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Dynamics of 3D-island growth on weakly-interacting substrates

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ABSTRACT

The growth dynamics of faceted three-dimensional (3D) Ag islands on weakly-interacting substrates are investigated—using kinetic Monte Carlo (kMC) simulations and analytical modelling—with the objective of determining the critical top-layer radius R_c required to nucleate a new island layer as a function of temperature T , at a constant deposition rate. kMC shows that R_c decreases from 17.3 to 6.0 Å as T is increased at 25 K intervals, from 300 to 500 K. That is, a higher T promotes top-layer nucleation resulting in an increase in island height-to-radius aspect ratios. This explains experimental observations for film growth on weakly-interacting substrates, which are not consistent with classical homoepitaxial growth theory. In the latter case, higher temperatures yield lower top-layer nucleation rates and lead to a decrease in island aspect ratios. The kMC simulation results are corroborated by an analytical mean field model, in which R_c is estimated by calculating the steady-state

adatom density on the island side facets and top layer as a function of T . The overall findings of this study constitute a first step toward developing rigorous theoretical models, which can be used to guide synthesis of metal nanostructures, and layers with controlled shape and morphology, on technologically important substrates, including two-dimensional crystals, for nanoelectronic and catalytic applications.

1. Introduction

Vapor condensation on weakly-interacting substrates leads to the formation of dispersed three-dimensional (3D) islands, which eventually form a continuous film that is characterized by roughness at the growth front with an average height of up to hundreds of atomic layers [1-3]. A notable example is deposition of metal films on two-dimensional (2D) crystals (e.g., graphene and MoS₂ [4-7]) and oxides (e.g., SiO₂, TiO₂, and ZnO) [8-10], for which the tendency toward the uncontrolled formation of 3D agglomerates is detrimental to the performance of a wide range of switching, catalytic, and optoelectronic devices [12-18]. Thus, understanding the dynamics of atomic-scale processes which govern 3D island formation and shape evolution is a key step toward controlling film morphology and, by extension, the functionality of devices based on weakly-interacting film/substrate materials systems.

From the viewpoint of thermodynamics, 3D film morphology is the result of interface energy minimization. Larger adatom/adatom than adatom/substrate interface energy provides a driving force to minimize the film/substrate contact area [1-2]. However, vapor-based film growth proceeds far from thermodynamic equilibrium. Thus, morphological evolution is primarily determined by the relative rates of competing atomistic structure-forming processes (i.e., by kinetics) [1,3]. In order to elucidate

these processes, we have recently used kinetic Monte-Carlo (kMC) simulation [19] to study shape evolution of single Ag islands on weakly-interacting substrates over the growth temperature range from 300 to 500 K, at a constant deposition rate of 10 monolayers/s (ML)/s, with an adatom/substrate pairwise bond strength equal to 50% of the corresponding adatom/adatom value. For these film-growth conditions, we find that 3D nuclei are initially formed due to facile adatom ascent at single-layer island steps, followed by the development of sidewall facets bounding the islands, which in turn facilitate upward diffusion from island bases to their tops. 3D island shapes then evolve via repeated cycles of in-plane expansion—mediated by layer growth on the sidewall facets—interspersed between out-of-plane growth events as upwardly migrating atoms nucleate a new layer on the island top.

The dynamic competition among in-plane and out-of-plane island growth is well-described in metal-on-metal homoepitaxial growth theory via the concept of top-layer critical radius, i.e., top-layer size required for two adatoms to form a stable cluster [20-23]. In homoepitaxial systems, the top-layer nucleation rate, and hence the critical radius are determined by the interplay among the rates of processes depicted schematically in Fig. 1(a): (i) vapor-atom deposition onto the island top (process 1); (ii) adatom diffusion across the island top (process 2); and (iii) downward step-edge crossing (process 3), which is governed by the Erlich-Schwöbel [20,21,24-26] barrier $E_a^{top \rightarrow sub}$ (position x_1 in Fig. 1(a)).

However, the homoepitaxial theoretical framework cannot describe the dynamic processes that govern the top-layer nucleation rate during film growth on weakly-interacting substrates. The reason for this is that the top-layer nucleation dynamics

are significantly modified by an upward atomic flux due to the low interatomic bond strength between deposited and substrate atoms. This, in turn, results in relatively small activation barriers for upward adatom interlayer transport from the substrate onto an island via, e.g., step ascent [27-29] (process 4 in Fig. 1(b) or sidewall facet ascent) [19]. Experimentally, upward mass transport is evidenced by the fact that 3D islands are initially formed even when 2D islands are too small for effective direct capture of vapor adatoms [30,31]. It should be noted that atomic step ascent is a highly unlikely process in homoepitaxial film/substrate systems [32], illustrated in Fig. 1 by the magnitude of the barrier $E_a^{sub \rightarrow top (a)}$ being larger than that of $E_a^{sub \rightarrow top (b)}$ at position x_2 (Figs. 1(a) and (b), respectively).

