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Keywords

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Disciplines

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Comments

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Formation of Irregular Al Islands by Room-Temperature Deposition on NiAl(110)

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ABSTRACT

STM studies reveal that irregular non-equilibrium two-dimensional Al islands form during deposition of Al on NiAl(110) at 300 K. These structures reflect the multiple adsorption sites and diffusion paths available for Al adatoms on the binary alloy surface, as well as the details of inhibited edge diffusion and detachment-attachment kinetics of Al adatoms for numerous distinct step edge configurations. We attempt to capture these features by multi-site lattice-gas modeling incorporating DFT energetics for adatoms both at adsorption sites and transition states. This formulation enables description and elucidation of the observed island growth shapes.

INTRODUCTION

A rich variety of complex far-from-equilibrium morphologies are known to form in homoepitaxial growth of single-component metal films (A on A) at lower deposition temperatures, T . This behavior occurs despite the feature that these systems have very simple equilibrium states [1,2]. The complex morphologies result from kinetic limitations on step edge diffusion or interlayer diffusion on the time-scale of film growth. Similar behavior is observed in heteroepitaxy (A on B) at least for lower lattice misfit, but distinct strain-induced features generally occur for higher misfit [3]. Rather than the single-component substrates employed in the above studies, our focus here is in the use of binary alloy substrates where a variety of far-from-equilibrium structures should also form under low- T deposition. We are motivated by the potential for these systems to provide new opportunities to guide the creation of thin film nanostructures with desired properties. Interestingly, despite this potential, well-controlled ultra-high-vacuum (UHV) analyses of film growth on binary alloys (A or B on BC) are rare [4-7].

In this paper, we consider submonolayer deposition of Al on NiAl(110) at low $T = 300$ K, corresponding to far-from-equilibrium growth with effectively frozen substrate dynamics. However, it is appropriate to comment on a previous study of Al deposition on NiAl(110) at high $T \approx 900$ K, where the NiAl substrate is actually quite dynamic or "reactive" [4]. In the initial stages of Al deposition at around 900 K, half the deposited Al replaces excess Ni residing at Al sites in the bulk. This displaced Ni diffuses to the surface and combines with the other half of the depositing Al to form a new stoichiometric NiAl(110) alloy adlayer [4]. Once the excess Ni concentration in the substrate is sufficiently reduced, the system turns to another mechanism involving bulk defects to bring Ni to the surface to perpetuate alloy growth [4]. One could imagine that at lower T , the depositing Al could at least extract excess Ni at Al sites in the surface layer. However, at 300 K, our density functional theory (DFT) analysis indicates that even this process is inactive, i.e., Al is effectively deposited on an inert substrate.

Our development of atomistic-level modeling for Al deposition on NiAl(110) is aided and validated by comparison with experimental STM observations. There are complications for

Al/NiAl(110) not seen, e.g., in Al homoepitaxy, such as multiple types of adsorption sites and diffusion pathways. Thus, a realistic description requires multi-site lattice-gas (LG) modeling [5,6]. Furthermore, an accurate treatment of far-from-equilibrium growth kinetics requires precise determination of diffusion barriers including those for edge diffusion and attachment-detachment for many local step edge configurations. This is achieved here utilizing high-level DFT to probe energetics for adatoms not just at adsorption sites but also at transition states for diffusion [5,6]. Model behavior can then be assessed via kinetic Monte Carlo (KMC) simulation.

EXPERIMENTAL DETAILS AND RESULTS

The experiments were performed in a UHV chamber with a base pressure of $\leq 4 \times 10^{-11}$ Torr. The chamber is equipped with an Omicron VT-STM as well as other standard facilities for sample preparation and characterization (Sputter gun, LEED, AES and XPS). The NiAl(110) single crystal was grown using the Bridgman technique. A sample was polished using standard metallographic techniques and mounted on an Omicron heater. The sample was cleaned by repeated cycles of 20 min of Ar^+ sputtering (1.5 keV at 300 K) followed by annealing to 1250 K for 1 h. This resulted in a clean surface with broad terraces with an average width of 200 nm. Al was evaporated from a homemade deposition source. The base pressure was below 9×10^{-10} Torr during deposition and the purity of the film was checked by XPS. Flux calibration of the source was achieved by measuring the coverage directly from the STM images in the submonolayer regime. Sample orientation was checked by co-deposition of Ag which forms bilayer islands elongated in the [001] direction [7]. STM data was analyzed using WSxM software.

