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Signature of multilayer growth of 2D layered Bi_2Se_3 through heteroatom-assisted step-edge barrier reductionYongsam Kim^{1,4}, Geunsik Lee^{2,4}, Nannan Li², Jikeun Seo³, Kwang S. Kim^{2*} and Namdong Kim^{1*}

During growth of two-dimensional (2D) materials, abrupt growth of multilayers is practically unavoidable even in the case of well-controlled growth. In epitaxial growth of a quintuple-layered Bi_2Se_3 film, we observe that the multilayer growth pattern deduced from in situ x-ray diffraction implies nontrivial interlayer diffusion process. Here we find that an intriguing diffusion process occurs at step edges where a slowly downward-diffusing Se adatom having a high step-edge barrier interacts with a Bi adatom pre-existing at step edges. The Se–Bi interaction lowers the high step-edge barrier of Se adatoms. This drastic reduction of the overall step-edge barrier and hence increased interlayer diffusion modifies the overall growth significantly. Thus, a step-edge barrier reduction mechanism assisted by hetero adatom–adatom interaction could be fairly general in multilayer growth of 2D heteroatomic materials.

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INTRODUCTION

Two-dimensional (2D) layered materials generally have weak van der Waals (vdW) interactions between layers.^{1–4} These systems possess strong anisotropic properties that are exploited to tailor optoelectronic, spintronic, and thermoelectric devices to meet practical requirements.^{5,6} Sizable growth of 2D atomic layers in high quality is required for application and it will be enabled by optimizing the growth kinetic parameters. The overall patterns of simple epitaxial growth have been explained with growth parameters such as interlayer diffusion, terrace diffusion, and 2D nucleation within the framework of the standard kinetic multilayer growth model.^{7–9} During complex layered-material growth, density of mobile atoms is enhanced on the dimensionally reduced surface, especially near steps that occur at the lateral-growth-front of islands on surface. In this situation, a simple hopping model of free adatoms may fail to describe the interlayer diffusion process. In other metal and semiconductor systems, cooperative exchange,^{10,11} kink channel or vacancy diffusion,^{12–14} and surfactant-assisted growth^{15–17} have been proposed to explain similar discrepancies. Moreover, the possible modification of step-edge barrier due to the interaction between heterogeneous adatoms near step edges can be considered.

Here, as a model system of the vdW epitaxial growth, we study Bi_2Se_3 , which is a three-dimensional (3D) topological insulator. Graphene is introduced between the substrate and the thin film as an epitaxial spacer.¹⁸ The graphene layer is most suitable for initial growth because the vdW interaction is weak enough to preserve the inert surface. A quintuple unit of Bi_2Se_3 forms a covalent monolayer (ML), which is also stacked periodically by weak vdW interaction (Fig. 1). According to our in situ x-ray diffraction, Bi_2Se_3 grew in a smooth multilayer pattern that was expected from the weak vdW interaction. In this study, the evolution of the surface morphology will be explored by a kinetic Monte Carlo (KMC) simulation, using inputs from density functional theory (DFT) calculations.^{19–22} Interlayer diffusion processes at step edges are

investigated based on the simplified kinetic multilayer growth model with an additional step-edge barrier.

During multilayer growth, one of the significant factors that determines the film morphology is the additional step-edge barrier ΔE_S or Ehrlich–Schwoebel (ES) barrier, which is the difference between the hopping energy barrier E_D at terraces and E_S at step edges that governs interlayer diffusion (Fig. 1a).^{23,24} Depending on barrier height and growth temperature, different film morphologies develop. High ΔE_S hinders the downward diffusion of adatoms at step edges and leads to rough 3D growth. However, if ΔE_S is small, the adatoms have sufficient thermal energy to overcome the step-edge barrier, so layer-by-layer (LBL) growth occurs and smooth surfaces are obtained.