The goal of this study is to establish the theoretical framework for describing the interplay among atomic-scale processes that govern top-layer nucleation dynamics in weakly-interacting film/substrate systems. To this purpose, we expand the capabilities of our previously-developed kMC code [19], in order to determine the mean critical top-layer radius R_c during Ag island growth on weakly-interacting substrates as a function of T at a constant deposition rate F . We find that R_c decreases from 17.3 to 6.0 Å as T is increased, at 25 K intervals, from 300 to 500 K, with $F = 10 \text{ ML/s}$. Thus, a larger T facilitates upward atomic diffusion along island sidewalls which, in turn, results in a larger top-layer adatom density and nucleation probability, causing the island to grow vertically. This is counter to established homoepitaxial growth theory, in which edge-adatom ascent is highly unlikely and temperature increase leads to enhanced in-plane growth and flatter islands, as adatoms more easily traverse down steps at island edges.

We also describe the dynamics of top-layer nucleation and we estimate R_c theoretically by developing and using a mean-field treatment, on the basis of the probabilistic approach originally devised by Krug *et al* [23], in order to calculate the steady-state adatom density on 3D islands bounded by smooth sidewall facets. The analytical results for R_c vs. T are consistent with experimental data for the growth of metal islands on weakly-interacting substrates [4-10], showing that films exhibit larger roughness with increasing growth temperatures.

The overall findings of this study constitute a first step toward the development of rigorous theoretical models that can be used to provide accurate predictions of the shapes of nanostructures on weakly-interacting substrates as a function of deposition conditions and, ultimately, to control the growth of functional films and nanostructures for catalytic, photonic, and nanoelectronic applications.

The paper is organized as follows. The kMC simulation methodology is described in Section 2 and the corresponding results presented in Section 3. The mean-field analytical model is described in Section 4; model results and comparison with kMC simulations are given in Section 5. The results are summarized in Section 6.

2. kMC simulation methodology

In order to investigate nucleation dynamics on the top layer of 3D islands on weakly-interacting substrates, we use our previously developed kMC code [19] which has been validated for homoepitaxial Ag/Ag(111) growth and employed to simulate Ag island shape evolution on weakly-interacting substrates. Process rates in the kMC

algorithm are calculated via the Arrhenius equation,

$$v = v_0 \exp \left(-\frac{E_a}{k_B T} \right), \quad (1)$$

in which v_0 is the atomic attempt frequency—taken to be $1.25 \times 10^{12} \text{s}^{-1}$, an average of published v_0 values for Ag diffusion on Ag(111) terraces [33-38]—and E_a is the activation barrier for a particular diffusion step. E_a values are calculated via a bond-counting scheme which is based upon both nearest and next-nearest neighbors and allows atoms to probe both *fcc* and *hcp* sites. Weakly-interacting substrates are implemented by lowering the pairwise adatom/substrate atom bond strength $E_{B,sub}$ relative to the corresponding adatom/adatom value $E_{B,film}$, thus resulting in a reduced activation barrier for adatom ascent onto the island second layer and sidewall facets. A list of activation barriers for key atomic-scale processes and $E_{B,sub}/E_{B,film} = 0.5$ is presented in Table A1 in the appendix. A more extensive barrier list, together with additional details concerning the physical model and algorithm implementation are found in Ref. 19. The critical radius is calculated by determining the size of the top layer, as a function of T and F each time a successful nucleation event takes place.

The kMC code is employed to simulate growth of single Ag islands on weakly-interacting substrates at temperatures T from 250 to 500 K with a deposition rate $F = 10 \text{ ML/s}$ for total coverages θ up to 1 ML. $E_{B,sub}/E_{B,film}$ ratios are varied from 0.50 to 0.75. We determine T and $E_{B,sub}/E_{B,film}$ values for which islands exhibit 3D morphology by evaluating their height-to-radius aspect ratio h/r , in which the radius is defined using a circle having an area equal to the base of the island. For

such sets of T and $E_{B,sub}/E_{B,film}$ values, R_c is computed as a function of θ . The Ovito software package [39] is used to visualize growth evolution, determine h/r values, and identify atomic-scale processes that govern island shape evolution and nucleation dynamics. Atomic-scale images are obtained with a resolution of 10^{-3} ML.

