Accelerated coarsening of Ag adatom islands on Ag(111) due to trace amounts of S: Mass-transport mediated by Ag–S complexes

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Abstract
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Keywords
Ames Laboratory, Materials Science and Engineering, Mathematics, adsorbed layers, density functional theory, monolayers, reaction kinetics theory, reaction-diffusion systems, scanning tunnelling microscopy, silver, silver compounds, surface chemistry, surface diffusion

Disciplines
Materials Science and Engineering | Mathematics | Physical Chemistry

Comments

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I. INTRODUCTION

Coarsening phenomena (also referred to as ripening or sintering) are ubiquitous in materials science and chemical physics for two-phase materials ranging from solid alloys to surface deposits to liquid droplets.1 Such processes frequently involve the evolution of distributions of clusters (or islands or droplets) of one phase embedded within another wherein the number of clusters decreases and their mean size increases. The driving force for such evolution is reduction of the excess free energy associated with the interface region between phases. The underlying mechanism is often Ostwald ripening (OR), which involves transfer of material between smaller and larger clusters, so that the latter grow at the expense of the former.

Coarsening of surface deposits is of particular interest in the context of nanofabrication processes, which typically utilize deposition techniques. Here, a key challenge and goal is to ensure stability of the surface nanostructures thus created. Extensive investigations have been performed into the coarsening of three-dimensional island distributions in heteroepitaxial systems2 and of two-dimensional (2D) island distributions in homoepitaxial systems.3,4 For the latter, which will be considered in this paper, a particularly detailed level of analysis and understanding has been possible. Most of these studies have been performed for pristine impurity-free systems under ultrahigh-vacuum (UHV) conditions. However, operation of nanoscale devices may involve non-UHV conditions where the presence of chemical additives in the environment could impact stability and coarsening. Thus, it is appropriate to perform systematic studies of the influence of different additives on nanostructure evolution.

In fact, observations exist for a variety of systems, indicating that the presence of even minute amounts of a chemisorbed additive can have a significant impact on mass transport on metal surfaces. Examples where the additive is a chalcogen (e.g., sulfur, S, or oxygen, O) either by design or by default include

(i) accelerated metal mass transport by exposure to S of Ag surfaces,7
(ii) enhanced sintering of supported Pt nanoparticles8 presumed due to the formation of PtO2,
(iii) accelerated decay of nanostructures on the Au(111) surface after exposure to air, most likely due to oxygen,9
(iv) extensive chemisorption-induced restructuring of Au(111) surfaces following exposure to organothiols,10 to S,11–13 and of O (Ref. 14). Here, mass transport of Au can be induced by lifting of the surface reconstruction and the associated mass density change in the surface layer and by the formation of surface sulphide for the case of S adsorption,
(v) enhanced release of Au adatoms from edges of small Au islands, and thus enhancing sintering of such nanoclusters, proposed to occur in the presence of S or O,15 and
(vi) massive S-induced transformation of arrays of Co nanoparticles on Au(111) into a cobalt sulfide phase mediated by the formation of Co3S2 complexes,16 as well as the transformation of Co nanoparticles at step edges on Ag(111) into various sulfide structures.17

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Systematic studies also exist for chalcogen-enhanced coarsening and decay of 2D adatom island distributions prepared by deposition, both for Ag/Ag(100) exposed to O (Refs. 18–20) and for Cu/Cu(111) exposed to S.21–23 The common proposal in these studies is that facile formation of a mobile metal-chalcogen complex or cluster enhances mass transport relative to that by metal adatoms. A basic requirement for such enhanced transport is that the sum of the formation energy and the diffusion barrier for the complex should be lower than that for metal adatoms.20,23 The latter sum determines the maximum attainable rate of coarsening, at least assuming that there is no additional barrier for attachment of the mass-transporting adspecies.

It is appropriate to also mention that a different additive, hydrogen, has been observed to both enhance24 and inhibit25 mass transport on metal surfaces and also to enhance mass transport on Si surfaces.26 In addition, there is a vast body of literature on the effect of additives on the thermodynamic properties of surfaces27,28 and on their impact as surfactants in modifying film growth modes.29

The current study explores the coarsening and decay of Ag adatom islands on Ag(111) at 300 K after exposure to S. The key observation is enhanced decay of these islands, but only above a critical coverage of S. This critical coverage corresponds to complete saturation of step edges with S. We propose that this accelerated coarsening is mediated by facile formation of metal-S complexes or clusters incorporating excess S, which cannot be accommodated at step edges. This picture is supported by density functional theory (DFT) analysis of the relevant energetics, as well as by reaction-diffusion equation modeling. Section II provides background information on our experimental and computational procedures. The key experimental observations on island coarsening and decay are then described in Sec. III. Then, in Sec. IV, we present our DFT results for relevant energies in the S + Ag/Ag(111) system and provide in Sec. V a basic analysis of the energetic driving force and kinetics for coarsening. Next, in Sec. VI, we describe a nonlinear reaction-diffusion equation formulation for coarsening kinetics and provide in Sec. VII the associated detailed analysis. Finally, Sec. VIII presents a discussion of related behavior in other systems and provides concluding remarks.

II. EXPERIMENTAL AND COMPUTATIONAL PROCEDURES

The Ag(111) sample used in these studies was grown at the Ames Laboratory, US-DOE Materials Preparation Center.30 The surface was oriented perpendicular to the (111) direction to within 0.25°. The sample was polished to a mirror finish using 6, 1, and 0.25 μm diamond paste. All experiments were carried out in a stainless steel UHV chamber with base pressure of 1 × 10⁻¹⁰ Torr, equipped with an ion gun and with a retarding field analyzer (RFA) for Auger electron spectroscopy (AES). One part of the chamber contained an Omicron variable-temperature scanning tunneling microscope (STM). All STM images were acquired using electrochemically etched W tips31 at the stated temperature, 300 K. Typical tunneling conditions were −2.0 V and 1.0 nA. The gap voltage was chosen to minimize interaction of the tip with the surface. The absence of tip effects was also determined by scanning both large and small areas of the surface in different directions, revealing no distortion of adlayer structures in the scanning direction. In the other part of the chamber, the sample was cleaned by repeated cycles of Ar⁺ sputtering (15 min, 20 mA, 1.0–1.5 kV, and T=300 K) followed by annealing. This procedure was carried out until no impurities could be detected by AES and until images acquired with the STM showed large terraces on the order of at least 100 nm in width, together with a very low density of apparent impurities, as evidenced by a lack of pinning sites of steps.

For our study of adatom island coarsening and decay, deposition of Ag on the Ag(111) single-crystal surface was performed using an Omicron EFM3 UHV evaporator containing Ag (99.99% pure) as the deposition source. The Ag flux was held fixed at 14–18 (mML)/s in all experiments. Sulfur deposition was then performed by exposing the sample to S₂ generated by a solid-state electrochemical Ag/AgCl/Ag₃S/Pt cell following the design of Wagner.32 Using this electrochemical doser, the S flux was in the range of 5–50 mML/min. To reduce the variability of the flux, we allowed extensive warmup of the doser and avoided performing experiments near the beginning and end of the chemical supply. Our recent work33 used this electrochemical cell to deposit S on the Ag(111) surface and then to study in detail the structure of S adlayers at 200 K.

Only Ag and S were detected by AES on the surface after S deposition—not iodine or oxygen. Sulfur coverage was determined after each run using the S(LMM)/Ag(MNN) AES intensity ratio, where the letters in parenthesis denote electronic energy levels, and the combination indicates the electronic transitions involved. We adopted a calibration that was published in Ref. 34 in 1979 derived largely from low energy electron diffraction but corroborated by temperature-programmed desorption and work function measurements and verified by another group.35

DFT calculations were performed using the vasp total energy code.36–38 We used the Perdue–Burke–Ernzerhof (PBE) form of the generalized gradient approximation (GGA).39 The ion-electron interactions were treated by the projector augmented-wave method.40 The energy cutoff was 280 eV for all calculations. The fcc Ag lattice constant was set to 0.417 nm, the theoretical value for the PBE-GGA functional (versus the experimental value of 0.409 nm). To represent the substrate, we used a (111)-oriented slab of Ag with thickness of five or six layers, fixing the lower two layers of atoms to their bulk positions. Adsorbates were attached only to the top side of the slab. Methfessel–Paxton smearing41 with a width of 0.2 eV was used for efficiency. The vacuum spacing between slabs was 1.2 nm. Most of the results were obtained using a (3 × 3) supercell, with the surface BZ sampled with a 4 × 4 grid of k-points, using the Monkhorst–Pack method.42 For consistency, we use the same number of irreducible k-points for the clean surface for all calculations, even though the presence of adsorbates can break symmetries.