RESULTS

We performed DFT calculations to find the most stable adsorption sites of adatoms and the hopping energy barriers (Fig. 1; see Supplementary information for details of calculation).³ Atomic positions of two top-surface-layers and edge-nearby atoms are fully relaxed. For a Bi atom adsorption on terrace, two stable configurations are identified as a metastable one with an adsorption energy $E_{\text{ad}} = -1.28$ eV at a bridge site of Se–Se and the most stable one with $E_{\text{ad}}^{(\text{Bi})} = -1.50$ eV. For a Se atom, only one stable configuration is found with $E_{\text{ad}}^{(\text{Se})} = -2.07$ eV (see Supplementary information for details). The transition energy barrier of the Bi adatom from the metastable to the most stable configuration is as small as 0.10 eV from the nudged elastic band (NEB) method calculation.²⁵ Although these are obtained from the 2D slab model, we obtained nearly the same results by using the ribbon model shown in Fig. 1b, that is, Fig. 1d(i) or (ii) for Bi, Fig. 1e (i) or (ii) for Se.

Migration of the adatoms can be described as a sequence of random hops on a periodic lattice with the binding sites. Transition state theory^{26–29} suggests that the activation energies for individual hops are determined by energy differences between

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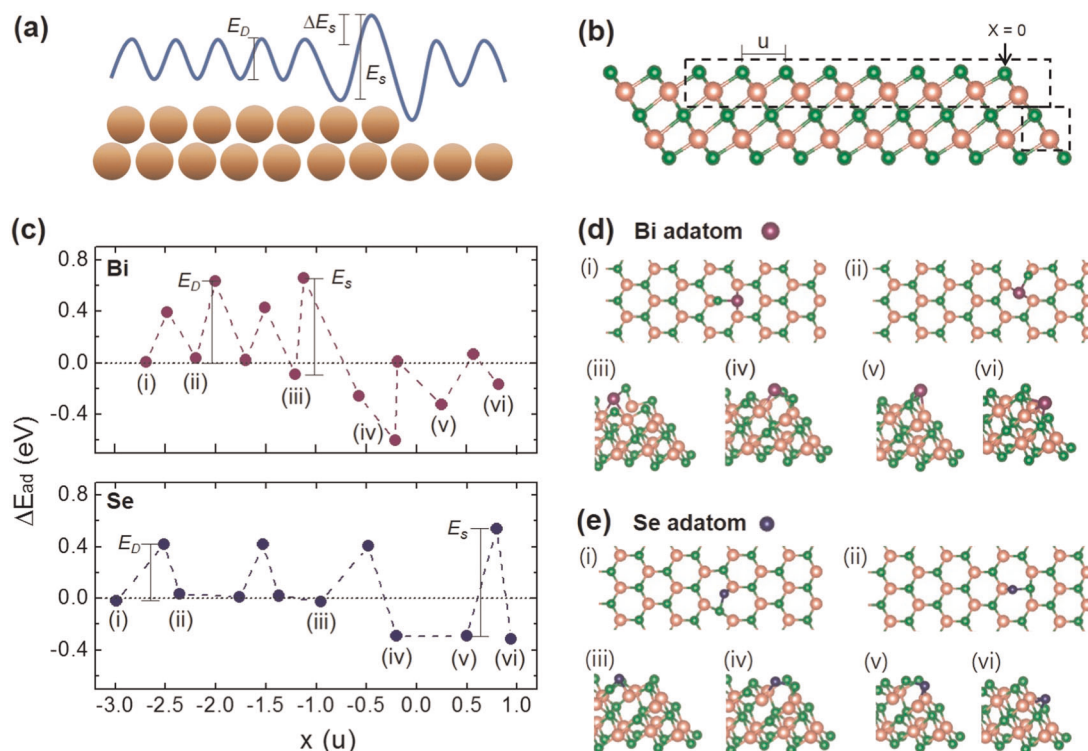


Fig. 1 Step-edge barrier. **a** Schematic of energy barriers for usual metallic surface. **b** Atomic model of Bi_2Se_3 as a quintuple unit composed of five atomic layers. The dashed rectangles indicate the surface and edge-nearby atoms to be optimized in DFT calculation. **c** Potential energy landscape for the diffusion path displayed by using relative adsorption energies ΔE_{ad} . E_D is 0.64 eV for Bi and 0.41 eV for Se, and $\Delta E_S \approx E_S - E_D$ is 0.11 eV for Bi and 0.42 eV for Se (u : lattice unit). **d, e** The most stable adsorption sites of Bi and Se adatoms. The calculated geometry of the Bi_2Se_3 with an adatom. Surface diffusion processes of Bi and Se adatoms on Bi_2Se_3 surface toward a step edge ($X = 0$) located at the right side.