3. kMC simulation results

Island h/r ratios are found to increase with θ and saturate for coverages $\theta \gtrsim 0.2$ ML toward a steady-state value $h/r|_{ss}$, which is plotted as a function of T and $E_{B,sub}/E_{B,film}$ in Fig. 2. There are two distinct $h/r|_{ss}$ regions in Fig. 2; the bottom-right quadrant in which $h/r|_{ss}$ ranges from 0.03 to 0.6 and the top-left quadrant in which $h/r|_{ss} \simeq 1.85$.

Island morphologies within the two $h/r|_{ss}$ regions in Fig. 2 are visualized in Fig. 3, which shows island-shapes after deposition of $\theta = 0.5$ ML at $T = 500$ K with $E_{B,sub}/E_{B,film}$ varied from 0.50 to 0.75. For $E_{B,sub}/E_{B,film} \gtrsim 0.70$ ($h/r|_{ss} \simeq 0.03 - 0.60$), the islands are rather flat, consist of 1-4 layers, and are bounded primarily by A-edges (see Appendix for edge nomenclature); while for $E_{B,sub}/E_{B,film} \lesssim 0.60$ ($h/r|_{ss} \simeq 1.85$), the islands exhibit pronounced 3D morphologies, with approximately 26 layers, and are bounded by large smooth (111) and smaller (100) sidewall facets. A transition between 2D and 3D island shapes is observed at $E_{B,sub}/E_{B,film} = 0.65$, for which the Ag island is 17 layers tall and encompassed by (111) and (100) sidewall facets of comparable sizes. Hence, the

bottom-right and top-left quadrants in Fig. 2 correspond to conditions that favor 2D and 3D island shapes, respectively, and the two regions are separated by a sharp boundary.

Detailed inspections of simulation visualizations reveal that for growth conditions which favor 2D islands (e.g., $E_{B,sub}/E_{B,film} \geq 0.70$ in Fig. 3), the rate of adatom attachment to island edges is high compared to the rate of direct deposition on the top island layer. The latter process is relatively infrequent due to small island sizes. Consequently, the bottom layer expands rapidly and 2D growth proceeds without facet formation. In contrast, for growth conditions which favor 3D island formation (e.g., $E_{B,sub}/E_{B,film} \leq 0.60$ in Fig. 3), edge-adatom ascent from the island base to the sites above is facile leading to sidewall facet formation. The presence of smooth facets allows rapid upward adatom diffusion from the base to the top of the island and thus causes an increase in top-layer adatom density [19,29], which in turn facilitates nucleation of new top layers and, hence, vertical out-of-plane island growth. The sharp boundary between 2D and 3D growth in Fig. 2 suggests that, for nearly all conditions at which edge adatoms can easily ascend from the substrate terrace and form a smooth sidewall facet, adatom crossing between facets and the top surface occurs sufficiently rapidly to increase the top layer adatom density [29] and enhance nucleation.

To quantify the dynamics of top-layer nucleation, R_c is determined for islands grown at temperatures T ranging from 300 to 500 K with $E_{B,sub}/E_{B,film} = 0.50$. R_c values presented here are averaged over the R_c values measured for each new layer

of a given island during deposition of 0.5 ML, from the moment at which the island aspect ratio h/r saturates. The results are plotted in Fig. 4, which shows that R_c decreases monotonically from 17.3 to 6.0 Å with increasing T and saturates at $T \simeq 375$ K. This trend is contrary to typical behavior during island growth in homoepitaxy, for which increasing T results in enhanced adatom downward diffusion over step edges leading to lower adatom densities on the top-layer, hence lower nucleation probabilities, and a corresponding *increase* in $R_c(T)$ [22].

R_c values for islands on weakly-interacting substrates are determined by the rate at which adatoms detach from island edges to diffuse along sidewall facets and cross to the top layers. Each process step is T dependent. However, since edge-adatom ascent has been shown to be facile [19], and Ag diffusion on dominant (111) facets is known experimentally to be rapid (i.e., with relatively low activation barriers) [3,40-42], the rate limiting step in 3D island growth is adatom crossing from sidewall facets to the top island layer.

