Temperature-dependent growth shapes of Ni nanoclusters on NiAl(110)

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Temperature-dependent growth shapes of Ni nanoclusters on NiAl(110)

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Scanning tunneling microscopy studies reveal that two-dimensional nanoscale Ni islands formed by deposition of Ni on NiAl(110) between 200–400 K exhibit far-from-equilibrium growth shapes which change systematically with temperature. Island structure reflects the two types of adsorption sites available for Ni adatoms, and island shapes are controlled by the details of adatom diffusion along island edges accounting for numerous local configurations. The temperature dependence of the island shapes is captured and elucidated by kinetic Monte Carlo simulation of a realistic atomistic-level multisite lattice-gas model incorporating precise diffusion barriers. These barriers are obtained by utilizing density functional theory to probe energetics not just at adsorption sites but also at transition states for diffusion. This success demonstrates a capability for predictive atomistic-level modeling of nanocluster formation and shape selection in systems that have a high level of energetic and kinetic complexity. © 2011 American Institute of Physics. [doi:10.1063/1.3626581]

I. INTRODUCTION

Nanostructure self-assembly processes, either in fluids or on smooth surfaces, are characterized by significant mobility of the aggregating components.1 In addition, some degree of mobility generally persists in the aggregated state2 which can both quench shape instabilities2 and control shape selection. The aggregation process driving nanostructure growth may be either attachment/reaction-limited or diffusion-limited. The former is common in liquid-phase nanoparticle and crystal growth, particularly in the presence of capping agents.3–5

The latter is more common for vapor deposition on surfaces, although some degree of attachment limitation may persist (e.g., an inhibition of atoms to incorporate at highly-coordinated kink sites as they cross steps or move around corners).6–9

There have been extensive efforts to control the formation of metal and semiconductor nanostructures, manipulating both size and shape. For liquid-phase formation, typically growth is controlled by surfactants and capping agents, which can produce an extraordinary variety of far-from-equilibrium growth shapes, e.g., pencil, arrow, tree-shaped, and hyper-branched semiconductor nanostructures.3,10 and polyhedral nanocrystals, nanorods, nanowires, platelets, etc., for fcc metal nanostructures.3,5,11 Certainly, a general appreciation of the factors controlling non-equilibrium growth morphologies has been established, e.g., a “kinetic control hypotheses” and insights from Cahn’s formulation of crystal growth.3 However, there is typically a lack of detailed atomistic-level understanding of the growth kinetics even though this would facilitate guided formation of functional nanostructures with tailored morphologies and “tuned” properties.

The focus of our study is on the formation of metal nanostructures, motivated by applications ranging from catalysis to plasmonics, where both size- and shape-control are desired. Specifically, we consider vapor deposition of metal atoms on flat single-crystal metal surfaces under the well-controlled conditions of ultrahigh vacuum (UHV). This process leads to self-assembly of epitaxial metal nanostructures mediated by rapid diffusion and aggregation of adsorbed atoms (adatoms) on broad terraces. Growth shapes are extremely sensitive to the degree and nature of relaxation in the aggregated state, either via diffusion of adatoms along the island edge or via detachment-reattachment of adatoms to/from surrounding terraces. Prominent early examples of exotic growth shapes for metal-on-metal deposition included “fat fractals” for Au on Ru(0001) exhibiting a diffusion-limited-aggregation-instability,12 and nano-width wires of Cu on anisotropic Pd(110).13 Dendrites with 3-fold symmetry in systems with equilibrium 6-fold symmetry, as well as transitions between various geometric non-equilibrium growth shapes, have also been observed for deposition on single-component substrates.6–9 Recent efforts have begun to utilize binary alloy substrates, hence opening new possibilities to guide the formation of metal nanostructures,14 which is the approach pursued here.

