Directing Anisotropic Assembly of Metallic Nanoclusters by Exploiting Linear Trio Interactions and Quantum Size Effects: Au Chains on Ag(100) Thin Films

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Directing Anisotropic Assembly of Metallic Nanoclusters by Exploiting Linear Trio Interactions and Quantum Size Effects: Au Chains on Ag(100) Thin Films

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Supporting Information

ABSTRACT: Discovery and understanding of mechanisms for kinetically controlled growth of metal nanoclusters can be enabled by realistic atomistic-level modeling with ab initio kinetics. KMC simulation of such a model for Au deposition on Ag(100) films reveals the formation of single-atom-wide Au chains below 275 K, even though 2D islands are thermodynamically preferred. Chain formation is shown to reflect a combination of strong linear trio attractions guiding assembly and a weak driving force and slow rate of transformation of 1D chains to 2D islands (or sometimes irreversible rounding of adatoms from chain sides to ends). Behavior can also be tuned by quantum size effects: chain formation predominates on 2-monolayer Ag(100) films supported on NiAl(100) at 250 K for low coverages but not on 1- or 3-monolayer films, and longer chains form than on bulk Ag(100). Our predictive kinetic modeling shows the potential for simulation-guided discovery and analysis of novel self-assembly processes.

Dramatic advances have been achieved in the experimental control of nonequilibrium shapes during the synthesis of metallic nanocrystals or nanoclusters (NCs). These shapes strongly impact, for example, catalytic or plasmonic properties. NC self-assembly via solution-phase synthesis or via deposition onto smooth surfaces can produce: 3D NCs with spherical, polyhedral, or other shapes (which are truncated for supported NCs); 2D plateslets in solution or monolayer islands on surfaces; and 1D NC rods, wires, or chains. For solution-phase synthesis, a substantial heuristic understanding has been developed for these kinetically controlled shapes accounting for, for example, the effect of capping agents on facet energies and growth kinetics and the role of inhibited periphery diffusion; however, such synthesis is still regarded as art versus science, and detailed molecular-level understanding is lacking. For assembly of epitaxial NCs on crystalline surfaces, a more detailed understanding has been achieved via atomistic lattice-gas modeling and kinetic Monte Carlo (KMC) simulation. Here there is an appreciation that the finer details of periphery diffusion, such as inhibited kink rounding, step edge crossing, or interfacet transport, strongly impact shape. Initial misperceptions regarding factors inducing nonequilibrium dendritic shapes and elongated shapes and the subtle effect on shape of additives decorating the NC periphery were corrected as a result of such modeling. Our focus in this study is on anisotropic NC shapes familiar for Au, Ag, and other metals. Specifically, we consider diffusion-mediated self-assembly of epitaxial Au NCs by deposition onto metal surfaces. Nanowires are often formed by deposition onto anisotropic metal or semiconductor surfaces or onto vicinal surfaces where steps direct assembly, however, we will demonstrate an alternative strategy that exploits many-body adatom interactions, anticipating that linear trio attractions could induce the formation of atomic chains even on isotropic surfaces. Although many-body interactions are generally weak, we show that they are significant for Au and can be tuned (together with other key energetics) by exploiting quantum size effects (QSEs) to facilitate anisotropic assembly. QSE in supported metal films of a few monolayers (MLs) is associated with electron confinement, the variation of energetics reflecting commensurability of the Fermi wavelength with nanoscale film thickness. Prominent examples of the influence of QSEs include the formation of ultralat deposited Ag films and tunable nucleation reaction and oxidation kinetics on thin metal films.

An obstacle to experimental identification of optimal surface systems for anisotropic assembly guided by many-body interactions and QSE is the many possible combinations of deposited atoms, metallic thin films, and supports. Thus, a capability for predictive atomistic-level modeling would greatly facilitate simulation-guided discovery of appropriate systems. However, a challenge for such modeling is the need to precisely describe both system thermodynamics and also distinct barriers for terrace diffusion and for edge diffusion and corner rounding for all relevant edge configurations (barriers to which NC...
formation is exquisitely sensitive). 26,27 We implement a procedure described below to obtain such barriers at the level of ab initio density functional theory (DFT). These provide precise input for KMC simulation of the NC assembly processes on the physical time scale. The Supporting Information (SI) provides details of our DFT and KMC analyses.