We should emphasize that there is some dependence of
DFT predictions for energetics on parameter choices (which we have examined) and intrinsic inaccuracy in the theory. For example, results below indicate a dependence of quantities such as binding or interaction energies on slab thickness. Such quantum size effects are, of course, expected for thin slabs typically used in calculations. However, even basic quantities such as the Ag nearest-neighbor (NN) pair interactions can vary quite strongly. Some of this variation may be due to the relatively coarse \( k \)-point grid used, although using a finer \((6 \times 6)\) grid shows more or less the same dependence on slab thickness. Comparing results for different thickness, etc., we believe that results such as those in Table III below should be accurate within \(-0.1\) eV. Despite this uncertainty, these results are still valuable in identifying basic trends in relevant energies.

III. ISLAND DECAY KINETICS: EXPERIMENTAL ANALYSIS

A common approach in analyzing coarsening kinetics is to quantify the decrease with time, \( t \), in the island number or density for large arrays of islands. Ideally, this type of analysis is performed on broad terraces where evolution is not significantly impacted by pre-existing extended steps on the surface. This approach can be applied either for OR, i.e., simultaneous dissolution of smaller islands and growth of larger islands mediated by mass transport across terraces between them, or for Smoluchowski ripening (SR), i.e., diffusion and coalescence of islands. However, such an analysis of the coarsening kinetics is sensitive to the presence of narrow terraces. Thus, here we utilize a more robust alternative for OR. Specifically, we characterize the decay with time, \( t \), of the area, \( A(t) \), of individual small adatom islands.

In an analysis of either the evolution of large island arrays or of individual island decay for OR, the key energetic parameters are the diffusion barrier, \( E_d \), and the formation energy, \( E_{form} \), for the species transporting mass across the surface. Often analyses of island area evolution exploit generic features of decay for small islands. For terrace diffusion (TD)–limited decay, one has that \( A(t)^{3/2} \sim A_0^{3/2} - R_{TTD} t \) for islands that are significantly smaller than their neighbors, so their chemical potential is correspondingly higher. The decay rate, \( R_{TTD} \), has an Arrhenius energy of \( E_{act} = E_d + E_{form} \). For the S-free surface, nonlinear decay of \( A(t) \), with \( t \) of this form, is apparent in our data, as it was in previous data. For attachment-detachment (AD)–limited decay, one has that \( A(t) \sim A_0 - R_{ADT} t \) for islands far smaller than the average size. Now the decay rate, \( R_{ADT} \), has an Arrhenius energy of \( E_{act} = E_d + E_{form} + \delta \), where \( \delta \) denotes the (additional) attachment barrier.

However, one complication for our system with nonzero S coverages, \( \theta_S > 0 \), is that we do not know \textit{a priori} whether decay is TD or AD limited, or in an intermediate transition regime, or described by a different mechanism. Thus, application of the above expressions is problematic, and we adopt a simpler versatile alternative (see Ref. 23). For adatom island distributions on Ag(111) surfaces with various S coverages, \( \theta_S \), we compare the decay times, \( \tau \), for “small” islands with a specific selected initial size or area, \( A_0 \), which are in similar environments. In our case, we will select \( A_0 = 300 \text{ nm}^2 \), sometimes interpolating or extrapolating \( \tau \)-data for other sizes, and choose islands that are \textit{always close to an ascending step}. Such a step provides a strong sink driving island decay, which is common to all cases. Islands further removed from such a step may decay more slowly depending on the details of their local environment.

Examples of the STM data used for this analysis of island coarsening and decay at 300 K are shown in Figs. 1 and 2. For our “benchmark” studies of the S-free surface where \( \theta_S = 0 \), Fig. 1(a) reveals coarsening with smaller islands shrinking and larger islands growing (at least initially). A very similar behavior is observed for \( \theta_S = 7 \text{ mML} \) in Fig. 1(b) for an array of islands on a terrace, which is similar in size to that in Fig. 1(a). In contrast, much faster decay of substantially larger islands is observed for \( \theta_S = 11 \text{ mML} \) in Fig. 2. Here, it should be noted that in all experiments with S coverages below 11 mML, STM images were acquired prior to S exposure and then again no earlier than 10 min after exposure. However, for experiments with \( \theta_S = 11 \text{ mML} \) and higher (the latter described below), STM scanning was per-
formed in situ during S deposition in order to capture the faster decay of islands. Thus, for example, in the experiment with \( \theta_S = 11 \) mML, the first image prior to exposure of S was taken only 1 min after completion of S deposition.

In Fig. 3, we present data for decay of island areas for various initial island sizes at \( \theta_S = 0 \) and 11 mML. For \( \theta_S = 0 \) and 7 mML, the nonlinear variation of \( A(t) \) with \( t \) is indicative of TD-limited decay, as established previously for the S-free surface.\(^{44,45} \) For \( \theta_S = 11 \) mML, \( A(t) \) appears to decrease linearly with \( t \), a behavior normally associated with AD-limited decay. However, other origins for such behavior are possible for systems including additives, as discussed below and in Ref. 23. From an analysis of island decay data of this type for various \( \theta_S \), we extract a decay rate, \( R \), based on the decay time, \( \tau \) (in minutes, say), for islands of initial size \( A_0 = 300 \) nm\(^2 \) as \( R = 300/\tau \) (in nm\(^2\)/min). The results, reported in Table I, indicate no systematic dependence of \( \tau \) or \( R \) on \( \theta_S \) between \( \theta_S = 0 \) and 7 mML. However, there is a dramatic increase in \( R \) by a factor of \( \approx 200 \) as \( \theta_S \) increases from 7 to 11 mML. For the latter, we have extrapolated decay times for larger islands down to \( A_0 = 300 \) nm\(^2 \). This prompts us to define a critical coverage, \( \theta_S(\text{crit}) \), \( \approx 8-10 \) mML, only above which coarsening or decay is enhanced.

Island decay for \( \theta_S \) significantly above 11 mML is so rapid that quantitative analysis of \( \tau \) or \( R \) is difficult. A major complication is that significant decay occurs on the time scale of S deposition, i.e., as \( \theta_S \) increases toward its final value. Also, decay can occur within a fraction of the time required to obtain a complete STM image of 100–200 s.

We now describe observations for a final \( \theta_S = 35 \) mML, where S is deposited relatively quickly in \( \approx 45 \) s. Figure 4 shows a distribution of islands on a S-free surface (left frame) and then the same area scanned during exposure of S (right frame). Acquisition of a complete image here takes 200 s. S deposition commences at the bottom of the right frame and thus is complete 20–25% through image acquisition. A few islands are still visible in this initial phase of scanning, but all have disappeared by the end of S exposure.

For example, a 613 nm\(^2 \) island on the lower right has disappeared when imaged \( \approx 45 \) s after exposure to S [i.e., \( \approx 30 \) s after reaching \( \theta_S(\text{crit}) \)]. From this observation, we make a strict upper estimate that \( \tau < 0.25 \) min, as indicated in Table I.

Next, we describe an additional experiment designed to explore island decay behavior in the regime of enhanced coarsening. Here, S was deposited relatively slowly at a rate of 0.2 mML/s up to a final coverage of \( \theta_S = 25 \) mML, which takes a total time of 125 s, allowing us to monitor the decay of islands during buildup of the sulfur coverage. Below, we use \( \delta \) to denote the time elapsed since \( \theta_S \) has reached \( \theta_S(\text{crit}) \) and \( \delta A \) the corresponding observed mean decrease in island area (effectively over a time interval \( \delta t \)). In the regime above the critical S coverage, the average island decay rates during buildup of S are given by \( R_{av} = \delta A/\delta t = 32, \) 40, 157, and 425 nm\(^2\)/min for \( \delta t = 30, \) 42, 65, and 80 s, where the final \( \theta_S = 14, \) 16.5, 21, and 24 mML, respectively. Behavior is consistent with that reported above. Another significant observation is that for the large array of islands observed during the enhanced coarsening phase of this experiment, one does not observe growth of larger than average islands. Rather, the areas of islands of all sizes decay in time.