the binding and the transition sites. Based on the potential energy landscape obtained from the most stable buckled geometry, the terrace hopping barrier calculated by the 2D slab model is $E_D = 0.64$ eV for Bi and 0.41 eV for Se adatoms. Actually this barrier corresponds to the energy cost to partially break the Bi–Bi or Se–Se bonds. The step-edge barriers E_S are calculated using our ribbon model (Fig. 1b; see Supplementary information). Each adatom migrates toward the step edge ($X = 0$) from the inner site ($X = -3$ lattice units) where the hopping barriers are close to those calculated for the terrace. The relative adsorption energies ΔE_{ad} of Bi and Se diffusing across the edge become higher than E_D , i.e., $E_S = 0.75$ eV for Bi and 0.83 eV for Se (Fig. 1c). Additional step-edge barriers^{3,23,24,30} $\Delta E_S \approx E_S - E_D$, are as large as 0.11 eV for Bi and 0.42 eV for Se. In this situation, the interlayer diffusion of Se adatoms would be a rate-determining process.

Our DFT calculations yielded the most important hopping barriers on terrace E_D and step edges E_S . These two barriers were then used in the construction of the KMC simulation model to simulate growth processes. In the LBL growth regime of a 2D layered material, i.e., the highly diffusive regime of $D/a^4F \sim 10^8 - 10^{10}$ (D : diffusion coefficient, F : deposition rate, a : lattice constant), we performed KMC simulations with various parameters to reproduce the film growth pattern. The simulation was simplified by assuming that a unit layer on a hexagonal lattice has not a quintuple unit of five atomic layers but monoatomic height with a single species.^{19–22} In the KMC code, the surface hopping barrier of an adatom is fixed at $E_D = 0.4$ eV, and the simulations were performed for various ΔE_S to trigger the rate at which atoms cross over step edges into the next lower level. Other periphery diffusions of adatom at island edges were prescribed to produce the triangular islands observed experimentally. At $T = 500$ K, simulation with $\Delta E_S = 0.1$ eV yielded LBL growth, whereas simulation with $\Delta E_S = 0.4$ eV yielded a 3D multilayer pattern

(Fig. 2a). When we used the higher barrier $\Delta E_S^{\text{(DFT)}} = 0.42$ eV for Se adatoms as the effective step-edge barrier, the film would grow in the form of strong 3D multilayer according to the simulation (Fig. 2b). However, this is unlike the actual case of smooth multilayer growth. This morphological discrepancy was pronounced in the results of x-ray diffraction below.

To examine the layer distribution in detail, in situ x-ray scattering was performed. We grew Bi_2Se_3 films epitaxially by thermal evaporation at varying deposition rates R_n and growth temperatures T under ultrahigh vacuum.¹⁸ The film growth was performed typically at a relatively slow $R_n < 0.001$ ML s^{-1} . During the film growth, we measured x-ray intensity (Fig. 3a) at an anti-Bragg point at moderate growth temperatures (420–560 K). The observed x-ray intensity was normalized by the initial intensity scattered before the deposition. After the deposition started, the intensity increased up to the high level as much as the first layer is grown. The oscillating anti-Bragg intensity indicates nearly-LBL growth, which is sensitive to morphological changes. Using a simple distributed growth model,^{31,32} we fit the data and extracted the coverage θ_n of each layer as a function of time.

From the anti-Bragg oscillation, the layer coverages can be retrieved based on a simple rate equation for the coverage change of the n th layer given by a diffusion equation in the Experimental section (see also Supplementary information). Several analytical fitting models have been developed; they differ in the kinetic parameters used to control the growth, which provide additional information as a result of fitting. We used the Cohen's model, which is a mean-field model that describes morphological evolution during thin film growth.³³ The fitting routine that uses the Cohen's model has been applied successfully to simulate the growth of organic film.³¹

Our experimental anti-Bragg oscillations I_{AB} (Fig. 3a) were fitted using a_n and $\theta_n(t)$. The effective distribution of the layer coverage

