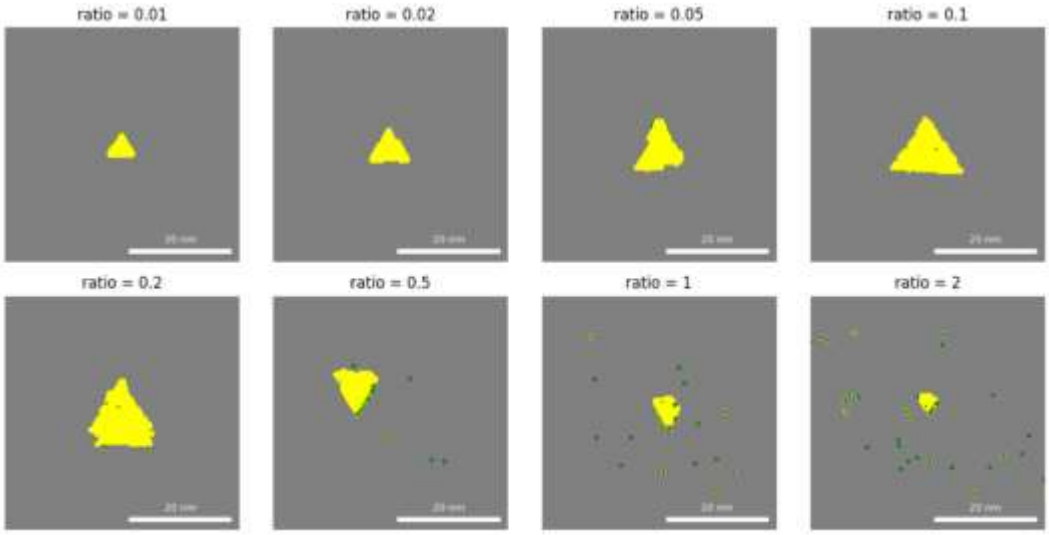

Figure 2. Kinetic Monte Carlo (KMC) simulated GaSe island morphologies at 1123 K across Ga/Se flux ratios ranging from 0.01 to 2. High diffusion rates promote the formation of triangular GaSe islands across a wide range of atomic flux ratios.

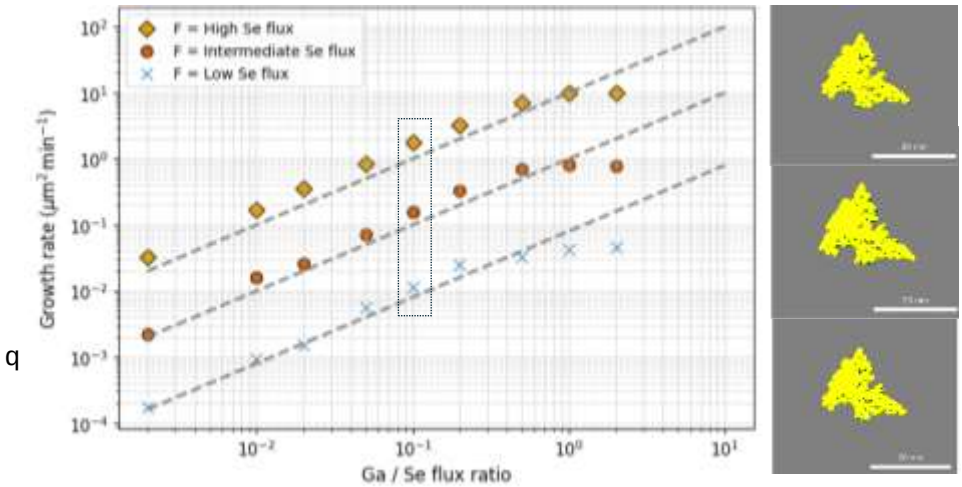

Figure 3. Average GaSe island growth rate as a function of the Ga/Se flux ratio at 723 K for three different Se flux regimes (high, intermediate, and low). The highlighted region marks the selected Ga/Se flux ratio used for the simulated snapshots in the right panels. These show representative simulated GaSe island morphologies at the same temperature and flux ratio with high (top), intermediate (middle) and low (bottom) Se flux.