It is also appropriate to compare our observations above with previous data for Ag adatom island decay on S-free clean Ag(111) surfaces: (a) Previous analysis of decay of a small isolated adatom island of initial area \( A_0 = 300 \) nm\(^2 \) inside a larger monolayer vacancy pit revealed a decay time of \( \tau \approx 80 \) min.\(^{44} \) This decay is slightly slower than but reasonably consistent with behavior observed here for \( \theta_S \approx 7 \) mML. (b) Previous analysis of decay of smaller islands within a large array of islands on broad terraces far from extended steps indicated decay times depending strongly on

### Table I. Decay time, \( \tau \), and decay rate, \( R \) (in units of nm\(^2\)/min), for islands of initial size \( A_0=300 \) nm\(^2 \) and for various amounts of S as indicated.

<table>
<thead>
<tr>
<th>( \theta_S ) (mML)</th>
<th>0</th>
<th>&lt;1</th>
<th>2</th>
<th>7</th>
<th>11</th>
<th>35</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \tau ) (min)</td>
<td>50</td>
<td>60</td>
<td>40</td>
<td>65</td>
<td>0.6</td>
<td>&lt;0.25</td>
</tr>
<tr>
<td>( R ) (nm(^2)/min)</td>
<td>6.0</td>
<td>5.0</td>
<td>7.5</td>
<td>4.6</td>
<td>( 1.0 \times 10^3 )</td>
<td>( &gt;2.4 \times 10^3 )</td>
</tr>
</tbody>
</table>
the local environment of the island, as expected for TD-limited decay. Selected examples reveal decay times of \( \tau = 70\) min when \( A_0 = 450\) nm\(^2\) (with a favorable local environment for decay) and \( \tau = 140\) min for \( A_0 = 300\) and 350 nm\(^2\) (with a less favorable environment).\(^{35}\) Again, this behavior is reasonably consistent with our observations for \( \theta_S = 7\) mML given the weaker driving force for decay within such island arrays. (c) Analysis of decay of a large isolated adatom island of initial area \( A_0 = 2600\) nm\(^2\) inside a large monolayer vacancy pit indicates a decay time of \( \tau = 12\) h.\(^{44}\) This should be compared with our observation of decay with \( \tau = 6\) min for \( A_0 = 2500\) nm\(^2\) when \( \theta_S = 11\) mML, illustrating again the dramatic enhancement of mass transport at this S coverage.

Next, to elucidate the above behavior, it is instructive to compare the S coverage with the total step edge population on the surface (i.e., the number of step edge sites available to accommodate S). This step edge population varies somewhat between experiments. However, for the surface prior to deposition of Ag islands, the step density is typically around \( 4-5\) nm per 100 nm\(^2\) of surface area, or \( 1.1 \times 10^{-2}\) edge atoms per surface atom or per fcc adsorption site. The step density increases to \( \sim 8\) nm per 100 nm\(^2\) of surface area, or \( 2.0 \times 10^{-2}\) edge atoms per site after Ag island formation. We have assessed step density on roughly 20 regions of size of \( 300 \times 300\) nm\(^2\) and find variations of about \( \pm 20\%\). Thus, we believe that a step density of \( 2.0 \times 10^{-2}\) edge atoms per site represents behavior on the region of the surface accessible to S in our coarsening studies. Since steps can accommodate one S adatom for every two step edge sites (see Sec. V), it follows that steps are not saturated for \( \theta_S \leq 7\) mML, but excess S is available for \( \theta_S = 11\) mML. Thus, the critical coverage, \( \theta_S(\text{crit}) \approx 8 - 10\) mML, introduced above, corresponds to the maximum \( \theta_S\), where all S can be accommodated at step edges.

Finally, we mention that in Appendix A, we present an analysis of the fluctuations in position of extended steps on the Ag(111) surface exposed to S. This analysis reveals behavior consistent with the existence of a critical coverage of S as introduced above.

### IV. Adspecies Interactions, Cluster Stabilities, and Diffusion Barriers: DFT Analysis

Below, for convenience, we denote Ag metal adatoms by M and sulfur adatoms by S. Our analysis of relevant energetics utilizes DFT, as described in Sec. II. First, we characterize a few basic interactions between these adspecies, which significantly impact overall coarsening behavior: (i) S binds at extended step edges on Ag(111) with strength of \( \phi_S^t > 0\) from 0.12 to 0.25 eV per S adatom. These results are obtained from calculating the adsorption energy of an S adatom on slabs representing the Ag(221) and Ag(332) surfaces, which mimic Ag(111) vicinal surfaces with (111)-microfaceted B steps and (100)-microfaceted A steps, respectively. In contrast, for M trimers decorated with three S adatoms, one finds a stronger binding per S adatom of \( \phi_S^t \approx 0.4\) eV at edges corresponding to (100)-microfacets, i.e., A steps, and \( \phi_S^t \approx 0.3\) eV at (111)-microfacets, i.e., B steps.\(^{33}\) We emphasize here that a simple short-range pairwise additive picture of M-S interactions is not adequate for this system. Energetics often reflects the unusual stability of linear S-M-S chains described below. (ii) The effective saturation population of step edges is one S atom per two M adatoms, as there are significant effective repulsions between S on adjacent step sites. (iii) Metal adatom interactions are described reasonably by effective NN M-M attractions of strength \( \phi_M \approx 0.2\) eV.\(^{33,44}\) These interactions imply an equilibrium state for Ag adlayers on Ag(111) corresponding to 2D condensed island phase coexisting with a dilute 2D gas phase on clean and S-exposed Ag(111) surfaces. They also drive island formation during deposition of Ag.\(^{46}\) (iv) There are also short-range repulsions between S adatoms on terraces, so there is no tendency for excess S (above the amount required to saturate step edges) to aggregate into islands.

In Appendix B, we provide a brief discussion of the equilibrium shape of decorated islands based on the above picture for energetics.

Next, we discuss the stability of various metal-sulfur complexes, \( C = M_S^n S_m^r \), which could potentially lead to enhanced coarsening. In Table II, we report (a) the total adsorption energy, \( E_{\text{ads}}(C) > 0\), relative to the separated constituents

### Table II. DFT values using a five-layer Ag slab for adsorption energy, \( E_{\text{ads}}(C) \); internal binding energy, \( E_{\text{bind}}(C) \); chemical potential, \( \mu(C) \), for S within, C; formation energy, \( E_{\text{form}}(C) \), incorporating terrace S; and diffusion barrier, \( E_d(C) \), for various clusters, \( C = M_S^n S_m^r \). Note that fcc sites are preferred for both isolated M and S.

<table>
<thead>
<tr>
<th>( C = M_S^n S_m^r )</th>
<th>( E_{\text{ads}} ) (eV)</th>
<th>( E_{\text{bind}} ) (eV)</th>
<th>( \mu ) (eV)</th>
<th>( E_{\text{form}} ) (eV)</th>
<th>( E_d ) (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag</td>
<td>2.24</td>
<td>0</td>
<td>( \cdots )</td>
<td>0.60</td>
<td>0.10</td>
</tr>
<tr>
<td>S</td>
<td>4.68</td>
<td>0</td>
<td>(-4.68)</td>
<td>0</td>
<td>0.19</td>
</tr>
<tr>
<td>AgS</td>
<td>6.95</td>
<td>0.03</td>
<td>(-4.11)</td>
<td>0.57</td>
<td>(-0.15)</td>
</tr>
<tr>
<td>AgS(_2) (linear)</td>
<td>12.24</td>
<td>0.64</td>
<td>(-4.70)</td>
<td>(-0.04)</td>
<td>(-0.1-0.2)</td>
</tr>
<tr>
<td>AgS(_2) (symm)</td>
<td>14.22</td>
<td>0.38</td>
<td>(-4.27)</td>
<td>0.81</td>
<td>0.11</td>
</tr>
<tr>
<td>AgS(_3) (bent)</td>
<td>14.54</td>
<td>0.71</td>
<td>(-4.43)</td>
<td>0.49</td>
<td>(\cdots)</td>
</tr>
<tr>
<td>AgS(_3)</td>
<td>19.62</td>
<td>1.10</td>
<td>(-4.65)</td>
<td>0.10</td>
<td>(\cdots)</td>
</tr>
<tr>
<td>AgS(_3) (hcp-t)</td>
<td>22.63</td>
<td>1.87</td>
<td>(-4.70)</td>
<td>(-0.07)</td>
<td>(-0.3)</td>
</tr>
<tr>
<td>AgS(_3) (fcc-t)</td>
<td>22.64</td>
<td>1.88</td>
<td>(-4.71)</td>
<td>(-0.08)</td>
<td>0.30</td>
</tr>
</tbody>
</table>
in the gas phase, which includes both adspecies-substrate bonding as well as adspecies interactions; (b) the total intern
al binding or interaction energy, $E_{\text{bind}}(\text{C}=\text{M}_n\text{S}_m) = E_{\text{ads}}(\text{C}) - nE_{\text{ads}}(\text{M}) - mE_{\text{ads}}(\text{S}) > 0$, which gives the difference in ad-
sorption energy between the cluster and its separated con-
stituent adspecies; (c) the chemical potential of each S ada-
tom within the complex $C$, $\mu_S(C) = (-E_{\text{ads}}(C) - n\mu(M))/m$, where $\mu(M)$ is the chemical potential of each M adatom in a complete surface layer. This quantity was introduced in a previ-
sous study, where lower chemical potentials reflect more effective ways to incorporate excess S into clusters in order to lower the free energy of the system. Within a NN interaction model, one has $\mu(M) = -E_{\text{ads}}(\text{M}) - 3\phi_M = -2.84$ eV, the second term reflecting the feature that each M adatom has six shared bonds to NN M adatoms.