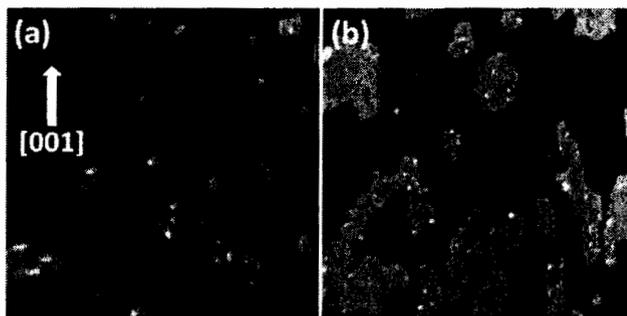


Figure 1. STM images ($50 \times 50 \text{ nm}^2$) of Al deposition on NiAl(110) at 300 K: (a) 0.1 ML with $F = 0.0033 \text{ ML/s}$; (b) 0.36 ML with $F = 0.0030 \text{ ML/s}$.

Al deposition at 300 K with flux $F = 0.003 \text{ ML/s}$ produces islands with a density of $\sim 1 \times 10^{-2} \text{ nm}^{-2}$ at $\sim 0.1 \text{ ML}$. However, this value mainly reflects the surface defect density as island formation is dominated by heterogeneous nucleation at such surface defects rather than by homogeneous nucleation [5]. The prominence of heterogeneous nucleation seems to be a general feature for deposition on alloy surfaces, as opposed to deposition on single-component single-

crystal surfaces [7]. Defects, such as those due to surface enrichment of one component, should generally be expected for alloys. In contrast to island density, island growth shapes are likely not significantly affected by the details of nucleation (e.g., the heterogeneous versus homogeneous pathway). From the STM images shown in figure 1, we see that smaller Al islands tend to be fairly compact and geometric with a propensity for [001] steps, but islands become irregular during growth. From these observations, it is clear that edge diffusion of aggregated Al adatoms is inhibited at 300 K. Provided that edge diffusion is somewhat operative, one expects a transition from compact shapes for smaller islands (which, in general, are growth rather than equilibrium shapes) to irregular shapes for larger islands. The latter reflects the longer distance which edge atoms must travel to reach more highly-coordinated kink sites [2,8].

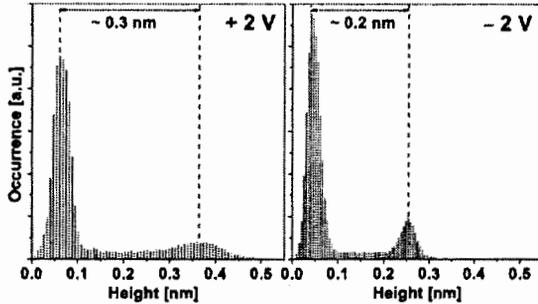


Figure 2. Tip-bias dependence of island height as reveals through film height distributions at 0.26 ML: lower (upper) peaks comes from the substrate (islands).

Another feature revealed in these studies is a strong tip bias-dependence of the measured apparent island height. This measured height is ~ 0.2 nm for a -2 V tip bias versus ~ 0.3 nm for a $+2$ V tip bias. Consistent results for this behavior come from either line scans or film height distributions. Data for the latter are shown in figure 2.

MULTI-SITE LATTICE-GAS (LG) MODEL DEVELOPMENT

DFT analysis, as well as comparison with STM observations, is invaluable in guiding model development. Specifically, DFT provides key energetic input parameters. Our analysis uses the plane-wave based VASP package [9] within the generalized gradient approximation using the PBE functional [10], and applying the PAW approach to treat electron-ion interactions [11].