4. Analytical description of 3D island shape evolution

As noted in Section 1, our previous kMC simulations showed that island shapes evolve via cycles of in-plane expansion, followed by out-of-plane growth when the critical radius R_c is reached for nucleating a new top layer [19]. In Section 3, we used our kMC code to calculate R_c as a function of T at a constant deposition rate. In the present section, we develop an analytical description of this process. The starting island shape is a faceted pyramidal island, bounded predominantly by (111) facets as

depicted based upon our kMC simulations in Fig. 2 for $E_{B,sub}/E_{B,film} \leq 0.60$. We approximate this shape in Fig. 5 by a cylinder of radius R and height h , whose sidewall is a surface accounting for both (111) and (100) fcc facets with areas A_{111} and A_{100} determined by our kMC simulation: $A_{100} \simeq 10ah$ and $A_{111} \simeq 2\pi hR - 10ah$. The term a is the nearest-neighbor interatomic distance, and the prefactor 10 is the typical total number of atoms comprising the bases of A_{100} facets observed in the simulations (see Fig. 3). The top island surface is a smooth fcc(111) facet.

Atoms are deposited at a mean rate F on both the island top layer, with area $A = \pi R^2$, and on the substrate for which the island has an effective capture area [23]

$$A' = \left(\frac{D_S}{F}\right)^{5/7} - \pi R^2, \quad (2)$$

in which D_S is the adatom diffusivity on the substrate surface [23],

$$D_S = \frac{1}{4} l^2 \nu_0 e^{\left(-\frac{E_a^{sub}}{k_B T}\right)}. \quad (3)$$

The term l in Eq. (3) is the mean length of an adatom jump on the substrate, $E_a^{sub} = 0.08 \text{ eV}$ [43,44] is the corresponding activation barrier, taken for simplicity as being equal to the Ag adatom diffusion barrier on Ag(111), and k_B is the Boltzmann constant. For $T = 500 \text{ K}$, $D_S = 2.44 \times 10^{10} \text{ \AA}^2/\text{s}$. The island density is assumed to be saturated [38,45] with no further nucleation on the substrate, the capture area remains constant as the island grows, and direct deposition on facets is neglected.

The time scale for adatom diffusion is orders of magnitude smaller than that associated with island morphological changes [23]. Thus, after each minor variation

in the island morphology, the adatom population immediately reaches a new steady-state density. Hence, it is sufficient to solve steady-state (i.e., time-independent) adatom diffusion equations for the top layer (Eq. (4)) and the facet (Eq. (5)).

$$\frac{D_{111}}{r} \frac{d}{dr} \left(r \frac{du_t}{dr} \right) + F = 0 \quad (\text{top}) \quad (4)$$

$$D_{eff} \frac{d^2 u_f}{dz^2} - \gamma u_f = 0 \quad (\text{facet}). \quad (5)$$

In Eqs. (4) and (5), u_t and u_f are the adatom densities per unit area on the island top surface and facets, respectively, D_{111} is the diffusivity of an Ag adatom on a top Ag(111) layer, and D_{eff} the average effective diffusivity on the 111 and 100 sidewall surfaces. Both diffusivities are calculated using Eq. (3) with the energy barriers $E_a^{111} = 0.08 \text{ eV}$ and $E_a^{100} = 0.45 \text{ eV}$ —obtained by nudged elastic-band (NEB) and action-derived molecular dynamics calculations [19,43,44]—while D_{eff} is taken to be equal to the area-weighted average of the diffusivities on each surface,

$$D_{eff} = \frac{A_{111}}{A_{111} + A_{100}} D_{111} + \frac{A_{100}}{A_{111} + A_{100}} D_{100}. \quad (6)$$

A complete description of adatom diffusion on the island must include the trapping effect of growing-layer edges on the sidewall facets (e.g., Fig. 3, $E_{B,sub}/E_{B,film} = 0.60$), which hinders transport between the substrate and top layer, and allows the island to expand laterally. However, a precise representation of the edges would result in an exceedingly complex model description, due to the wide variety of shapes that each new layer can adopt. We circumvent this problem by defining a coefficient γ which represents the mean rate at which adatoms irreversibly attach to the edge of a growing layer. Hence, the shape of the model island is a smooth cylinder (Fig. 5). It

follows that γ must be dependent on the average rate at which adatoms migrate over the facets, as well as the rate of crossing between facets,

$$\gamma = \left(\alpha \frac{D_{eff}}{2\pi R h} + \frac{v^{facet \rightarrow facet}}{h} \right). \quad (7)$$

In Eq. (7), α is a proportionality constant which accounts for different rates of adatom attachment to sidewall facets that exhibit different densities of highly-coordinated sites (i.e., roughness) at which atoms can attach. $v^{facet \rightarrow facet}$ denotes the facet/facet crossing rate obtained from Eq. (1), in which $E_a^{facet \rightarrow facet} = 0.33 \text{ eV}$ [43,44] is the average activation barrier for crossing from (111) to (100) facets and vice versa.