Another challenge is that most DFT analyses of thin films consider unsupported slabs due to both computational efficiency and uncertainty regarding the film-support interface; however, predictive modeling requires more demanding analysis for supported films with correct interface structure. Thus, while performing efficient exploratory analysis for unsupported slabs, we focus on judiciously selected supported thin film systems with known interface structure. In addition, we select a low-strain system as approaches for efficient precise determination of various edge diffusion barriers in the presence of significant strain are not available.

The specific systems considered here involve deposition of Au on Ag(100) thin films supported on Al-terminated NiAl(100), 28 and for comparison on freestanding Ag(100) slabs and bulk Ag(100). The near-perfect lattice match between fcc Au and Ag, and between Ag(100) and NiAl(100) implies minimal lateral mismatch strain. (Flat Ag(100) thin films on NiAl(100) can be created by deposition at ∼300 K due to facile interlayer diffusion on Ag(100).) 5 Surface diffusion involves hopping of Au adatoms between nearest-neighbor (NN) 4-fold-hollow (4fh) adsorption sites through bridge-site transition states (TS). DFT analysis finds terrace diffusion barriers for isolated Au adatoms of Ef = 0.45, 0.55, and 0.50 eV for 1–3 ML supported Ag(100) films, Ef = 0.55, 0.54, 0.52, and 0.53 eV for 2–5 ML Ag(100) slabs, and Ef = 0.53 eV for bulk Ag(100), respectively. Diffusion barriers at island or chain edges are determined from Eact = Ef + ΦTS − Φint, where Φact (ΦTS) denotes the total lateral interaction energy in the initial state (in the TS). Φint (ΦTS) is obtained by summing conventional (unconventional) ω (φ) interactions between the hopping adatom at its initial site (at the TS) and other adatoms at nearby 4fh sites. 26 See below. Our stochastic KMC simulations of Au island and chain formation include random deposition of Au and hopping between NN 4fh sites with probabilities proportional to the physical rates: F = 0.006 ML/s for deposition and h = ne−E(s)/kT for hopping at surface temperature T with ν = 3 × 1012 s−1. We thereby track the diffusion-mediated nucleation, growth and possible coalescence of islands or chains on the surface (starting from a clean surface without any preassigned bias in the pathways for NC formation).

System thermodynamics is determined by ω interactions between adatoms at 4fh adsorption sites. For fcc(100) systems, the magnitude of second NN pair- and compact trio-interactions is usually only ∼10% of NN pair interactions; 15 however, we find stronger linear trio interactions for Au on bulk Ag(100), which are further enhanced by QSE for Ag(100) thick films, thereby guiding NC formation. The dominant ω interactions are NN attractions (ωT1 < 0 for separation d = a), second NN pair attractions (ωT2 for d = √2a), and also linear (ωT1) and bent (ωT2) trio interactions. Determination of barriers for edge diffusion also requires a knowledge of ϕ interactions, with one adatom at the bridge TS for hopping and other adatoms at nearby 4fh sites. The dominant ϕ interactions are short-range pairs (ϕ_{T1} for d = √5a/2) and three types of trios (ϕ_{T12}, ϕ_{T13}, ϕ_{T23}). See Scheme 1 and Table 1 for ω and ϕ values used in our KMC simulations.

The selected sets of interactions can be calculated directly for isolated pairs or trios of atoms in a large supercell, but this neglects some longer-range and many-body interactions. For our analysis, it is critical that the chosen ω interactions exactly recover the thermodynamic driving force for conversion of 1D chains to 2D islands. This is not achieved for any subset of directly calculated ω values. Thus, instead we use (slightly) modified effective ω values that recover exactly DFT values for the lateral interaction energy per adatom for single-atom wide chains, E1D, and for a complete 2D adlayer, E2D. We find that E2D < E1D, so 2D islands are always thermodynamically preferred over 1D chains for our systems. In addition, we determine the lateral interaction energy per atom for a (2 × 2) adlayer, E_{(2×2)}, and for an isolated 2 × 2 square island, E_{square}. Then, effective ω values follow from E_{1D} = ω_{P1} + ω_{T11}; E_{2D} = 2ω_{P1} + 2ω_{P2} + 2ω_{T1} + 4ω_{T2}; E_{(2×2)} = 2ω_{P2} and E_{square} = ω_{P1} + ω_{P2}/2 + ϕ_{T12} (see SI).