Our primary interest here is in determining particularly stable clusters (see Table II) and their configurations (see Fig. 5). Our DFT results shown in Table II were obtained using a five-layer Ag slab and revealed that MS clusters ($E_{\text{bind}} = 0.03$ eV) are not very stable compared to linear MS$_2$ clusters ($E_{\text{bind}} = 0.64$ eV). The “symmetric” M$_2$S$_2$ cluster, with M on adjacent fcc sites and S bonded at (100) and (111) microfacets on both sides, is stable ($E_{\text{bind}} = 0.38$ eV), as is an analogous cluster with M on hcp sites. However, a distinct “bent” M$_2$S$_2$ configuration, which is es-
sentially a linear MS$_2$ with an M attached in one corner ($E_{\text{bind}} = 0.71$ eV), and also an M$_2$S$_2$ cluster ($E_{\text{bind}} = 1.10$ eV) are signifi-
cantly more stable. The enhanced stability of these clusters derives from the feature that they both incorporate linear MS$_2$ subconfigurations.

Finally, we note that certain M$_3$S$_3$ clusters are even more stable. One of these consists of an M$_3$-trimer with M on fcc sites and its center of mass above a top site (fcc-top), deco-
rated by three S on (100) microfacets ($E_{\text{bind}} = 1.88$ eV). An-
other, which is almost as stable, consists of an “inverted” M$_3$
trimer with M on hcp sites and its center of mass also above a top site (hcp-top), decorated by three S again on (100) microfacets ($E_{\text{bind}} = 1.87$ eV). Both M$_3$S$_3$ configurations in-
corporate three linear MS$_2$ subconfigurations. Estimates for these binding energies using a six-layer Ag slab tend to be somewhat higher.

Of key importance for coarsening is the formation energy, $E_{\text{form}}(\text{C})$, for creating various metal-containing clusters, $\text{C}=\text{M}_n\text{S}_m$ with $n > 0$. $E_{\text{form}}(\text{C})$ will control the equilibrium population of these species, which can potentially facilitate mass transportation. Creation of an isolated metal (M=Ag) adatom by removal from kink or corner sites requires breaking of three Ag–Ag bonds, so $E_{\text{form}}(\text{M}) = 3\phi_M = 0.6$ eV. For other clusters, one can consider two separate scenarios:

(i) **Cluster creation by extracting both M and S from the step edge for $\theta_S < \theta_S(\text{crit})$.** Here, formation energy is determined from the difference between the total cost of extracting M and S from step edges and the gain in binding energy for the cluster, i.e., $E_{\text{form}}(\text{C}=\text{M}_n\text{S}_m) = nE_{\text{form}}(\text{M}) + mE_{\text{form}}(\text{S}) - E_{\text{bind}}(\text{C})$. This process is ener-
getrially costly given the need to break multiple M–M bonds and lack of a major gain in M–S bond-
ing. Thus, e.g., one finds that $E_{\text{form}}(\text{M}_3\text{S}_3) = 0.67$ eV is prohibitive high for there to be a significant ter-
face population of M$_3$S$_3$. This feature underlies the absence of enhanced coarsening in the regime where $\theta_S < \theta_S(\text{crit})$.

(ii) **Cluster creation utilizing “excess” S already on ter-
race for $\theta_S > \theta_S(\text{crit})$.** Now, the formation energy is determined by $E_{\text{form}}(\text{C}=\text{M}_n\text{S}_m) = mE_{\text{form}}(\text{M}) - E_{\text{bind}}(\text{C})$, which is lower than that above since there is no cost to extract S from step edges and a major gain in M–S bonding upon incorporating S into M–S clusters. Thus, e.g., one finds a slightly negative formation energy $E_{\text{form}}(\text{M}_3\text{S}_3) = -0.08$ eV. Note also that $E_{\text{form}}(\text{C})$ is simply related to the S chemical potential, $\mu_S(C)$, defined in Ref. 33 and above by $E_{\text{form}}(\text{C}) = m[\mu_S(C) + E_{\text{ads}}(\text{S})]$. Table II shows that several clusters have lower formation energies than M adatoms in this regime. Not just $E_{\text{form}}(\text{M}_3\text{S}_3)$ but also $E_{\text{form}}(\text{MS}_2)$ may even be slightly negative, in which case such clusters would form spontaneously in the presence of excess S on terraces.

Finally, Table II also reports DFT results for the diffusion barriers, $E_d(C)$, for various clusters. C. Previous DFT and experimental analyses consistently indicate that $E_d(M) = 0.10$ eV. We now also briefly comment on the diffusion of M$_3$S$_3$, which has two particularly stable configurations, fcc-top and hcp-top, described above. Two less stable config-
urations, hcp-3fh and fcc-3fh, exist with the center of mass of the M$_3$ trimer now above a threefold hollow (3fh) site, in both cases decorated by three S on (111) microfacets. One expects that a dominant diffusion path for M$_3$S$_3$ clusters involves a quasi-rigid translation between fcc-top and hcp-3fh config-
urations. A simple estimate for $E_d(M_3S_3)$ comes from the energy difference between these configurations of $\sim 0.3$ eV, which is mainly due to the difference in binding strength for S at the different types of microfacets. We have con-
firmed the validity of this picture for the diffusion path and associated energy barrier with a DFT-nudged elastic
band analysis (see Fig. 6). Such a diffusion path has also been proposed for undecorated M$_3$ clusters on M(111) surfaces$^{40,49}$ and also for Cu$_3$S$_3$ clusters on Cu(111).$^{22}$

V. COARSENING OF Ag ISLANDS: ANALYSIS OF KEY ENERGETICS

Here, we first analyze the energetic driving force for coarsening both with and without S. In general, coarsening is driven by a reduction in the total free energy associated with steps due to a decrease in the overall perimeter length of islands.$^{1-14}$ This energy decrease is determined from the step energy, $\gamma$, where a reduction in perimeter length of L M atoms produces a decrease in energy of $\Delta E_L = -L \gamma$. For the S-free fcc(111) surface, one has $\gamma = \phi_M$ per atom, as two shared bonds are broken for each step atom in creating a step. We now present a modified analysis to obtain the relevant energy decrease, and thus effective step energy, for steps that are saturated with S. In this case, S is ejected onto the terrace due to perimeter length reduction during coarsening.