The mathematical constraint for diffusion equations Eqs. (4) and (5), which accounts for the boundary between the substrate and the island edge is

$$\left. \frac{du_f}{dz} \right|_{z=0} = - \frac{1}{2\pi R} \frac{F A'}{D_S}. \quad (8)$$

The term $F A' / D_S$ represents the fraction of adatoms diffusing on the substrate in close vicinity to the island, assuming that edge adatom ascent from the substrate to the sidewall facet occurs sufficiently fast to neglect growth at the island base. The constraints associated with the boundary between the sidewall facet and the island top surface are

$$F\pi R^2 + 2\pi R a v_c u_f(h) = 2\pi R a v_c u_t(R) \quad (9)$$

$$\left. \frac{du_t}{dr} \right|_{r=R} = - \left. \frac{du_f}{dz} \right|_{z=h}. \quad (10)$$

Eq. (9) is obtained by noting that, in order to fulfill the steady-state requirement of the present model (i.e., to ensure that the adatom density remains constant over time), the total incoming adatom flux to the top layer must be equal to the total outgoing flux, since no nucleation occurs for $R < R_c$. In this way, all adatoms deposited on the top island surface or crossing from the sidewall facet to the top layer (left side of the equation) must cross in the opposite direction at the same rate (right side). Eq. (10) expresses the continuity condition for the adatom density derivatives of the facet/top-layer boundary to ensure mass conservation.

With the boundary conditions (9) and (10), analytical solutions for steady-state adatom densities on the top and sidewall facets (Eqs. (4) and (5)) read

$$u_t(r) = F \left\{ \frac{1}{4\pi} \left[2\pi R \left(\frac{1}{\alpha} + \frac{1}{D_{111}k \tanh(kh)} \right) + \frac{\pi(R^2 - r^2)}{D_{111}} \right] + \frac{A'}{2\pi R D_S k \sinh(kh)} \right\} \quad (11.a)$$

$$u_f(z) = \frac{F}{k \sinh(kh)} \left\{ \frac{R}{2D_{111}} \cosh(kz) + \frac{A'}{2\pi R D_S} \cosh(k(z - h)) \right\}, \quad (11.b)$$

in which $k = \sqrt{\gamma/D_{eff}}$. Integration of Eqs. (11.a) and (11.b) over the island surface yields the mean number of adatoms diffusing on it, which is of the order of 10^{-3} . This indicates that the island surface is sparsely populated during most of the growth process.

The two time-scales governing the top-layer nucleation probability [23] are (i) the mean time interval between two subsequent adatom arrivals at the island top, which is the inverse of the sum of the arrival rate from direct deposition and the upward diffusion via sidewall facets,

$$\Delta t = \left(F\pi R^2 + 2\pi R a v_c u_f(h) \right)^{-1}, \quad (12)$$

and (ii) the mean residence time τ of a single adatom on the island top prior to forming a stable nucleus. Expressing the mean number of adatoms simultaneously present on the island top as $N = \tau/\Delta t = \pi R^2 \bar{u}_t$, it follows that

$$\tau = \frac{\bar{u}_t}{F + \frac{2a}{R} u_f(h)}, \quad (13)$$

for which $\bar{u}_t$ is the mean adatom density on the island top surface.

The top-layer nucleation probability p_{nuc} is then defined as the probability of two adatoms simultaneously populating the island top at a given time. We approximate the time the atoms need to find each other as being negligible compared to the arrival and exit times. Hence, letting t_1 be the time at which an adatom escapes from the top and t_2 the time at which a new adatom arrives, p_{nuc} becomes the probability of $t_1 > t_2$, i.e. the probability that the first atom remains on the top when the second one arrives. t_1 and t_2 are exponential random variables with mean values τ and Δt , respectively [21]. Thus, p_{nuc} becomes

$$p_{nuc} = Prob[t_1 > t_2] = \frac{1}{\tau \Delta t} \int_0^\infty dt_1 e^{-t_1/\tau} \int_0^{t_1} dt_2 e^{-t_2/\Delta t} = \frac{\tau}{\tau + \Delta t} \quad (14)$$