Epitaxial growth on single-crystal surfaces offers a special advantage in facilitating detailed and realistic...
atomistic-level modeling due to two factors. First, localization of adatoms at a periodic array of adsorption sites enables the use of lattice-gas (LG) modeling for which non-equilibrium evolution can be efficiently analyzed on the appropriate time- and length-scales via kinetic Monte Carlo (KMC) simulation. Conventional molecular dynamics cannot access relevant time scales. The possibility of different types of adsorption sites on binary alloy surfaces is accommodated by multisite LG models. Second, ab initio density functional theory (DFT) analysis can provide two key classes of energetic input parameters: (i) adatom adsorption and interaction energies, which control nanostructure thermodynamics; (ii) diffusion barriers, which control formation kinetics. It should be emphasized that not just terrace diffusion, but edge diffusion and attachment-detachment barriers are required for large numbers of island edge configurations.

Specifically, in this contribution, we consider Ni deposition on the single-crystal NiAl(110) surface. The structure of bulk NiAl crystal is CsCl-type (bcc-like) with an experimental lattice constant of $a_{\text{NiAl}} = 0.2887$ nm, which is in very good agreement with our DFT value of 0.2896 nm. The NiAl(110) surface unit cell is rectangular with dimensions $a_x = \sqrt{2}a_{\text{NiAl}}$ and $a_y = a_{\text{NiAl}}$, as will be shown in Fig. 3 below. For consistency, the [001] direction on this surface, corresponding to the direction of shorter periodicity of $a_y$, is aligned in the direction of the “vertical” y-axis in all of our scanning tunneling microscopy (STM) and KMC simulation images, as well as in our schematics. The orthogonal [110] direction corresponding to the longer periodicity of $a_x$ is always aligned in the direction of the “horizontal” x-axis. Ni deposition is considered for two reasons. First, strain build-up is minimized, because there is a very good lattice match between Ni(100)-type epitaxial structures and the NiAl(110) surface. This lattice match follows from the experimental value of $a_{\text{Ni}} = 0.3520$ nm for the bulk fcc Ni lattice constant, as discussed further below. This feature is valuable since while atomistic-level modeling of strain effects is advancing, one cannot yet incorporate realistic diffusion kinetics, a key requirement for our analysis of far-from-equilibrium growth shapes. Second, Ni nanostructures have potential for use as inexpensive catalysts, particularly for steam reforming.

However, we should note that our focus here is on structure rather than catalytic properties.

In Sec. II, we describe the experimental details for our studies, and present some information on the DFT analyses which provides input to our atomistic modeling. Next, in Sec. III, we describe our STM observations of Ni nanocluster growth at different surface temperatures ($T$), as well as our analysis of both the thermodynamics and growth kinetics of this system. Finally, in Sec. IV, we provide further discussion and conclusions.

II. EXPERIMENTAL DETAILS AND MODELING APPROACH

In our experimental studies, the NiAl single crystal was grown using the Bridgeman technique. The surface was oriented to within ±0.25$^\circ$ of the (110) orientation and then polished using standard metallographic techniques. The sample was cleaned by repeated cycles of Ar$^+$ sputtering (20 min, 1.5 keV) followed by annealing to 1200 K for 2 hours until the surface was judged clean. Subsequent STM analysis reveals surfaces with a terrace-step morphology, with terraces obtained by this procedure up to 0 $\mu$m wide. The sample was introduced into an UHV chamber with an Omicron variable-temperature STM, as well as Auger electron spectroscopy (AES) and x-ray photoemission spectroscopy (XPS). The base pressure of the chamber was $2 \times 10^{-11}$ Torr.

Evaporative deposition of Ni was performed from a commercial (Mantis) source, with deposition rates $F$ around 1–2 $\times 10^{-3}$ monolayer (ML) per second, where 1 ML corresponds to 2 Ni atoms per NiAl(110) unit cell. Coverages, $\theta$, of Ni range from 0.1–0.2 ML. See below for details. Flux calibration was achieved by direct STM measurement of the coverage. Film composition and purity were checked with AES and XPS. STM imaging of Ni island morphologies was performed with a tunneling current of 0.5 nA, and either positive or negative tip biases ranging from 0.5–2 V in magnitude. However, we find no significant dependence of film features on tip bias. For example, the Ni island height has the value $\sim 0.23$ nm over the entire range of bias corresponding to monolayer islands. In these studies, sample orientation within the surface plane was checked by codeposition of Ag, exploiting the feature that Ag forms bilayer islands which are highly elongated in the [001] direction.