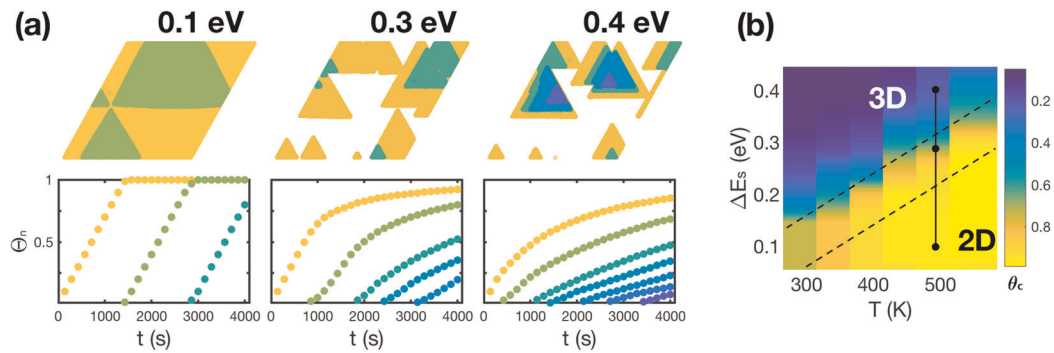


Fig. 2 KMC simulation. **a** The KMC simulation of growth for ES barriers $\Delta E_S = 0.1, 0.3,$ and 0.4 eV. $E_D = 0.4$ eV is used according to the DFT calculation. Experimental temperature $T = 500$ K and deposition rate $R_n = 0.0007$ ML s^{-1} were fixed. The simulated area is a 600×600 lattice. **b** Phase diagram of ΔE_S vs T , KMC suggests that 2D and 3D growth separated gradually. Region between dashed lines: smooth multilayer growth. θ_c : critical coverage at which a new layer starts to form.