First, we consider the scenario where step length reduction of S-saturated step edges during coarsening ejects S onto the terraces and where S is not incorporated into metal-sulfur clusters. In this case, for a reduction of L M atoms in step length, there is an energy reduction due to the gain in M–M bonding of $-L \phi_M$ within islands (just as for the S-free surface) and an increase in energy due to the loss of bonding of $\frac{1}{2} L \phi_S$ to the step edge of $+\frac{1}{2} L \phi_S$. Thus, the total energy change, $\Delta E_L = -(\phi_M - \frac{1}{2} \phi_S)L$ (so $\Delta E_L < 0$ for $\phi_S < 2 \phi_M = 0.4$ eV) is relatively small compared to the S-free system. Second, consider length reduction of S-saturated step edges where the ejected S is incorporated into M$_3$S$_3$ clusters created by net dissolution of M atoms from the islands. For a reduction of L M atoms in perimeter length, again $\frac{1}{2} L$ sulfur atoms are ejected from the step edge, but now dissolution of $\frac{1}{2} L$ M atoms is also required to create $L/6$ M$_3$S$_3$ clusters. Detailed analysis reveals no net change in the amount of M–M bonding but a net increase in M–S bonding since S is bound more strongly at (100) microfacets in small clusters than at extended step edges. Thus, one has an overall decrease in energy of $\Delta E_L = -(\phi_M - \phi_S)L < 0$. In either case, the effective step energy, $\gamma = |\Delta E_L|/L$ is relatively small compared to the S-free system. This reduced energy is consistent with enhanced step fluctuations described in Appendix A, at least if there is sufficient excess S to saturate the extended length of the wandering steps.

Next, we consider the rate of coarsening, which must include both a thermodynamic component (reflecting the energetic driving force for coarsening) and a kinetic component (reflecting the efficiency of mass transport). Consequently, one anticipates that the maximum possible rate of coarsening, $R_c$ (max), where mass transport is mediated by an M-containing species or cluster, $C=M_nS_m$, can be estimated from the product

$$R_c$ (max) = $\gamma D_C \theta_C^{eq},$ (5.1)

where $D_C = D_0 \exp[-\beta E_N(C)]$ is the diffusion coefficient for C with inverse temperature $\beta = 1/(k_B T)$, and $\theta_C^{eq}$ is the equilibrium concentration or coverage for C. When all cluster formation energies, $E_{form}(C)$ are non-negative, i.e., taking $E_{form}(M_3S_3) = 0$ and $E_{form}(MS_2) = 0$, one can write $\theta_C^{eq} = \exp[-\beta E_{form}(C)]/\Delta \theta_S$, where $\Delta \theta_S = \theta_S - \theta_S$(crit) is the coverage of excess S free to participate in cluster formation. For a significantly negative $E_{form}(M_3S_3)$, the equilibrium population of M$_3$S$_3$ is controlled by the amount of excess S, i.e., $\theta_{M3S3}^{eq} \approx \Delta \theta_S/3$; i.e., most excess S is incorporated in M$_3$S$_3$ clusters. The populations of smaller clusters are now determined accounting for the difference in their binding or formation energy relative to M$_3$S$_3$. Finally, we emphasize that the above maximum possible rate might not be achieved even if coarsening is dominated by mass transport of C,$^{23}$ a subtlety discussed in the following sections.

Using the above rate estimates, we consider a coarsening behavior in two distinct regimes:

(i) Low S coverages $\theta_S < \theta_S$(crit): Since all S can be incorporated at step edges, the populations of M-containing clusters on the terraces are very low, and coarsening must be mediated by M adatom transport. Thus, the rate for coarsening scales as $R_M$ = $R_{M}$(max) = $\exp[-\beta E_{eff}(M)]$, where $E_{eff}(M) = E_A(M) + E_{form}(M) = 0.7$ eV just as for the S-free surface. Indeed, experimental data in Sec. II indicate that coarsening occurs at a rate similar to that for S-free surface for $\theta_S < \theta_S$(crit).

(ii) Higher S coverages $\theta_S > \theta_S$(crit): Now step edges are saturated with S, and extra S populates terraces as adatoms and as part of various clusters C = M$_n$S$_m$. This allows for the possibility of enhanced coarsening with rate potentially as high as $R_{C}$(max) = $\exp[-\beta E_{eff}(C)]$, where $E_{eff}(C) = E_A(C) + E_{form}(C)$ is below $E_{eff}(M)$ = 0.7 eV for various $C$ including MS$_2$, MS$_3$, or M$_3$S$_3$. However, such enhanced coarsening also requires sufficiently strong coupling between spatial gradients in the diffusion field for M adatoms and those for C (see Secs. VI and VII and Ref. 23).
VI. COARSENING OF Ag ISLANDS: REACTION-DIFFUSION EQUATIONS

Ling et al. argued that even if metal-sulfur clusters cannot directly attach and detach from step edges, sufficiently strong coupling of the spatial gradients in the diffusion field for metal adatoms, M, to those for certain clusters such as M₂S₃, could enhance coarsening. Denoting the coverage of clusters C = M₃S₃ₙ by θₐ (in units of ML), they analyzed a simplified coupled pair of linear reaction-diffusion equations for θₐ and θₐ₋₁ in the steady-state regime but did not specify the basis of the linearization or the details of the coupling mechanism. Elaboration of these issues is important for a full validation of the theoretical model. For example, one cannot regard the primary creation mechanism for M₃S₃ as involving simultaneous collision of three M adatoms and three S adatoms, as the associated coupling would be too weak. Instead, one should explore possibilities for coupling mediated through “reactions” involving smaller clusters, e.g., M+M₂S₃ → M₃S₃. In fact, various other reaction pathways should also be considered, which couple the diffusion field for M adatoms to those for M₃S₃ clusters and to other clusters capable of enhancing coarsening.

In order to assess these various mechanisms for enhanced coarsening, we develop a coupled set of nonlinear reaction-diffusion equations for the spatially varying coverages of relevant metal-containing clusters, C. The nonlinearity derives from the form of the rates of various cluster formations. Let K(C + C') denote the rate for formation or creation of the cluster CC' via C+C' → CC, and F(C + C') the rate for the reverse fragmentation process. The reaction-diffusion equations must account for gain and loss in local adspecies populations due to all relevant reaction processes (i.e., cluster formation and fragmentation), as well as due to diffusion for spatially nonuniform systems. Leaving implicit the terms for many reaction processes and focusing for simplicity on the reaction M+M₂S₃ → M₃S₃, these equations in the relevant steady-state regime have the form

\[ \frac{\partial}{\partial t} \theta_{M} = D_{M} \nabla^{2} \theta_{M} - K(M + M_{2}S_{3}) + F(M + M_{2}S_{3}) \]

\[ + \cdots = 0, \]  

(6.1a)

\[ \frac{\partial}{\partial t} \theta_{M_{2}S_{3}} = D_{M_{2}S_{3}} \nabla^{2} \theta_{M_{2}S_{3}} - K(M + M_{2}S_{3}) \]

\[ + F(M + M_{2}S_{3}) + \cdots = 0, \]  

(6.1b)

\[ \frac{\partial}{\partial t} \theta_{M_{3}S_{3}} = D_{M_{3}S_{3}} \nabla^{2} \theta_{M_{3}S_{3}} + K(M + M_{2}S_{3}) \]

\[ - F(M + M_{2}S_{3}) + \cdots = 0. \]  

(6.1c)

The total diffusion flux for metal across the surface either as adatoms or in clusters,

\[ J_{\text{MTOT}} = \sum_{n=1}^{\infty} \sum_{m=0}^{\infty} D_{M_{n}S_{m}} \nabla \theta_{M_{n}S_{m}}, \]  

(6.2)

naturally satisfies \( \nabla \cdot J_{\text{MTOT}} = 0 \) in the steady-state regime.