DFT calculations are performed to provide energetic input to our atomistic modeling using the plane-wave based Vienna ab initio simulation package (VASP). We use the Perdew-Burke-Ernzerhof form of the generalized gradient approximation, and electron-ion interactions are described by the projector augmented wave approach. The energy cutoff for the plane-wave basis set is selected to be the VASP default value. In all calculations, the NiAl(110) substrate is represented by slabs of four NiAl(110) layers, separated from adjacent slabs by vacuum regions of thickness 1.5 nm. We use a supercell with the lateral size of $3 \times 4$ unit cells, and a $\Gamma$-centered $4 \times 4 \times 4$ k mesh. In standard calculations, except for atoms in the bottom-most NiAl(110) layer which are fixed, all atoms are relaxed until the converged magnitudes of the forces on all free coordinates reach 0.1 eV/Å.

DFT analysis is used to assess the relative stability of various possible structures for complete adlayers. DFT is also used to determine adsorption energies for isolated Ni adatoms at the two possible stable adsorption sites on NiAl(110) as well as at transition states (TS) for hopping. In addition, DFT is used to assess interactions between nearby pairs of adatoms with prescribed lateral positions. In conventional analyses of lateral interactions, both adatoms are at stable adsorption sites. However, in our analysis we also consider the case where one adatom is fixed at a TS. In DFT calculations of adatom adsorption energies at TS, and in calculations of adatom-adatom interactions, we also fix the lateral positions of adatoms.

These DFT energetics are incorporated into a multi-site lattice-gas model accounting for the different types of stable adsorption sites and also for the appropriate diffusion pathway between these sites. Realistic diffusion
barriers for terrace diffusion, and also for edge diffusion and attachment-detachment processes for all possible step-edge configurations, are determined as described below. KMC simulation is performed to assess model behavior where deposition and hopping are implemented with the appropriate relative probabilities based on Arrhenius hop rates with the above barriers and a common prefactor of $v = 10^{13}/s$.

III. STM ANALYSIS AND ATOMIC MODELING

A. STM observations

Figures 1(a)–1(d) summarize our STM observations of the $T$-dependence of two-dimensional (2D) Ni island growth shapes. Specifically, the result of deposition of: 0.2 ML Ni at 200 K with a flux of $F = 1.33 \times 10^{-3}$ ML/s is shown in Fig. 1(a); 0.15 ML Ni at 300 K with $F = 1.7 \times 10^{-3}$ ML/s in Fig. 1(b); and 0.18 ML Ni at 400 K with $F = 1.2 \times 10^{-3}$ ML/s in Fig. 1(c). We should note that heterogeneous nucleation is dominant at 300 K and above, so that the island density at these temperatures is controlled by the density of surface defects. This issue will be discussed in more detail elsewhere as our focus here is on island shape. Figure 1(d) shows the result of annealing island distributions formed by deposition at 400 K to a temperature of 500 K. Specifically, heating from 400 to 500 K took ~3 min, and the sample was held at 500 K for 30 min. The coarsening process which occurs during annealing only slightly reduces the island density. However, one portion of the islands grow significantly larger at the expense of others which shrink.

In our discussion of island shapes below, we will refer to step edges aligned in the [001] direction (which corresponds to the $y$-axis in all of our images) as “vertical”. We will refer to steps aligned in the orthogonal [110] direction, corresponding to the $x$-axis in all of our images, as “horizontal.” Finally, steps aligned with the diagonal of the rectangular NiAl(110) unit cell shown below, and thus having the slope of $\pm 1/\sqrt{2}$ relative to the $x$-axis in our images, are described as “diagonal.”