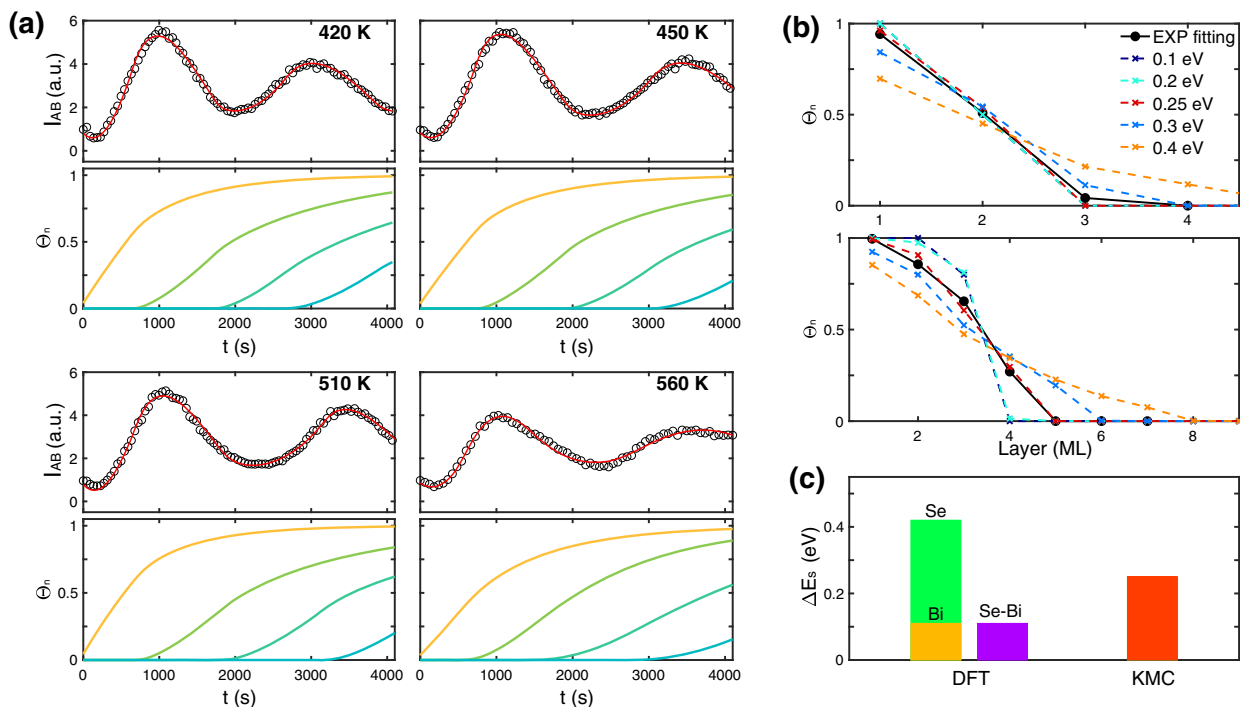


Fig. 3 Anti-Bragg oscillations. **a** Anti-Bragg oscillations (open circles) measured at an anti-Bragg $(00\bar{3})$ position during growth at different temperatures. The layer coverages as a function of the growth time are recovered from the fitting; red curves are best-fits. **b** Experimental layer coverage (black solid line) obtained from anti-Bragg oscillations for total coverage of 1.5 and 2.8 ML, compared with layer profiles (dotted lines) produced by KMC simulations with various ES barriers. **c** The DFT calculations ($\Delta E_S^{(DFT)}$) for ES barriers of single species are much different from the result of the KMC simulation ($\Delta E_S^{(KMC)}$). The DFT barrier for Se–Bi will be discussed in Fig. 4.

$\theta_n(t)$ was deduced from the anti-Bragg fits. Indeed, the $\theta_n(t)$ in Fig. 3a reveals that Bi_2Se_3 film grows rather in smooth multilayers. Furthermore, θ_n from the anti-Bragg fit indicates that the effective ES barrier should be $\Delta E_S^{(KMC)} \sim 0.25$ eV by comparison with the simulated layer coverage profiles (Fig. 3b). Even if the layer coverage profile looks quite similar to the case of $\Delta E_S^{(KMC)} = 0.25$ eV, the effective $\Delta E_S^{(KMC)}$ is much different from $\Delta E_S^{(DFT)} = 0.42$ eV from the DFT calculation.

DISCUSSION

We now discuss the cause of discrepancy of the above DFT calculation from the effective barrier $\Delta E_S^{(KMC)}$. Most effectively, single adatoms were assumed to diffuse on surfaces by simple hopping from one favorable adsorption site to the next on top of

an atomic terrace.^{20,21} However, this simple model fails to describe the interlayer diffusion process in our heteroatomic vdW system. Some nontrivial diffusion processes such as exchange processes, surfactants, and downhill diffusions through kink channel or vacancy, might be taken into account as a cause to reduce the energy barriers.^{10–17} However, such processes seem to be inapplicable to our system because it possesses quintuple-layered steps that are much different from the usual monoatomic height steps. The relatively wide facet area, at which step edges form, consists of heteroatomic alternating stacked layers. A new diffusion process associated with such a structural feature might be required in order to account for the discrepancy. An adatom that arrives at a laterally growing facet may encounter pre-existing isolated adatoms at step edges. As a secondary process at step edges, a diffusion process that is characterized by the