Given that spatial variations in coverages during coarsening are small, it is natural to linearize the above equations by expanding coverages about their equilibrium values, i.e., \( \theta_{C} = \theta_{C}^{\text{eq}} + \delta \theta_{C} \) (where “eq” will be used to denote equilibrium values of various quantities). An analogous expansion of the relevant rates then yields

\[ K(C + C') = (D_{C} + D_{C'})\theta_{C}\theta_{C'}, \]

\[ \approx K^{\text{eq}}(C + C') + \alpha_{C}(C') \delta \theta_{C} + \alpha_{C'}(C) \delta \theta_{C'}, \]

(6.3a)

\[ F(C + C') = (D_{C} + D_{C'})\exp[-\beta \Delta E(C + C')] \theta_{CC'}, \]

\[ = F^{\text{eq}}(C + C') + (\beta C + C') \delta \theta_{CC'}. \]

(6.3b)

where \( \alpha_{C}(C') = (D_{C} + D_{C'})\theta_{C}^{\text{eq}} \), \( \beta (C + C') = (D_{C} + D_{C'}) \times \exp[-\beta \Delta E(C + C')] \), and \( \Delta E(C + C') \) is the binding energy difference between the separated C + C' configuration and the CC' configuration. Our notation (specifically, the use of \( \alpha \) and \( \beta \)) is chosen to mimic that of Ref. The note the identities \( K^{\text{eq}}(C + C') = F^{\text{eq}}(C + C') \) and \( \beta (C + C')^{eq} = \alpha_{C}(C)^{eq} = \alpha_{C'}(C)^{eq} \). It is also instructive to introduce diffusion lengths and modified equilibrium constants as \( L_{C}(C') = [D_{C}/(\alpha_{C}(C'))]^{1/2} \)

\[ R_{CC'}^{eq} = (D_{C}^{eq}/(D_{CC'}\theta_{CC'}^{eq})). \]

(6.4)

Here \( L_{C}(C') \) denotes the diffusion length for C before reaction with C' to form CC'. The magnitude of these lengths relative to the typical island separation, \( L_{\text{iso}} \sim 100–300 \) lattice constants, will be key in determining the strength of coupling between different diffusion fields. In the case of high populations of clusters on the terraces, one should replace the “bare” value of diffusion coefficient \( D_{C} \) for isolated clusters, C, with an effective value for the populated terrace. This would likely reduce \( D_{C} \) and perhaps also \( L_{C}(C') \).

Our goal in obtaining linearized steady-state reaction-diffusion equations is to cast them in a form that highlights the key factors controlling coarsening behavior. To this end, we rescale the spatially varying component of the coverages introducing \( \rho_{C} = D_{C} \theta_{C}^{eq}/L_{M} \) and also utilize the above characteristic lengths and equilibrium constants. One then obtains the equations

\[ 0 \approx \nabla^{2} \rho_{M} - \rho_{M}/L_{M}(M_{2}S_{3})^{2} - \rho_{M_{3}S_{5}}/L_{M}(M_{5}S_{3})^{2} \]

\[ + \rho_{M_{3}S_{3}}R_{M_{3}S_{3}}/L_{M}(M_{5}S_{3})^{2} + \cdots , \]

(6.5a)

\[ 0 \approx \nabla^{2} \rho_{M_{2}S_{3}} - \rho_{M}/L_{M}(M_{2}S_{3})^{2} - \rho_{M_{3}S_{5}}/L_{M}(M_{5}S_{3})^{2} \]

\[ + \rho_{M_{3}S_{3}}R_{M_{3}S_{3}}/L_{M}(M_{5}S_{3})^{2} + \cdots , \]

(6.5b)

\[ 0 \approx \nabla^{2} \rho_{M_{3}S_{3}} - \rho_{M}/L_{M}(M_{2}S_{3})^{2} + \rho_{M_{3}S_{5}}/L_{M}(M_{5}S_{3})^{2} \]

\[ - \rho_{M_{3}S_{3}}R_{M_{3}S_{3}}/L_{M}(M_{5}S_{3})^{2} + \cdots , \]

(6.5c)

again leaving implicit terms describing the rates for many processes. Note that

\[ \rho_{\text{MTOT}} = \sum_{n=1}^{\infty} \sum_{m=0}^{\infty} \rho_{M_{n}S_{m}} \] satisfies \( \nabla^{2} \rho_{\text{MTOT}} \approx 0. \) (6.6)
We must also impose appropriate boundary conditions for these equations. Suppose that only M adatoms attach and detach from islands with no attachment barrier (see Ref. 23). Then, \( \rho_M \) equals the excess equilibrium adatom density at the island edge, which from the Gibbs-Thompson condition satisfies \( \rho_M = \rho^* (1/r - 1/r_w) \) for an island of radius \( r \). \(^{23} \) Here \( r_w \) is the average island radius. The \( \rho_C \) for other clusters \( C \) satisfy zero-flux boundary conditions. One cannot discount the possibility of complex processes involving direct detachment from the step edge, e.g., of a MS perhaps facilitated by S on the terrace. If such processes are competitive, then one must modify the boundary condition for the detaching cluster at the island edge.

VII. COARSENING OF Ag ISLANDS AT 300 K: ANALYSIS OF KINETICS

Here, we first consider the scenario where only M adatoms attach and detach from step edges. Lengths are reported in dimensionless units of surface lattice constants. Below, we let \( \rho_M^* \) denote the typical magnitude of \( \rho_M \) at edges of smaller or larger islands, and \( r \) denotes the distance across terraces measured from the edge of an island where \( r \rightarrow 0 \). One could potentially assess the impact of various clusters on coarsening from the complete solution of Eq. (6.5a), (6.5b), and (6.5c). See Appendix C. However, below we adopt a simpler and perhaps more instructive approach.

Our simplified analysis will first focus on the reaction pathway \( M+M_2S_3 \rightarrow M_3S_3 \) to illustrate the potential coupling of the diffusion field \( \rho_M \) to \( \rho_{M_2S_3} \). Thus, we initially ignore the many terms implicit in Eqs. (6.1a), (6.1b), (6.1c), (6.5a), (6.5b), and (6.5c). A detailed analysis in Appendix D indicates that

\[
L_M(M_2S_3) = (\Delta \theta_3)^{1/2} \left( L_{M_2S_3}(M) \right) \gg L_{isl}, \]

\[ R_{M_2S_3} \ll 1 \text{ at } 300 \text{ K}, \]  

(7.1)

except that the latter breaks down for extremely small \( \Delta \theta_3 = \theta_3 - \theta_3(\text{crit}) \). Accounting for these inequalities, Eq. (6.5a) adopts the particularly instructive approximate form

\[
0 = \nabla^2 \rho_M - \rho_M/L_M(M_2S_3)^2. \]

(7.2)

For small \( \Delta \theta_3 \leq 0.025 \text{ mML} \), we have that \( L_M(M_2S_3) \approx L_{isl} \approx 200 \) from Eq. (7.1). Then Eq. (7.2) effectively becomes \( \nabla^2 \rho_M = 0 \), which implies negligible coupling of \( \rho_M \) to the cluster diffusion field. Consequently, one has TD-mediated coarsening dominated by diffusion of metal adatoms with a quasilinear variation of \( \rho_M \) across terraces, so that

\[
\delta \theta_M(r) = \rho_M(r) \sim \rho_M^* r/L_{isl} + \text{ const} \quad \text{and} \quad J_{MTOT} \sim D_M \rho_M^* /L_{M_2S_3}, \]

(7.3)

with suitable adjustment of the constant to match the boundary conditions.

For larger \( \Delta \theta_3 \gg 3 \text{ mML} \), say, one now has that \( L_M(M_2S_3) \ll 18 \) from Eq. (7.1), which is well below \( L_{isl} \approx 200 \). An analysis of Eq. (7.2) in this regime implies that

\[
\delta \theta_M(r) = \rho_M(r) \sim \rho_M^* \exp\left[-r/L_M(M_2S_3)\right] \quad \text{and} \quad J_{MTOT} \sim D_M \rho_M^* /L_{M_2S_3}, \]

(7.4)

for \( r \) below \( \sim 1/2 L_{isl} \) in the first result. The result [Eq. (7.4)] for \( J_{MTOT} \) follows from two observations. First, this flux is essentially constant across terraces. Second, since there is no contribution to this flux from S-containing clusters at the island edge, it must correspond to the flux of M adatoms at the island edge. Another consequence of Eq. (7.4) is that \( \rho_M \) is very small (and spatially uniform) in the middle of terraces, i.e., for distances greater than \( \sim L_{M_2S_3} \) from island edges. Thus, again since \( J_{MTOT} \) is essentially constant, there must be a quasilinear variation in \( \rho_{M_2S_3} \sim \rho_M^* \) across the middle of terraces. The result [Eq. (7.4)] for \( J_{MTOT} \) constitutes a significant enhancement over Eq. (7.3) since \( L_M(M_2S_3) \ll L_{isl} \). Finally, since the mass flux in this regime of \( M_2S_3 \)-dominated transport is independent of the distance \( L_{isl} \) between islands, one expects coarsening kinetics similar to AD-limited behavior, including linear decay of island areas.