Deposition at 200–300 K produces Ni islands that are rather irregular, and on average are elongated along the [001] direction. Correspondingly, there is some preference for step orientations between vertical and horizontal which are significantly steeper (with a magnitude of their slope measured from the $x$-axis above unity) than the diagonal orientation defined above. In contrast, deposition of Ni at 400 K produces much more geometric quasi-six-sided Ni monolayer islands predominantly bounded by diagonal step edges (in the sense defined above) and [001] vertical edges. Thus, these 400 K shapes can be regarded as distorted octagons missing [110] horizontal edges. However, the 400 K shapes do not correspond to equilibrium shapes. Annealing to 500 K produces Ni islands which are more rounded, and which might be better described as eight-sided, distorted octagons. These shapes should be closer to equilibrium (see below).

Next, we report mean island aspect ratios to provide one basic measure quantifying the variation of island shape with $T$. Specifically, if the maximum linear dimension (or caliper length) of the island in the [001] direction ($y$-axis) is $Y$, and that in the [110] direction ($x$-axis) is $X$, then we measure the aspect ratio $R = Y/x$. See Fig. 2 for an illustration of these lengths. Islands formed by deposition at 200 K are small, so distortion of their shapes due to STM tip effects precludes reliable analysis. For higher $T$, islands are larger reducing this distortion, but we still restrict our analysis to the larger $\sim 50\%$ of islands in images. At 300 K, we obtain an aspect ratio of $R = 1.43 \pm 0.05$ for 29 larger islands in a $200 \times 200$ nm$^2$ region including Fig. 1(b). At 400 K, we obtain $R = 1.00 \pm 0.03$ for 26 larger islands in a $200 \times 200$ nm$^2$ region including Fig. 1(c). At 500 K, we obtain $R = 1.03 \pm 0.03$ for 25 larger islands in a $200 \times 200$ nm$^2$ region including Fig. 1(d). The uncertainty in the average value is taken as one standard deviation of the distribution of measured values divided by the square root of the number of islands sampled.

Finally, we provide a more sophisticated analysis which can distinguish between the average geometric island shapes at 400 K and 500 K. Our strategy is to obtain the best fit of each island to a distorted octagon where the four “diagonal” sides are aligned with the diagonals of the NiAl(110) unit cell as defined above. We determine the

![FIG. 1. STM images of monolayer Ni islands on NiAl(110) for deposition at (a) 200 K ($F = 1.33 \times 10^{-3}$ ML/s, $\theta = 0.20$ ML); (b) 300 K ($F = 1.7 \times 10^{-3}$ ML/s, $\theta = 0.15$ ML); (c) 400 K ($F = 1.2 \times 10^{-3}$ ML/s, $\theta = 0.18$ ML); and annealing to (e) 500 K. STM images show a significant fluctuations or variations in shapes for the latter. (e)-(g) KMC simulation images corresponding to (a)-(c), respectively. (h) KMC simulation image for deposition at 500 K ($F = 1.2 \times 10^{-3}$ ML/s, $\theta = 0.08$ ML).](image1)

![FIG. 2. STM images of representative Ni islands on NiAl(110) at (a) and (b) 300 K; (c) and (d) 400 K; (e) and (f) 500 K. A coarse-grained smooth fit to the shape is shown for 300 K, and optimal fits to distorted octagons are shown for 400 K and 500 K. We also indicate the various linear dimensions mentioned in the text. The size of each image is $25 \times 25$ nm$^2$.](image2)
average length of the [110] horizontal, [001] vertical, and diagonal sides for each island. These averages are denoted by $Y_{av} = (Y_1 + Y_2)/2$, $X_{av} = (X_1 + X_2)/2$, and $D_{av} = (D_1 + D_2 + D_3 + D_4)/4$, respectively. See Fig. 2 for these lengths. Then, we evaluate the averages of ratios of these quantities over the same sets of islands used above in our analysis of the aspect ratio $R$. For the islands at 400 K, one obtains $Y_{av}/D_{av} = 0.86 \pm 0.05$, $X_{av}/D_{av} = 0.39 \pm 0.04$, and $X_{av}/Y_{av} = 0.47 \pm 0.05$. In contrast, for the islands at 500 K, one obtains $Y_{av}/D_{av} = 1.24 \pm 0.07$, $X_{av}/D_{av} = 0.71 \pm 0.05$, and $X_{av}/Y_{av} = 0.59 \pm 0.04$. This confirms the claim that islands at 400 K are closer to 6-sided (corresponding to shorter horizontal sides associated with, e.g., a significantly smaller $X_{av}/D_{av}$ value) compared to those annealed to 500 K (which are more octagonal).