As a preliminary analysis, we assess ω interactions for Au on bulk Ag(100) and the dependence on thickness for freestanding Ag(100) slabs. For bulk Ag(100), the linear trio attraction ω_{T1} = −0.065 eV is unusually strong relative to the NN pair attraction ω_{P1} = −0.201 eV (∼30% versus the typical ∼10%). Furthermore, ω_{T1} is enhanced due to QSE in thin Ag(100) slabs: ω_{T1} = −0.069, −0.088, −0.102, and −0.087 eV compared with ω_{P1}=−0.164, −0.111, −0.121, and −0.197 eV for 2–5 ML Ag(100) slabs, respectively (with ω_{T1}/ω_{P1} highest for 3–4 ML slabs). KMC simulations show that these strong ω_{T1} do guide the formation of single-atom-wide chains at 250 K, more prominently on a 4-ML slab than bulk Ag(100); see Figure 1ab.

Behavior for supported films generally differs from that for unsupported slabs due to strain (absent for Au/Ag/NiAl(100)), differing chemical environments (a minor effect for ≥2 ML films), and QSE. Electron confinement in metal-on-metal films, a requirement for QSE, can still occur due to a gap or pseudo gap in the normal direction or just a depletion in the density of states near the Fermi level (as expected for NiAl); however, one expects a “phase shift” in the variation of energetics with thickness relative to that for a freestanding slab. 35 Different boundary conditions for the electron wave functions at the film-substrate versus the film-vacuum interface produce this shift. We have performed computationally demanding DFT analyses of energetics for Ag(100) films on Al-terminated NiAl(100). Indeed, curves for ω versus thickness show the same trends for Ag(100) slabs and supported films but are shifted relative to each other by 1 to 2 ML. See SI Figure 1. Simulated island and

Scheme 1. Conventional (ω) and Unconventional (ϕ) Interactions between Au Adatoms Incorporated into KMC Simulations

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Table 1. ω and ϕ Interactions (in eV) Used in KMC Simulations for Au on 1–3 ML Supported and 4 ML Unsupported Ag(100) Films and Bulk Ag(100)

<table>
<thead>
<tr>
<th></th>
<th>1 ML/NiAl</th>
<th>2 ML/NiAl</th>
<th>3 ML/NiAl</th>
<th>4 ML</th>
<th>∞ ML (bulk)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ωP1</td>
<td>−0.276</td>
<td>−0.131</td>
<td>−0.183</td>
<td>−0.121</td>
<td>−0.201</td>
</tr>
<tr>
<td>ωP2</td>
<td>−0.006</td>
<td>+0.052</td>
<td>+0.047</td>
<td>+0.071</td>
<td>+0.030</td>
</tr>
<tr>
<td>ωT1</td>
<td>−0.103</td>
<td>−0.115</td>
<td>−0.104</td>
<td>−0.102</td>
<td>−0.065</td>
</tr>
<tr>
<td>ωT2</td>
<td>+0.062</td>
<td>+0.011</td>
<td>+0.011</td>
<td>−0.001</td>
<td>+0.016</td>
</tr>
<tr>
<td>ϕP1</td>
<td>−0.335</td>
<td>−0.237</td>
<td>−0.211</td>
<td>−0.130</td>
<td>−0.141</td>
</tr>
<tr>
<td>ϕT1</td>
<td>+0.244</td>
<td>+0.105</td>
<td>+0.100</td>
<td>+0.078</td>
<td>+0.044</td>
</tr>
<tr>
<td>ϕT2</td>
<td>+0.043</td>
<td>−0.013</td>
<td>−0.032</td>
<td>−0.031</td>
<td>−0.012</td>
</tr>
<tr>
<td>ϕT3</td>
<td>−0.055</td>
<td>−0.056</td>
<td>−0.073</td>
<td>−0.086</td>
<td>−0.031</td>
</tr>
</tbody>
</table>