Figure 7 provides a schematic of the behavior of \( \rho_M \) and \( \rho_{M_2S_3} \) in the two distinct regimes described above. Note that gradients are possibly induced in other diffusion fields. Significantly, the above analysis indicates that the key diffusion length, \( L_M(M_2S_3) \), will decrease below \( L_{isl} \) when \( \Delta \theta_3 \) increases to a few millimolayer. This is qualitatively consistent with the observed enhanced coarsening and linear island decay for \( \theta_3 \approx 11 \text{ mML} \). The above identification of distinct regimes for coarsening kinetics corresponds to the scenario for the simpler model in Ref. 23. The analysis in Ref. 23 also identified another possible regime where \( L_M(M_2S_3) \approx L_{isl} \approx R_{M_2S_3} \) promoting local equilibration, i.e., \( \rho_M = \rho_{M_2S_3} \rho_{M_3S_3} \). Here, both densities would vary quasilinearly across terraces, and \( J_{TOT} \) would be further enhanced. However, this regime may not be realized for our system. \(^{51} \)

We emphasize that the above analysis does not treat all possible reaction pathways, which might couple \( \rho_M \) to \( \rho_{M_2S_3} \). Furthermore, it does not treat reaction pathways coupling \( \rho_C \) to other \( \rho_{PC} \) with \( R_C(\max) \approx R_M(\max) \), which could also potentially enhance or dominate mass transport. One such possibility is \( M+S \rightarrow MS \) and \( MS+S \rightarrow MS_2 \), noting the unusual stability of \( MS_2 \). Detailed analysis in Appendix D indicates
that the relevant diffusion lengths satisfy $L_{\text{AD}}(S) = L_{\text{MS}}(S) = 2(\Delta \theta_b)^{-1/6}$ at 300 K. Typically, one has $L_{\text{M}}(S)/L_{\text{isl}}$ $\ll R_{\text{MS}}$ so it follows that $\theta_M$ and $\theta_{\text{MS}}$ are well equilibrated (see Ref. 23). Also, the key diffusion length, $L_{\text{MS}}(S) \approx 5$, for MS to react with S to form MS$_2$ is well below $L_{\text{isl}} = 200$ for $\Delta \theta_b \approx 3$ mML. This feature, together with the inequalities $R_{\text{M},\text{MS}} < L_{\text{MS}}(S)/L_{\text{isl}} < 1$, implies a particularly strong enhancement of coarsening with linear decay of island areas associated with mass transport via MS$_2$ (see above and Ref. 23).

Another possibility, mentioned at the end of Sec. VI, is that certain clusters might be formed by direct detachment from step edges. Indeed, detachment of MS aided by S on the terrace would seem most likely to have a relatively low energetic cost. However, under this scenario, one would expect a standard TD-limited behavior, i.e., nonlinear decay of island areas, unless diffusion fields for these clusters are suitably coupled to other clusters such as M$_x$S$_y$.

VIII. DISCUSSION AND SUMMARY

As noted in Sec. I, additive-enhanced mass transport and coarsening appear to be general phenomena. Accelerated coarsening in the S+Cu/Cu(111) system$^{21-23}$ was proposed to derive from the low formation energy and significant mobility of Cu$_x$S$_y$ clusters. Specifically, it was shown that$^{25} E_{\text{eff}}(\text{CuS}_3) = 0.63$ eV for Cu$_x$S$_y$-mediated mass transport versus $E_{\text{eff}}(\text{Cu}) = 0.84$ eV for mass transport mediated by Cu adatoms.$^{32}$ Experiments at 215 C indicated TD-limited coarsening similar to the S-free system for $\theta_b \approx 2$ mML, enhanced AD-like coarsening for 2 mML $< \theta_b < 6.5$ mML [similar to that observed for S+Ag/Ag(111) at 11 mML], and enhanced TD-like coarsening for $\theta_b > 6.5$ mML. No critical coverage of S was identified, i.e., $\theta_b (\text{crit}) = 0$, although it is possible that a low $\theta_b (\text{crit}) > 0$ may exist. The coarsening rate was proposed to scale like $(\theta_b)^{3}$, although this should only apply for additive-enhanced coarsening. Furthermore, our own DFT analysis reveals a particularly stable Cu$_x$S$_y$ species, which could contribute to enhanced coarsening. A detailed analysis will be presented elsewhere.

For the O+Ag/Ag(100) system, we proposed that enhanced coarsening via OR (versus SR for the O-free surface) was due to facile mass transport by a $\text{Cu}_x\text{O}_m$ complex, where $E_{\text{eff}}(\text{C}) < E_{\text{eff}}(\text{Ag})$. The O coverage is very low in this system, and presumably most O is strongly bonded at kink sites on island edges. Our kinetic picture involved detachment of C from step edges, thereby transporting Ag to other islands. However, C could perhaps form spontaneously on terraces incorporating Ag detaching from step edges, at least when kinks are saturated by O. However, an alternative scenario proposed recently for enhanced coarsening in this system is that the presence of O at kink sites along the island edges reduces the barrier for interlayer vacancy attachment and thus catalyzes OR via TD of vacancies.$^{6}$

This current study provides another example of additive-enhanced mass transport involving formation of metal-additive complexes. Trace amounts of S were shown to greatly enhance coarsening of Ag adatom islands on Ag(111) but only above a critical coverage where all step edges are saturated with S. This picture is consistent with our DFT results demonstrating the stability and mobility of various metal-S clusters, together with our quantitative analysis of coarsening kinetics based on nonlinear reaction-diffusion equations incorporating appropriate mechanisms and rates for cluster formation. In contrast to the other systems mentioned above, one of the stable clusters, Ag$_3$S$_5$, which can contribute to enhanced coarsening has been observed directly by STM as a component of S adlayer structures on Ag(111) at around 200 K.$^{33}$ (Again, we note that other clusters such as Ag$_2$S$_2$ could provide even greater enhancement.) Interestingly, another recent STM study$^{53}$ revealed formation of aggregates, likely Ni$_3$S$_3$ clusters with a structure analogous to that of Ag$_3$S$_3$ clusters, on a Ni(111) surface exposed to S.

ACKNOWLEDGMENTS

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APPENDIX A: FLUCTUATIONS OF S-DECORATED STEPS

Our STM images of the Ag(111) surface exposed to various amounts of S indicate an increase in the amplitude of the fluctuations of step edges as $\theta_S$ increases at and above 25 mML. To quantify such behavior, one could consider the spatial correlation function, $G(y)$, which gives the mean-square difference in displacement from the average step position (i.e., in the direction orthogonal to the step) for two points on the step edge separated by a distance $y$ in the direction of the step edge.$^{34}$ For smaller separations, $G(y)$ increases linearly with $y$ with a coefficient proportional to the step diffusivity, $b^2$, which is inversely proportional to step stiffness. Instead, we consider the mean-square roughness of the step, $\sigma^2(L)$, simply measured as the variance of the distribution of step displacements from the average position (in the direction orthogonal to the step) for a segment of the step of length $L$. This quantity will also reflect the step diffusivity.

One complication for an analysis of step fluctuations on nonvicinal surfaces (where step orientations can vary) is that step stiffness or diffusivity depends on orientation. For a model of a fcc(111) surface with nearest-neighbor interactions of strength $\delta_{\text{step}}$, variation in diffusivity with step orientation has been determined for various $T$ below the critical temperature for phase separation, $T_c$, where $kT_c = \frac{1}{2}\delta_{\text{step}}/\ln(3).$ We apply these results for S-free Ag(111) surfaces at 300 K, where $\delta_{\text{step}} = 0.2$ eV,$^{35,36}$ and $T = 300$ K $= T_c/7$, and where the stiffness of close-packed steps has been measured previously.$^{56}$ One finds that $b^2$ increases by a factor of $\sim 4$ ($\sim 9$) as the step orientation varies from the close-packed direction to a 10° (30°) misorientation. Note that the maximum is achieved at 30°, midway between close-
shape analysis, some results from geometry are relevant. A distorted hexagonal island with sides of alternating length $L_e=(1+\delta)L$ and perimeter length of $P=6L$ has an area of

$$A = \left(3/4\right)(1+\delta)(9-6\delta+\delta^2)^{1/2} + (1-\delta)(9+6\delta + \delta^2)^{1/2}L^2 \sim (3\sqrt{3}/2)(1-\delta^2)\overline{L}^2$$

as $\delta \to 0$.