In Subsections III B and III C, we will provide more detailed insight from modeling and theory into what controls the observed island shapes and their $T$-dependence.

## B. Adlayer and nanostructure thermodynamics

To develop a detailed atomistic-level understanding of island structure and shape, we first characterize relevant adlayer thermodynamics for Ni/NiAl(110). Isolated Ni adatoms prefer the Ni bridge (Ni-br) site with adsorption energy $E_{ads,Ni} = -4.66$ eV, over the Al-bridge (Al-br) site where $E_{ads,Al} = -4.50$ eV, as shown in Fig. 3(a). Here, the Ni-br (Al-br) site refers to the adsorption site between two neighboring Ni (Al) separated by $a_x = 0.2887$ nm in the [001] direction. In contrast to the preferred Ni-br site for isolated Ni, in an equilibrated stoichiometric alloy adlayer, Ni resides at Al-br sites on NiAl(110) thereby propagating the bulk alloy ordering.

Ni island structure also depends on adatom interactions. Assuming dominant pairwise interactions [DFT values are given in Fig. 3(b)], the total energy per adatom for large, dense islands with Ni populating both Ni-br and Al-br sites equals $E_{tot} = -5.36$ eV. This is lower than the corresponding energy per adatom for dilute islands with Ni populating only Ni-br sites (by 0.66 eV), or only Al-br sites (by 0.71 eV). These total energies are obtained by summing the adsorption energy and half of the shared lateral interactions. The energy differences obtained from this analysis match well those from direct DFT determination of complete adlayer energetics incorporating many-body interactions of 0.68 eV for islands populating only Ni-br sites, and 0.75 eV for only Al-br sites. This comparison supports the validity of our pairwise interaction model. We conclude that the dense Ni island structure is more favorable than the dilute structures since the cost of populating the less favorable Al-br site is more than offset by enhanced adatom interactions. We have also checked that the dense structure is more favorable than other, more complex, intermediate-density structures sometimes preferred for other metals.  

Additional support for this dense island model follows from consideration of the height of the Ni islands. STM line-scan measurements give a value of $0.23 \pm 0.03$ nm which is consistent the value from DFT analysis of the “height” for dense islands of 0.19 nm. The latter is measured from the height difference between nuclei for Ni adatoms and Ni in the surface layer of NiAl(110).

The distance between Ni on diagonally adjacent Ni-br and Al-br sites on the NiAl(110) surface of $\sqrt{a_x^2 + a_y^2}/2 = 0.2500$ nm matches well with that of neighboring Ni atoms on the Ni(100) surface of $\sqrt{a_{Ni}/2} = 0.2489$ nm. Again, $\sqrt{a_{Ni}} = 0.3520$ nm is the experimental bulk fcc Ni lattice constant. Thus, the dense structure suffers relatively little strain, with only a 4.86% areal compression relative to Ni(100).

Determination of equilibrium Ni island shapes for the preferred dense structure is a natural precursor to analysis of growth shapes. For an appropriate analysis, we first evaluate the total energy per atom at Ni-br sites within a dense island of $E_{tot,Ni} = -5.38$ eV as the sum of $E_{ads,Ni}$ and half the shared interactions to all neighbors. Similarly, one has that $E_{tot,Al} = -5.33$ eV at Al-br sites. Note that the energy quoted above in assessing the stability of dense Ni islands relative to other structures is given by $E_{tot} = (E_{tot,Ni} + E_{tot,Al})/2$. The standard 2D Wulff construction must be modified due to the non-zero difference in adsorption energies of $\Delta = E_{tot,Al} - E_{tot,Ni} = 0.05$ eV for the two distinct types of adsorption sites. For an island of $M$ atoms, we let $\delta M$ denote the excess population of Ni-br sites over Al-br sites. Then, the overall island energy is given by

$$E_{island} = MF_{tot} - \frac{1}{2} \delta M \Delta - \{\text{edge cost}\},$$

where $\{\text{edge cost}\}$ is half the cost of broken bonds at the island edge. For [110] horizontal edges, this edge cost is $\phi_2 = 1.05$ eV/nm for edge atoms residing either on all Ni-br or all Al-br sites. The corresponding value is $\phi_4 = 1.22$ eV/nm for [001] vertical edges. For diagonal steps (in the sense described above), the cost is $\phi_2 = 0.88$ eV/nm. These values are determined from the pair interactions reported in Fig. 2(b).