chain distributions are shown in Figure 1c−e for Au deposition at 250 K on 1−3 ML supported Ag(100) films. Short chains form in all systems at 0.01−0.02 ML; however, by 0.04 ML, prominent formation of longer chains occurs only for 2-ML supported films, with a tendency to form 2D islands on 1- and 3-ML films. This behavior does not simply correlate with the strength of ωT1.

One can also assess the T dependence of self-assembly. For sufficiently high T, thermodynamics should dominate producing 2D islands. For lower T, inhibited terrace diffusion should limit chain length or 2D island size. These expectations are confirmed by the KMC simulation results shown in Figure 2 for 2-ML supported films and bulk Ag(100). In both cases, 2D islands dominate at 275 K. Chain length grows upon increasing T from 225 to 250 K, especially for 2-ML supported films where 2D islands also form at 250 K.

To provide a deeper understanding of the essential features controlling chain self-assembly, we now go beyond just reporting KMC results to dissect the kinetics of key processes controlling behavior.

Chain End-to-Side Edge Diffusion. Previous studies of chain formation on anisotropic fcc(110) surfaces suggested that a key factor is anisotropic corner rounding (facile edge diffusion from chain sides-to-ends and inhibited diffusion from ends-to-sides) and inhibited detachment from chain ends (thereby blocking reattachment on sides). Earlier studies incorrectly identified anisotropic terrace diffusion as key. Thus, here we characterize edge diffusion in Figure 3a and Table 2. The barrier, E_e, for diffusion along chain sides is always much lower than E_d, and the barrier, E_e→s, for side-to-end rounding is much lower than that for end-to-side rounding, E_e→s. Thus, corner rounding is anisotropic. Of particular relevance is the rate for the slowest end-to-side rounding process, h_e→s = ν_e−E_e→s/(k_BT), relative to the typical rate k_agg = F/N_ch for aggregation of deposited adatoms with individual chains for chain density N_ch. Naturally, k_agg will exceed h_e→s at the onset of deposition where
N\textsubscript{ch} is low, so edge-to-side rounding is effectively irreversible promoting initial chain formation; however, for 1–3 ML supported films (and for freestanding slabs), the rate for the slowest end-to-side rounding process, $h_{\text{end}}$, at 250 K is well above the typical $k_{\text{agg}} \approx 1.5–6$ s$^{-1}$ for $N_{\text{ch}} \approx (1–4) \times 10^3$ site at coverage 0.04–0.1 ML with $F = 0.006$ ML/s. Thus, end-to-side rounding is facile on the time scale of chain growth. In contrast, this is not the case for Au on bulk Ag(100). Finally, the rate for detachment from chain ends, $h_{\text{det}} = e^{-E_{\text{det}}/k_{\text{B}}T}$ with $E_{\text{det}} = E_0 - \omega_1 - \omega_2$ (well above $E_{\text{end}}$), is always very low on the time scale of deposition, so this process is inactive.

Additional insight comes from “atom tracking” KMC.\textsuperscript{29,31} See Figure 3b,c. Here initially deposited Au atoms are colored yellow and subsequently deposited atoms are red. With no detachment or end-to-corner rounding, the center of chains would be yellow and the ends red; however, simulations for 2-ML supported films reveal color mixing. This reflects active end-to-side rounding: earlier deposited yellow atoms leave ends, just aggregated red atoms then join ends, and the gold atoms subsequently rejoin the end by side-to-end rounding. We find significantly less color mixing for Au deposition on bulk Ag(100) consistent with irreversible side-to-corner rounding.