The top-layer nucleation rate is then obtained simply by multiplying this probability by the mean number of atoms arriving at the top per surface unit time,

$$\omega_{nuc} = (\Delta t)^{-1} \frac{\tau}{\tau + \Delta t} \approx \frac{\tau}{\Delta t^2}. \quad (15)$$

Finally, we define the average critical radius R_c of an ensemble of islands as the radius at which the top layer nucleation rate ω_{nuc} equals the monolayer formation rate ω_{ML} on the side-wall facets

$$\omega_{nuc}(R_c) = \omega_{ML}(R_c) , \quad (16)$$

which contains information about the in-plane expansion of the island. ω_{ML} can be obtained by considering mass conservation at steady-state; since nucleation on the top layer does not occur for $R < R_c$, the only sink for adatoms in the island/substrate system is attachment to the sidewall facet. Hence, all adatoms deposited in the island capture area A_{cap} during time τ_{ML} will migrate toward the island and eventually occupy the available $\left(\frac{\sqrt{3}}{2}\right) A_{facet}$ sidewall sites. Thus,

$$\omega_{ML} = \tau_{ML}^{-1} = \frac{FA_{cap}}{\sqrt{3}\pi R h} . \quad (17)$$

5. Analytical model results and discussion

By inserting Eqs. (11.a) and (11.b) into Eqs. (12) and (13), and both sets into Eq. (15), we extract R_c and plot it in Fig. 6 as a function of T over the range 300 to 500 K for different values of the proportionality constant α . The model parameter values for 300 and 500 K are listed in Table A2 in the appendix. With $\alpha = 0.02$, R_c exhibits a steady decrease from 17.1 to 8.1 with increasing T ; while for $\alpha = 0.8$, R_c increases from 37.3 until it saturates at a value of $100 \text{ \AA}$ at $T \simeq 450 \text{ K}$. With an intermediate

value of $\alpha = 0.2$, R_c is found to increase from 34.1 Å at 300 K to 56.2 Å at 400 K, above which it decreases again to 47.3 Å with $T = 500K$.

The very low values of α (e.g., $\alpha = 0.02$) represent sidewall facets with a low density of highly-coordinated sites which increase the mean adatom lifetime before attaching to a growing layer. In this case, increasing T translates into larger adatom diffusion lengths on the sidewall facet; hence, higher probabilities of reaching the island top layer without encountering attachment sites. This, in turn, increases the top-layer nucleation probability and decreases R_c .

Conversely, a high density of stable positions at the sidewall facet, e.g. $\alpha = 0.8$, means that adatoms deposited on, and migrating from the substrate are trapped longer on sidewall facets before they can diffuse to the island top layer. Upward mass transport is therefore hindered, and direct deposition becomes the primary source of adatoms on the island top layer. The adatom density is then controlled by the rate at which adatoms cross down to the facets. Hence, increasing temperature in this regime enhances down-stepping, leading to a decrease in the average adatom density, and a lower island top-layer nucleation probability (i.e., a larger R_c).

In the latter case of high α , the island exhibits a morphological evolution similar to a monolayer island growing on a homoepitaxial substrate, since a large value of the coefficient γ is analogous to that of a high activation energy for ascending across the step edge of a monolayer island. In both cases, trapping of adatoms in the region between the top layer and substrate blocks upward mass transport. The dynamic

competition between adatom attachment to the facet and crossing to the island top-layer is reflected in a non-monotonic variation in R_c vs T at intermediate α values, indicating a transition between the two atomistic pathways which determine the island growth morphology.

An island with a low value of α in the analytical model corresponds in the kMC simulation code (Fig. 3) to $E_{B,sub}/E_{B,film} \lesssim 0.60$. The simulated islands are bounded by smooth sidewall facets with a small number of trapping sites, and adatoms can easily diffuse from the substrate to the top layer; therefore, the probability of adatoms on the facets attaching to a growing sidewall layer is low. Similarly, in the analytical model a low value of α also represents a surface with minimal hindrances to adatom migration and implies low adatom probabilities for sidewall attachment. Thus, both kMC and analytical models are consistent in predicting the decrease in R_c with increasing T . In addition, the results presented herein are in qualitative agreement with experimental data for the microstructural evolution of metal films growing on weakly-interacting substrates, which show an increase in film roughness with increasing deposition temperature [4-10], while providing insights into the responsible atomic-scale mechanisms.