The equilibrium shape minimizes $E_{island}$ for fixed $M$, so it is clear that preferred horizontal and vertical steps have edge atoms on Ni-br sites (as this choice produces a lower energy than populating Al-br sites). The complication (cf. a standard Wulff analysis) is that changing island shape for fixed $M$ also changes $\delta M$ and this affects $E_{island}$ since $\Delta \neq 0$.

Next, as in conventional equilibrium analyses for geometric island shapes, we restrict our attention to large islands...
ignoring distinct contributions for edge atoms at corners and also ignoring step edge fluctuations. Then, for the expected distorted octagonal island shapes with [110] horizontal (001) vertical) edge length \( X \) and diagonal edge length \( D \), one can show that \( \delta M = X/\psi_x + Y/\psi_y \). This yields

\[
E_{\text{island}} = ME_{\text{tot}} + 2X\psi_x + 2Y\psi_y + 4D\psi_d, \tag{2}
\]

with effective or renormalized step energies \( \psi_{x,y} = \phi_{x,y} - \Delta/(4\psi_d) \) and \( \psi_d = \phi_d \). Thus, the effective step energies for horizontal and vertical steps (but not diagonal steps) are reduced relative to the case \( \Delta = 0 \). This reflects the feature that all edge atoms for these steps are on preferred Ni-br sites, in contrast to diagonal steps with equal populations at Ni-br and Al-br sites. Despite this feature, diagonal steps still have the lowest effective energy due to small \( \psi_d = 0.88 \) eV/nm. versus \( \psi_x = 1.02 \) eV/nm and \( \psi_y = 1.18 \) eV/nm.

Solving the constrained minimization problem via Lagrange multipliers yields for the equilibrium shape

\[
D : Y : X = \sqrt{\frac{3}{2}}(\sqrt{2}\psi_x + \psi_y - \sqrt{3}\psi_d) : 2(\sqrt{3}\psi_d - \psi_y) : (\sqrt{3}\psi_d - 2\psi_x) = 8.1 : 3.0 : 1. \tag{3}
\]

It is instructive to note that the edge length inequality, \( Y > X \), occurs despite the step energy inequality \( \psi_y > \psi_x \). This reflects the feature that the diagonal island edges are not symmetrically oriented at 45° relative to the \( x \)- and \( y \)-axes. However, the relative strengths of the horizontal and vertical effective step energies are clearly reflected in the simple and natural relation \( Y : X = \psi_y : \psi_x \) which follows directly from Eq. (3). Again, \( Y_c \) and \( X_c \) denote the maximum linear dimensions or caliper lengths of the island in the \( y \)- and \( x \)-direction, respectively.

We can also estimate the stiffness, \( \sigma \sim e^{\kappa_{\text{kink}}/(k_B T)} \), for steps with various orientations from the corresponding kink creation energies, \( \kappa_{\text{kink}} \). (Here, \( k_B \) is the Boltzmann constant.) Our DFT interactions give \( \kappa_{\text{kink}} \) values of \( \sigma = 0.17, 0.03-0.07, 0.005-0.01 \) eV for diagonal, vertical, and horizontal steps, respectively. The very small latter value implies extensive meandering for horizontal steps [cf. Fig. 1(h)].

It is clear that the above geometric analysis of equilibrium island shape does not fully capture island shapes observed by STM at 500 K, or the corresponding simulated shapes from our atomic model. Both the latter have more prominent horizontal [110] edges. It should be emphasized that likely the experimental islands and certainly the simulated islands are not fully equilibrated. Also, we note that the geometric equilibrium analysis neglects step edge fluctuations which are quite prominent in experimental and simulated islands, particularly for horizontal [110] edges.