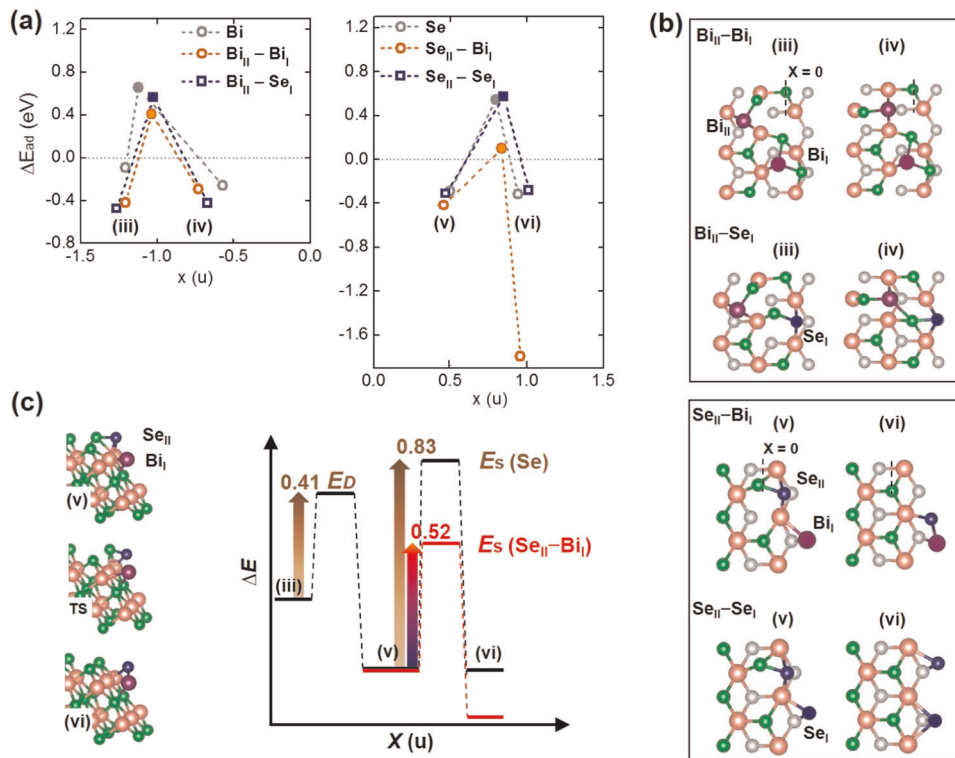


Fig. 4 Adatom–adatom interaction. **a** Edge barrier variation for the diffusion of the second Bi_{II} and the second Se_{II} adatom interacting with already-present adsorbed Bi_I or Se_I adatom nearby (orange circle, blue square); single-adatom edge barrier without adatom–adatom interaction for comparison (gray circle). **b** Initial and final atomic structures for each case, with step edges located at $X = 0$. **c** Diffusion process of Se_{II} adatom interacting with Bi_I adatom at step sides. TS denotes transition state. The step-edge barrier for Se_{II} adatom is reduced significantly by ~ 0.3 eV compared with single-adatom diffusion so that the reduced ES barrier becomes $\Delta E_S \sim 0.1$ eV.

heteroatomic interaction between Se and Bi adatoms at step edges might reduce the additional step-edge barrier of $\Delta E_S^{(\text{Se})} = 0.42$ eV (Fig. 4). In such a process, the Se–Bi adatom interaction would have an important function in crossing over steps. Among various dynamical processes at steps, the most plausible situation would be that a Se adatom approaching a step edge encounters a pre-existing Bi adatom at the step, or vice versa. Indeed, incoming Se adatoms experience a much-reduced ES barrier down to 0.1 eV ($\Delta E_S^{(\text{Se})} \sim 0.1$ eV) compared to the case of single-adatom diffusion (Fig. 4). A Se adatom diffuses down over the step-edge barrier as easily as if no additional barriers exist. The reduced step-edge barrier affects overall growth pattern significantly. No proper growth model for such heteroatomic systems has been developed so far. However, our DFT result in Fig. 4 emphasizes that the interaction between two heteroatomic species could lower the step-edge barrier. Thus, the heteroatom-assisted reduction of step-edge barrier is strongly reliable for a possible mechanism.

In summary, we performed in situ x-ray scattering to study the growth kinetics of layered Bi₂Se₃ film. The x-ray intensity at an anti-Bragg position was fitted using the Cohen's model to obtain kinetic parameters, which reveals an effective step-edge barrier through KMC simulations. Among the step-edge barriers of each diffusing species, large ES barriers should be effectively reduced down to the level of $\Delta E_S^{(\text{KMC})} \sim 0.25$ eV. The heteroatom-assisted reduction of step-edge barrier drastically modifies the overall growth mechanism for 2D heteroatomic materials. Adatom–adatom interaction may sufficiently reduce high barriers at step edges and such a reduction leads easily to the LBL mode resulting in 2D scalable growth. We thus believe that the new mechanism makes an important step to extend understanding of the kinetics in chemical vapor deposition (CVD) or molecular beam epitaxy (MBE) growth of heteroatomic vdW epitaxial layers.

METHODS

DFT calculation

DFT calculations were performed by using the Vienna ab initio simulation package³⁴ with the PBE-type generalized gradient approximation.³⁵ A cutoff energy of 210 eV was used for the plane wave expansion. The terrace and edge hopping barriers were calculated by using one quintuple unit of Bi₂Se₃ ribbon with the periodic boundary condition along the {100} axis (Fig. 1b; see Supplementary information for details), with sufficient vacuum sizes between periodic images, i.e., 15 Å along [210] and 13 Å along [001]. This substrate model is suitable given that commonly observed islands are triangular and that our result with a step edge is most energetically favorable with the fewest dangling bonds. With the four times larger supercell along the y-direction, the k -mesh size is $1 \times 2 \times 1$. Atomic positions of the two top-surface layers and the edge-nearby atoms in a lattice unit were optimized until the force was <0.02 eV Å⁻¹. The vdW interaction was included by using the Grimme's method, and we also confirmed that the hopping barriers change within the difference of 0.05 eV by using the Tkatchenko–Scheffler dispersion correction. The adsorption energy is defined as