To develop a detailed atomistic-level understanding of Al/NiAl(110), we first consider the binding and diffusion of an *isolated* Al atom on NiAl(110), the behavior of which is illustrated schematically in figure 3(a). Al prefers the short bridge site between two Ni aligned in the [100] direction (which is vertical in our schematics). This site is denoted as Ni-br below. Isolated Al diffuses preferentially in the [001] direction between Ni-br sites over an on-top Ni site transition state (TS) with a barrier of $E_d = 0.30$ eV. Al can also hop in the [110] direction from the on-top Ni site (Ni-top) over an Al short bridge (Al-br) site with a barrier of $E_d = 0.51$ eV. In contrast to behavior for isolated adatoms, diffusion of *aggregated* Al along island edges occurs

predominantly via diagonal hops where the TS is a bridge-site between diagonally neighboring Ni and Al atoms (NiAl-br). We will describe the associated barrier determination below.

We consider a multi-site LG model where Al atoms within islands can populate both the Ni-br and Al-br sites, but we do not allow population of other sites. (See below for a critique of this limitation.) To prescribe the associated *adlayer thermodynamics*, we assess from DFT the interactions between Al adatom pairs at both types of sites for various separations. See figure 3(b). First, we describe consequences for island structure in this model incorporating just these pair interactions. The energy per adatom is lower for complete “dense” adlayers of Al populating *both* Ni-br and Al-br sites than for complete “dilute” adlayers populating just Ni-br or just Al-br sites: -4.68 eV vs. -4.00 eV (Ni-br) or -3.36 eV (Al-br) per Al adatom. This behavior tracks DFT energetics for complete adlayers for these three possibilities. The preference for “dense” over “dilute” islands reflects the presence of strong attractions between Al at diagonally neighboring Ni-br and Al-br sites which off-set the cost of populating the less favorable Al-br sites. Finally, we note that knowledge of these pair interactions also allows prediction of other key thermodynamic features. For example, for dense Al islands, one finds that [100]-oriented steps with Al on Ni-br sites are slightly favored over diagonal or horizontal steps.

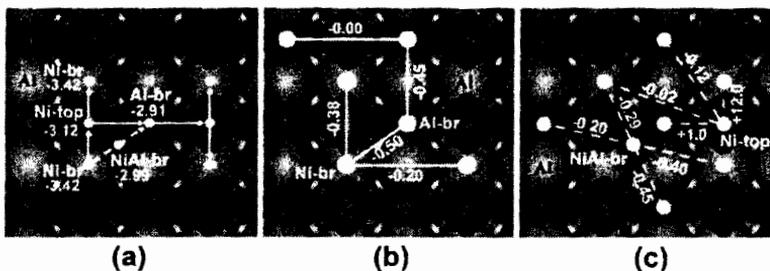


Figure 3. (a) Al adsorption energies in eV at various sites (binding < 0) and Al diffusion paths; pair interactions in eV (attractions < 0) between Al adatoms: (b) with both Al at adsorption sites; (c) with one Al at a TS and the other at an adsorption site.

Correct treatment of non-equilibrium *growth kinetics* also requires an accurate description of diffusion not just for isolated adatoms, but also for edge diffusion and attachment-detachment processes for all relevant pathways and for all local island edge configurations. Our model includes hops between Ni-br and Al-br sites with barriers determined from $E_{\text{act}} = E_{\text{TS}} - E_{\text{init}}$, where E_{init} (E_{TS}) is the total energy in the initial (transition) state. Both energies are obtained from a sum of the relevant adsorption energy and all pair interaction energies. The adsorption energies are provided in figure 3(a). Pair interactions relevant for the initial state are provided in figure 3(b). However, to determine E_{TS} , we must also assess a distinct class of pair interactions with one adatom at a TS and another at nearby adsorption sites. See figure 3(c). One caveat with the above formulation is that the true TS could be an initial or final unstable Al-br site (rather than a Ni-top or NiAl-br site), a feature checked for each Al hop. Finally, Arrhenius hop rates are selected with the above barriers and with prefactors $\nu = 10^{13}/\text{s}$. Detailed-balance is automatically satisfied. These rates provide input to KMC simulation of our atomistic multi-site LG model in which adatoms can reside at both Ni-br and Al-br sites, and where deposition and hopping are

implemented with the appropriate relative probabilities. This formulation provides a powerful general strategy for modeling kinetics in epitaxial alloy thin film systems.