C. Non-equilibrium nanostructure growth kinetics and shapes

Our central interest here is in the modeling and elucidation of the experimental observations of growth kinetics. This requires an accurate characterization of diffusion pathways and barriers. Isolated Ni adatoms make diagonal hops between neighboring Ni-br and Al-br sites. The adsorption energy at the TS is \( E_{\text{ads,Ts}} = -4.26 \) eV, so terrace diffusion has an isotropic barrier of \( E_d = E_{\text{ads,Ts}} - E_{\text{ads,Ni}} = 0.40 \) eV. See Fig. 3(a). General edge diffusion and attachment-detachment barriers are determined from \( E_{\text{act}} = E_{\text{TS}} - E_{\text{init}} \), where \( E_{\text{init}} \) (\( E_{\text{TS}} \)) is the total energy in the initial (transition) state. This form automatically satisfies detailed-balance. Both energies are obtained from a sum of the relevant adsorption energy and all pair interaction energies. For \( E_{\text{init}} \), DFT values of relevant pair interactions are shown in the top part of Fig. 3(b). For \( E_{\text{TS}} \), we must also unconventionally assess pair interactions with one adatom at the TS and another at a nearby adsorption site. DFT values for this case are shown in the lower part of Fig. 3(b). Application of this approach for accurate determination of \( E_{\text{act}} \) opens the possibility for realistic treatment of kinetics in a broad range of complex multi-component epitaxial systems.

KMC simulation is performed to describe the process of island formation during deposition using our multisite LG model allowing population of adatoms at both Ni-br and Al-br sites. As indicated in Sec. II, we incorporated the above activation barriers into Arrhenius hopping rates. Experimental deposition fluxes are also used. One caveat is related to the feature that island formation in this system is dominated by heterogeneous nucleation, at least for 300 K and above. Thus, rather than model homogeneous nucleation on a perfect surface, we initially seed the surface with the appropriate density of islands to match experiment.

Our model is particularly effective at capturing and elucidating observed growth shapes. Irregular, vertically-elongated shapes are generated for deposition at 200–300 K as in experiment. See Figs. 1(e) and 1(f). To explain this behavior, note that edge diffusion is most active along diagonal steps with an effective barrier of \( E_e = 0.36 \) eV calculated for hopping from the most stable Ni-br site (see Fig. 4). In contrast, edge...
diffusion is strongly inhibited along horizontal or vertical steps where $E_c \sim 0.8 \text{ eV}$. Thus, one might expect a preference for Ni island growth shapes with diagonal steps, but no horizontal or vertical steps. This speculation is based on an analogy with square island growth shapes in fcc metal(100) homoepitaxy where diffusion is rapid along [011] horizontal/vertical close-packed steps (which dominate island growth and equilibrium shapes) and limited along [001] diagonal kinked steps (which are not prominent).

However, the detailed form of the Ni island growth shapes (in particular the tendency for vertical elongation of Ni islands) is more complicated, and not captured by the analogy with fcc metal(100) homoepitaxy. We find that corner rounding from diagonal to horizontal [110] steps is easier than to vertical [001] steps. In the TS for corner rounding, there is a “missing” pair interaction relative to diffusion along the diagonal edge. The magnitude of this missing interaction corresponds to the additional “kink Ehrlich-Schwoebel (ES)” barrier for corner rounding. See Fig. 3. The more vertically aligned missing interactions associated with rounding to vertical [001] steps are stronger than the more horizontally aligned missing interactions for rounding to horizontal [110] steps. Thus, edge atoms are more easily fed to the top and bottom of the growing island, producing elongation. Simulated islands for 300 K have an aspect ratio of $R = Y_v/X_v \sim 1.2$ (with very limited statistics) which substantially exceeds $R \sim 0.9$ for those at 400 and 500 K. This matches the trend in experiment where $R \sim 1.4$ at 300 K is well above $R \sim 1.0$ at 400 K and 500 K. Furthermore, the persistent flux of atoms to the top and bottom results in a typical step orientation at 300 K which is much steeper (measured relative to the x-axis) than the nominal slope of $\pm 1/\sqrt{2}$ for diagonal steps.