6. Summary and outlook

We investigated the dynamics of 3D islands grown on weakly-interacting substrates as a function of temperature using both simulations and analytical modelling, with the goal of determining the critical top-layer radius R_c required to nucleate a new island layer. kMC simulations of Ag island growth were carried out using film/substrate to

film/film atomic bond strength ratios $E_{B,sub}/E_{B,film}$ ranging from 0.50 to 0.75, deposition temperatures from 250 to 500 K, and an atom growth flux of 10 ML/s . All islands were grown to a coverage Θ of 1 ML . The results clearly show two distinct regions in growth-parameter space, with a narrow boundary, corresponding to island 3D vs. 2D growth. At $T = 500 \text{ K}$ with $E_{B,sub}/E_{B,film} \gtrsim 0.70$, islands grow in-plane with a 2D morphology, due to a low rate of edge-adatom detachment from the substrate. For lower bond strengths ($E_{B,sub}/E_{B,film} \lesssim 0.60$), islands are 3D, since facile substrate detachment from the substrate allows fast upward adatom diffusion across island sidewall facets leading to nucleation of new top layers. To quantify the dynamics of top-layer nucleation, we compute R_c for islands grown at $E_{B,sub}/E_{B,film} = 0.50$ at $T = 300 - 500 \text{ K}$ and find that R_c decreases from 17.3 to $6.0 \text{ \AA}$ as T is increased. This is in stark contrast to the trend exhibited by 2D islands grown under homoepitaxial conditions, for which R_c increases with temperature.

In addition to the simulations, we developed an analytical model, which includes primary atomistic processes involved in the formation of 3D islands on weakly-interacting substrates, in order to compute R_c for different deposition conditions and intrinsic physical parameters of the film/substrate system. The variation of the rate at which adatoms attach to the sidewall facets with respect to direct top-layer deposition accounts for R_c trends during both 2D and 3D growth; high attachment rates result in higher R_c values with increasing T , and low attachment rates yield lower R_c values at high temperatures, in agreement with the kMC simulations.

Overall, our results are consistent with previous experimental observations which show that increasing growth temperatures during metal deposition on weakly-interacting substrates—including Ag/SiO₂ [46,47], Ag/ZnO [30], Cu/ZnO [31], Pd/TiO₂ [48], and Dy/graphene [49]—gives rise to an increase in surface roughness. The results of this study represent a first step toward developing rigorous theoretical models that can be used to provide accurate predictions of the morphological evolution of nanostructures on weakly-interacting substrates and, by extension, to optimize the performance of devices based on weakly-interacting film/substrate materials systems. An area of particular interest is the growth of thin metal films on 2D materials, in which flat metal layers are a prerequisite for leveraging the unique physical properties of 2D crystals in high-performance nanoelectronic devices [4,50]. Moreover, the atomic-scale processes highlighted and the methodology presented here may also be useful for investigating the kinetics of island formation in strongly-interacting film/substrate systems for which 3D morphology has been observed, including Pb/Si(111) [51-53] and Ag/Si(111) [54].

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FIGURES AND FIGURE CAPTIONS

Fig. 1. (Color online) Schematic illustrations of atomic structure, potential energy landscape, and atomic-scale migration processes during top-layer nucleation on a (a) homoepitaxial and (b) weakly-interacting substrate. (1) Vapor-atom deposition on island top, (2) adatom diffusion, and (3) downward step-crossing are common processes on both homoepitaxial and weakly-interacting substrates. In addition, on weakly interacting substrates (4) upward atomic transport is possible, since $E_a^{\text{sub} \rightarrow \text{top}}(b) < E_a^{\text{sub} \rightarrow \text{top}}(a)$ at position x_2 . Green spheres represent atoms in stable lattice sites, grey spheres represent atoms of the weakly-interacting substrate in (b), while light green spheres with dashed contour represent migrating atoms. The diffusion direction is indicated by arrows, and the letter “X” represents an energetically unfavorable pathway.

Fig. 2. (Color online) 3D plot of steady-state height-to-radius aspect ratios $h/r|_{ss}$ for Ag islands on weakly-interacting substrates as a function of film-growth T and $E_{B,sub}/E_{B,film}$ (see text for definition). The bright region (top-left quadrant) corresponds to conditions which promote large $h/r|_{ss}$ values, and hence 3D island morphologies, while dark regions (bottom-right quadrant) correspond to the 2D island morphology regime.

Fig. 3. (Color online) Ag island morphologies for growth at $T = 500K$ on weakly-interacting substrates with $E_{B,sub}/E_{B,film}$ varied from 0.75 to 0.50 at film coverages $\theta = 0.5 ML$. The film deposition rate is $F = 10 ML/s$.