Finally, we briefly comment on some issues and limitations for our modeling. DFT, which is used to guide selection of energetic input parameters, has its limitations, and adjusting some interactions can better describe finer details of island shapes. We do not include trio, quartet, etc. adatom interactions, noting that the pairwise contributions capture key adlayer thermodynamics. Also, exchange with the substrate and concerted terrace diffusion processes are not included, but we have checked that they are energetically prohibitive at 300 K. More significantly, we neglect strain effects although dense Al islands are subject to compressive strain due to lattice mismatch with NiAl(110). Local strain relief induces Al at Al-br sites to sit higher than those at Ni-br. We also neglect alternative energetically-competitive monolayer island structures with so-called "square-hex motifs", where 3-fold-type sites in addition to Ni-br and Al-br sites are populated. These structures have been discussed for Au and Ag on NiAl(110) [6,7].

MULTI-SITE LG MODELING: KMC SIMULATION RESULTS

Results from KMC simulations of the model described above are presented here and compared with experiment. Our central focus is description of the nucleation and growth of Al islands. This process is mediated by strongly anisotropic terrace diffusion. The most stable dimer is vertically aligned on Ni-br sites with a binding energy of $E_b = 0.38$ eV (the vertical dimer on Al-br sites being destabilized by a large adsorption site penalty). This large E_b would imply irreversible island formation for homogeneous nucleation [2]. However, as noted above, heterogeneous nucleation dominates in this system, the enhanced stabilization of larger islands implying effectively irreversible island formation at 300 K. The simulated island density at 300 K from our model including only homogeneous nucleation (i.e., no defects) is far below experiment. This result indicates the dominance of heterogeneous nucleation in experiment.

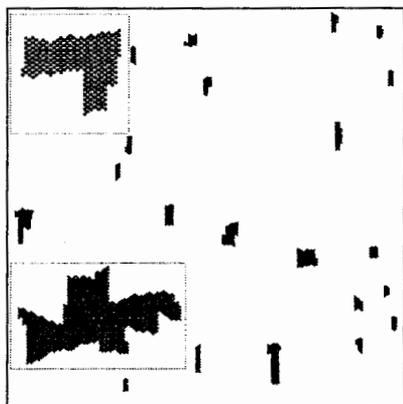


Figure 4. Simulation (size: 43×43 nm²) of growth of multiple Al islands at 300 K with $F = 0.0033$ ML/s. Insets show structures of two larger islands.

Our simulations do recover trends in experimental island shapes despite the model limitations described above. Note that the island density determines the typical area of “capture zones” surrounding islands. This area controls the rate at which islands incorporate aggregating atoms, which in turn has some influence on island shape (higher aggregation rates inhibiting shape relaxation). Thus, to appropriately describe experimental conditions, we seed the system with a suitable density of Al island nuclei. Then, islands grow irreversibly about these during subsequent deposition. Results shown in figure 4 are consistent with experiment, i.e., a tendency for [001] steps at least in smaller islands, and the development of irregular growth of larger islands. Note that in simulations incorporating only the vertical and horizontal diffusion pathway for isolated Al, edge diffusion becomes effectively inoperative producing highly ramified fractal islands. Edge diffusion is activated via diagonal hops, especially along vertical edges ($E_{\text{edge}} \sim 0.5$ eV), facilitating formation of the island structures seen in experiment. Thus, multi-site multi-diffusion-path LG modeling is essential to capture growth behavior in this system.

SUMMARY

Deposition of Al at 300 K on NiAl(110) produces far-from-equilibrium dense monolayer islands. Multi-site LG modeling incorporating DFT-guided energetics for both interactions and barriers allows a realistic treatment of far-from-equilibrium growth in this complex system. This approach has general applicability for single- and multi-component epitaxial systems.

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