For deposition at $\sim 400$ K, the model also recovers the experimental observation of quasi-six-sided islands with prominent [001] vertical and diagonal steps. To understand growth behavior, we note that diffusion along horizontal and vertical steps becomes active at 400 K, potentially allowing such steps to form. (Actually, these high diffusion barriers are comparable to detachment barriers, so transport along the edges should occur via a combination of direct edge diffusion and detachment-reattachment.) However, anisotropic corner rounding induces a higher flux of edge atoms to [110] horizontal steps. As a result, these steps grow faster and thus “grow out” and disappear, resulting in quasi-six-sided islands as observed by STM [Fig. 1(g)]. As seen from experiment, simulation, and theory, these compact geometric islands at 400 K do not correspond to the equilibrium island shapes.

Depositing at 500 K in our simulations produces closer-to-equilibrated islands relative to deposition at lower $T$. We caution that detailed comparison between the experimental shape in Fig. 1(d) obtained from annealing at 500 K and the simulated shape obtained from deposition at 500 K in Fig. 1(h) is inappropriate given the different procedures for island preparation. It is computationally expensive to run the simulation for 30 min of post-deposition annealing at 500 K, motivating our choice to instead deposit at 500 K.) In any case, our simulated shapes tend to be better described as distorted eight-sided octagons rather than quasi-six-sided.

These simulated island shapes could be fit to distorted octagons as for the experimental shapes in Sec. III A. Indeed, it should be noted that for growth shapes, the distortion or lack of reflection symmetry about central horizontal or vertical axes is a natural consequence of the non-symmetric capture zones surrounding the islands.3 Note that the capture zones are primarily determined by island locations, which reflect randomness in nucleation or in defect locations. On average, atoms deposited in a capture zone are fed to the nearest edge of the corresponding island. Thus, asymmetry in capture zones produces distortion in island growth shapes for inhibited island shape relaxation. However, quantitative analysis by fitting is inhibited by very limited statistics, and comparison with experiment is dubious for 500 K as indicated above. Nonetheless, one does confirm an enhanced prominence of horizontal edges in simulated shapes with increasing $T$, e.g., with $X_{av}/Y_{av}$ increasing from $\sim 0.3$ at 400 K to $\sim 0.7$ at 500 K.

IV. DISCUSSION AND CONCLUSIONS

To summarize our study, we have demonstrated that with realistic atomistic multisite LG modeling, it is possible to obtain a detailed understanding of complex far-from-equilibrium growth shapes of epitaxial Ni nanostructures on NiAl(110). We can even succeed in capturing dramatic transitions in these shapes with varying $T$.

From a broader experimental perspective, the deposition of Ni analyzed here can be used as the first step to create more exotic nanostructures. For example, deposition of Ag subsequent to that of Ni on NiAl(110) can create imperfect “Ni core + Ag ring” structures. Such core-ring structures, which have been formed in previous sequential deposition studies,27,28 might be regarded as the 2D analogue of 3D core-shell
nanostructures. Figure 5(a) reveals a prominent Ag ring surrounding the Ni core in a caldera-like core-ring morphology, the taller ring reflecting a bilayer Ag(110) structure. For higher Ag doses, we find Ni islands are encapsulated within elongated bilayer Ag(110) islands or adlayers. See Fig. 5(b). As noted previously, formation of these structures can be used to check substrate orientation within the surface plane. The “Ni core + Ag ring” structures may be of particular interest since, e.g., decorating Ni step edges with Ag (or Au) can inhibit graphite formation and associated poisoning in steam reforming catalysis. This example also serves to illustrate the breadth or variety of possible atomic-scale island structures which might be obtained using binary alloy (versus single-component) crystalline substrates, in part due to multiple types of adsorption sites.

From a broader theoretical or modeling perspective, suitably general multisite LG models have the capability to describe diverse complex epitaxial heterostructures, including their far-from-equilibrium growth kinetics. We are also pursuing this approach in fundamental studies of alloy self-growth position.

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