Fig. 4. Evolution of the top-layer critical-nucleation radius R_c for growth of Ag islands on weakly interacting substrates ($E_{B,sub}/E_{B,film} = 0.50$) as a function of the film growth temperature T . The film deposition rate is $F = 10 \text{ ML/s}$.

Fig. 5. Model of a 3D island on a weakly-interacting substrate during film growth. F is the deposition flux, A' is the effective island capture area, γ is the rate of adatom attachment to a growing layer on the sidewall facet, R and h are the radius and height of the island, and u_t and u_f are the adatom densities per unit area on the top and the sidewall facets, respectively.

Fig. 6. (Color online) Evolution of the top-layer critical radius R_c for nucleation on a 3D Ag island on a weakly-interacting substrate as a function of the film growth T for different values of the proportionality constant α for the rate γ (Eq. (7)) of adatom attachment to a growing layer on the sidewall facet. The film deposition rate is $F = 10 \text{ ML/s}$. Note the break in the vertical axis.

APPENDIX

A hexagonal monolayer island on an fcc(111) substrate is bounded by alternating A and B edges, in which the A edges are composed of $\langle\bar{1}10\rangle/\{100\}$ nanofacets and B edges consist of $\langle01\bar{1}\rangle/\{111\}$ nanofacets, as shown schematically in Figure A1 [55]. Continued island growth leads to the island being bounded by alternating 100 and 111 sidewall facets. Note that A and B edge atoms have different numbers of nearest-neighbor terrace atoms.

Adatom diffusivities along the two types of edges, and across the two sidewall facets, are not the same—the activation s for edge and facet diffusion used in this work [19] are $E_a^{A-edge} = 0.26 \text{ eV}$, $E_a^{B-edge} = 0.31 \text{ eV}$, and $E_a^{100} = 0.45 \text{ eV}$, $E_a^{111} = 0.08 \text{ eV}$, respectively. Thus, island morphological evolution is strongly affected by the initial asymmetric edge configuration.

A list of activation barriers for key atomic processes and $E_{B,sub}/E_{B,film} = 0.5$ is presented in Table A1, while Table A2 lists the values of the parameters of the analytical model for the lowest and the highest temperature used in the calculations (300 and 500 K, respectively).

Fig. A1. (Color online) Monolayer heptamer island on a (111) fcc surface. A and B island edges are defined as in Ref. 53. The dashed lines connect island and nearest-neighbor substrate atoms.

Table. A1. Activation energies for selected Ag adatom migration processes. Symbol definitions are: t = terrace, f = facet, and e = edge. The process denoted as $f \rightarrow f$ refers to an adatom migrating between two facets, via an overhanging position in which the adatom has only two nearest neighbors. The process denoted as $e \rightarrow f$ refers to an atom detaching from the edge of an island, which resides on a weakly-interacting substrate, and moving to an island facet. A more extensive list of activation barriers is presented in Ref. 19.

Migration path	Activation barriers (eV)
$t(111) \rightarrow t(111)$	0.081
$t(100) \rightarrow t(100)$	0.452
$f \rightarrow f$	0.322
$e \rightarrow f$	0.082
Step ascent (weakly-interacting substrate)	0.210
Step-descent (weakly-interacting substrate)	0.322
Step-ascent (homoepitaxy)	0.836
Step-descent (homoepitaxy)	0.322

Table. A2. Parameter values for the analytical model, of an island with radius R and height h . Symbol definitions are: A' = effective island capture area, $D_{S,111}$ = diffusivity on the substrate and on the Ag(111) surface, D_{eff} = effective diffusivity on the sidewall facet of the island; and γ_α = adatom attachment rate to edges of growing facets (the subscript α is the proportionality constant). Additional details on the model parameters can be found in the text.

Analytical model parameters ($R = 16 \text{ \AA}$, $h = 20 \text{ \AA}$)		
	$T = 300 \text{ K}$	$T = 500 \text{ K}$
$A' (\text{\AA}^2)$	1450	2600
$D_{S,111} (\text{\AA}^2/\text{s})$	$1.15 \cdot 10^{11}$	$4.01 \cdot 10^{11}$
D_{eff}	$9.11 \cdot 10^{10}$	$3.20 \cdot 10^{11}$
$\gamma_{\alpha=0.8} (\text{atom}/\text{s})$	$2.37 \cdot 10^5$	$2.70 \cdot 10^7$
$\gamma_{\alpha=0.2}$	$2.33 \cdot 10^5$	$1.64 \cdot 10^7$
$\gamma_{\alpha=0.02}$	$1.80 \cdot 10^5$	$2.86 \cdot 10^6$