To summarize, Au formation on bulk Ag(100) derives from effectively irreversible side-to-end rounding ($E_{\text{end}} = 0.643$ eV) and negligible detachment from chain ends ($E_{\text{det}} = 0.796$ eV). For other systems, end-to-side rounding is facile (but not end detachment) except for very low coverage, and we propose that differing behavior partly derives from differing driving forces, $\Delta E_{1D \rightarrow 2D} = E_{2D} - E_{1D}$ for the formation of 2D islands from 1D chains; see Table 2. Specifically, those cases with the most prominent chain formation have the weakest driving force, but because end-to-side rounding is facile for 1-ML supported films, how can chains survive conversion to thermodynamically preferred 2D islands?

**Transformation from 1D Chains to 2D Islands.** Chain survival when end-to-side rounding is facile must reflect the feature that there is a significant effective barrier for the transformation of 1D chains into hybrid 1D-2D structures and finally into 2D islands. This transformation involves stochastic evolution in the complex space of possible nanocluster configurations. Thus, it is convenient to consider a simplified scenario wherein a long chain transforms to hybrid 1D–2D structures, $\{m\}$, by moving various numbers, $m$, of atoms from one end to one side (so $m$ is the “reaction coordinate”). The energy cost, $\Delta E_{\text{trans}}$, increases from $\Delta E_{\text{trans}} = 0$ over the effective barrier before decreasing like $\Delta E_{\text{trans}} \approx m \Delta E_{1D \rightarrow 2D} < 0$, for large $m$. Larger $|\Delta E_{1D \rightarrow 2D}|$ makes it more likely that the “biased walk” through configuration space will evolve to a 2D island versus returning to the chain. To concretely illustrate this behavior, consider the special subset of configurations where $m = n(n - 1)$ atoms at the end of a long chain are moved to form an $n \times n$ square located at the end of the chain; see Figure 4a. One can show that

$$\Delta E_{\text{trans}} = \Delta E_{\text{trans}} = e_0 + (n - 2)e_1 + (n - 2)^2e_2,$$

for $n \geq 2$

where $e_0 \equiv \Delta E_{1D \rightarrow 2D} = 0$, $e_1 \equiv 2\omega_1 + 2\omega_2$, and $e_2 \equiv \Delta E_{1D \rightarrow 2D} = E_{2D} - E_{1D}$. The variation of $\Delta E_{\text{trans}}$ with $n$ for supported films is shown in Figure 4b and mimics classic 2D nucleation theory.\textsuperscript{32} From Table 2, it is clear that $\Delta E_{\text{trans}}$ is highly sensitive to $n$, but it shows the most strongly from $E_{\text{end}} = 0$ and has the weakest dependence for 2-ML-Ag/NiAl (and for 4-ML slabs) versus 1-ML- and 3-ML-Ag/NiAl. The extent of increase reflects the strength of both linear trio attractions and of second NN pair and bent trio repulsions. Thus, the transformation to 2D islands is most difficult in the first two cases.

The above analysis shows explicitly energetics of the 1D to 2D transformation pathway only for a special subset of configurations; however, there is some evidence from simulations that these configurations are relevant for the transition to 2D islands. Thus, the above behavior might reflect the minimum energy path through the complex configuration space but likely also reflects trends in energetics for more complex pathways. Note also that relative to the above quasi-equilibrium analysis, evolution from 1D chains to 2D islands is
enhanced by deposition, which creates a supersaturation of adatoms on chain sides. This feature should facilitate the formation of new rows in 2D structures.

In summary, unusually strong linear trio attractions are shown to drive the formation of single-atom-wide Au chains on bulk Ag(100) and also on certain Ag(100) thin films sometimes enhanced by QSE. This behavior is demonstrated by KMC simulations of a predictive atomistic model with ab initio kinetics; however, deeper understanding of this behavior follows from a targeted analysis of kinetics of key edge diffusion and 1D-to-2D NC transformation processes. For Au deposited on bulk Ag(100), side-to-end rounding is effectively irreversible, naturally inducing chain formation. For Au deposited on thin Ag(100) films, modified energetics due to QSE impact chain formation. Often end-to-side rounding is facile, so chain formation and survival here is more subtle, reflecting an effective barrier for transformation from 1D to 2D structures.

**REFERENCES**