$$E_{\text{ad}} = E_{\text{adsorbed}} - E_{\text{clean}} - E_{\text{atom}}, \quad (1)$$

where E_{adsorbed} and E_{clean} are the total energies of adsorbed and clean surfaces, respectively, and E_{atom} is the total energy of an isolated atom to be adsorbed. Relative adsorption energies, ΔE_{ad} , are defined as the relative values from the terrace adsorption energy. The relative adsorption energies display the potential energy landscape for the diffusion path with the transition state energies found by using the NEB method with the climbing image.²⁵ Overall accuracy of E_{ad} and the hopping barrier is about 0.01 eV. For E_D and E_S , we have chosen the largest barrier at terrace—far away from step edge by a few lattice units—and at step edge, respectively.

KMC simulation

The simulation surface consisted of a lattice of 600×600 atoms, in a face-centered cubic (111) surface with straight monoatomic steps.¹⁹ The simulation was simplified by assuming that a unit layer on a hexagonal lattice is a monoatomic layer, rather than a set of five atomic layers. In the

KMC code, the terrace diffusion parameters, such as $E_D = 0.4$ eV for hopping of a single adatom, an attempt frequency $\nu_0 = 3 \times 10^{12} \text{s}^{-1}$, and a deposition rate $R_n = 0.0007 \text{ ML s}^{-1}$, were used. To reproduce the experimental triangular islands, other hopping barriers along step edges of island were determined (see Supplementary information for details). We have used effective step-edge barriers because step edges are simplified. Thus, a rate catalog contains a predetermined set of possible configurations and transitions. In addition to diffusion rates and a deposition rate, a sticking coefficient affects the morphological evolution as well. However, the use of such effective barriers simplified on the fcc(111) surface does not affect the morphology of the resulting film significantly.

X-ray diffraction and anti-Bragg oscillation fitting

Two graphene substrates were prepared: (i) CVD graphene on SiO_2 and (ii) epitaxial graphene grown on 6H-SiC(0001) surface.¹⁸ The CVD graphene grown on a copper foil was transferred to the SiO_2 substrate after an etching process. Epitaxial graphene was grown in an ultrahigh vacuum (UHV) chamber. The substrates were mounted in an in situ x-ray scattering chamber at $< 1 \times 10^{-9}$ Torr. Bi_2Se_3 pieces wrapped with tungsten wire were thermally evaporated by heating the tungsten filament resistively. Film growth was performed typically at an effective growth rate ($< 0.05 \text{ ML min}^{-1}$) with the substrate maintained at 420–560 K. During the film growth, intensity oscillations were measured at an anti-Bragg point (0 0 1.5). Measurements were performed at the 5D BL of Pohang Light Source. We performed more than two runs of measurement on each substrate. We collected three effective datasets in total for different substrates, which are within the fit error. The kinetic parameters were obtained using the Cohen's model.^{31,32} In this model, adatoms arrive at the film at an effective deposition rate R_n and adsorb to the surface. Adatoms that land on top of a surface layer may diffuse and incorporate on the uphill steps, or transfer down to the top of the next layer. The rate of change for the coverage θ_n of the n th layer is then given by

$$\frac{d\theta_n}{dt} = R_n(1 - a_{n-1})(\theta_{n-1} - \theta_n) + R_{n+1}a_n(\theta_n - \theta_{n+1}), \quad (2)$$

where R_n is the effective deposition rate on the n th layer. R_1 is affected by the sticking probability of substrate. a_n is the probability of interlayer mass transport into the n th layer, and measures the rate at which adatoms transfer from the $(n+1)$ th to the n th layer.

DATA AVAILABILITY

The data that support the findings of this study are available from the corresponding author upon reasonable request.

CODE AVAILABILITY

Detailed information of the used DFT, KMC, and fitting codes is available from the corresponding author upon reasonable request.

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AUTHOR CONTRIBUTIONS

Y.K. and N.K. designed and conducted the experiment. G.L. and N.L. performed the DFT calculation. Y.K., N.K., and J.S. performed the KMC simulation. Y.K., G.L., K.S.K., and N.K. wrote the manuscript. Y.K. and G.L. contributed equally to this work.

COMPETING INTERESTS

The authors declare no competing interests.

ADDITIONAL INFORMATION

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