Special cases are $A=(3\sqrt{3}/2)L^2$ for a perfect hexagon of side length $L(\delta=0)$ and $A=\sqrt{3}L^2$ for an equilateral triangle of side length $2L(\delta=1)$.

We now present some observations on zero-temperature equilibrium shapes of decorated islands where S bonding is assumed stronger at (100) than (111) steps by an amount of $\Delta\phi_S^e>0$:

(i) S coverage low enough so that less than half the island perimeter is covered. All S should decorate the (100) steps. The island remains hexagonal since this minimizes the perimeter length.

(ii) S coverage slightly above that needed to completely cover the (100) steps. The hexagonal island should distort (maintaining fixed $A=A_0$) to acquire longer (100) step edges, allowing accommodation of extra S with stronger bonding. Introducing a small first-order difference in the lengths of (100) and (111) step edges, $L_e=(1-\delta)L$, produces only a second-order increase in $L=L_0(1+\delta^2/6)$ and in perimeter length $P = P_0(1+\delta^2/6)$, where $P_0=6L_0=2.5\overline{M}\overline{A}_0^{1/4}(A_0)^{1/2}$ is the perimeter length of the undistorted hexagon (see above). Thus, there is minimal additional energy cost associated with this perimeter length increase.

(iii) S coverage high enough to exactly cover a perfect hexagon of side length $L_0$. Consider area-conserving conversion to a distorted hexagon with (100) sides of length $2L_0$ fully covered by S and uncovered (111) sides of length $0.1414L_0$ (see above). This produces an energy decrease of $3L_0\Delta\phi_S^e$ from enhanced S bonding and an energy increase of $3 \times 0.1414L_0\phi_M$ from increased uncovered perimeter length. Thus, the energy is lowered, and this “complete” distortion is preferred if $\Delta\phi_S^e>0.14\phi_M$. For smaller $\Delta\phi_S^e$, the minimum energy shape is less distorted.

Finally, we comment on experimentally observed shapes. There appears to be no substantial deviation from hexagonal shapes in the presence of S up to $\theta_S=7$ mML (although we cannot be certain that these shapes are fully equilibrated). This suggests that $\Delta\phi_S^e$ is small.

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**APPENDIX B: EQUILIBRIUM SHAPES OF DECORATED ISLANDS**

Energies of (100) and (111) steps on the S-free M(111) surface, for M=Ag or Cu, are almost equal, resulting in near-perfect hexagonal equilibrium island shapes.\(^5\) The presence of S could modify these equilibrium shapes, given an enhanced bonding by $\Delta\phi_S^e$ to (100) versus (111) steps. For a

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**TABLE III. Variance of step position distribution (orthogonal to step direction) for $L=48$ nm in unit of Å\(^2\).**

<table>
<thead>
<tr>
<th>$\theta_S$ (mML)</th>
<th>0</th>
<th>2.4</th>
<th>11</th>
<th>25</th>
<th>30</th>
<th>35</th>
<th>50</th>
<th>95</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\sigma^2$ (var)</td>
<td>6.7</td>
<td>5.8</td>
<td>5.3</td>
<td>53</td>
<td>132</td>
<td>155</td>
<td>235</td>
<td>302</td>
</tr>
<tr>
<td>Orientation</td>
<td>10(^{-4})-A</td>
<td>6(^{-4})-B</td>
<td>16(^{-4})-B</td>
<td>13(^{-4})-A</td>
<td>9(^{-4})-B</td>
<td>6(^{-4})-A</td>
<td>10(^{-4})-B</td>
<td>10(^{-4})-A</td>
</tr>
</tbody>
</table>

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APPENDIX C: ANALYSIS OF ONE-DIMENSIONAL LINEARIZEDREACTION-DIFFUSION EQUATIONS

One could potentially assess the impact of various clusters on coarsening from a complete solution of the linearized equations [Eq. (6.5a), (6.5b), and (6.5c)] for the $N_c$ distinct cluster densities, $\rho_c$. This approach would most readily be explored in a one-dimensional setting solving Eq. (6.5a), (6.5b), and (6.5c) in an interval of $0 < r < L_{\text{sl}}$ imposing different $\rho^c_{\text{eq}}$ values and zero gradients for $\rho^c_{\text{c}+\text{m}}$ at the end points (see Ref. 23). In this case, one seeks linearly independent solutions of the form $\rho^c = a_c \exp(\lambda r)$, setting $a_M = 1$. Eliminating $a_c$ yields a secular equation of the form $\lambda^2 A_0 + A_1 \lambda^2 + \ldots + A_{N_c-1} \lambda^{2(N_c-1)} = 0$. Physical symmetry demands that both $\pm \lambda$ are solutions producing a polynomial in $\lambda^2$. The degenerate case $\lambda = 0$ incorporates both the spatially uniform (equilibrium) solution and a solution where $\rho_c$ vary linearly. A complete solution to the boundary value problem can be obtained from a suitable linear combination of all these solutions.

APPENDIX D: ANALYSIS OF DIFFUSION LENGTHS AND EQUILIBRIUM CONSTANTS

For the reaction $M + M_2S_3 \rightarrow M_3S_1$, the diffusion length satisfies $L_M(M_2S_3) = (\theta_{M}S_{\text{eq}})^{-1/2}$, noting that $D_M \gg D_{M_2S_3}$. We use the result $\theta_{M_3S_1} \approx \Delta \Theta / 3$, where $\Delta \Theta = \theta_s - \theta_s(\text{crit})$ (see Sec. V) together with the identity $\theta_{M_3S_1}^{\text{eq}} = \exp(\beta \Delta \Theta) \theta_{M_3S_1}^{\text{eq}}$ to determine $\theta_{M_3S_1}^{\text{eq}}$. Here, $\Delta \Theta \approx 0.6-0.8$ eV is the difference in binding energies for $M_3S_1$ and $M_2S_3$ accounting for uncertainty in DFT estimates. This analysis, together with the result that $\theta_{M}^{\text{eq}} = \exp(-\beta \Theta)$, implies that at 300 K

$$L_M(M_2S_3) \approx (\Delta \Theta)^{-1/2} \text{ (a lower estimate),}$$

$$L_{M_2S_3}(M) \approx (D_{M_2S_3}/D_M)^{1/2} (\theta_{M_2S_3}^{\text{eq}})^{-1/2} \\ \approx 10^{-7}(D_{M_2S_3}/D_M)^{1/2} \gg L_{\text{sl}},$$

$$R_{M_3S_1} = (D_M/D_{M_2S_3}) (\theta_{M_2S_3}^{\text{eq}}/\theta_{M_3S_1}^{\text{eq}}) \\ \approx 10^{-7}(\theta_{M_2S_3}^{\text{eq}})^{-1} \ll 1 \text{ (except for } \Delta \Theta \ll 1).$$

For the pathway $M + S \rightarrow MS$ and $MS + S \rightarrow MS_2$, the relevant diffusion length satisfies $L_M(S) = L_MS(S) = (\theta^S_{\text{eq}})^{-1}$ since $D_M \gg D_S$ and $D_MS \gg D_S$. To evaluate these quantities, we determine the population, $\theta^S_{\text{eq}}$, of $S$ on terraces, which is free to participate in such reactions from the identity $\theta_{M_2S_3}^{\text{eq}} = \exp(\beta \Theta)(\theta^S_{\text{eq}}) / (\theta^S_{\text{eq}})^3$ using the above expression for $\theta_{M_3S_1}^{\text{eq}}$. We conclude that $\theta^S_{\text{eq}} = \exp(-\beta \Theta)(\Delta \Theta / 3)^{1/3} \approx (\Delta \Theta / 3)^{1/3}$ at 300 K, which implies that

$$L_M(S) = L_MS(S) = 2(\Delta \Theta / 3)^{-1/6} \Delta \Theta / 3.$$
DFT analysis for a six-layer Ag slab yields $E_{ads}/E_{bind} = 2.22/4.63/6.92/0.07/12.19/14.54/19.50/11.57\text{ eV}$ for Ag, S, AgS, AgS$_2$ (linear), Ag$_2$S$_2$ (bent), Ag$_3$S$_3$, and Ag$_4$S$_4$ (fcc-t).

Note also the identity $R_{CC}/L_{CC}\theta_{eq} = \theta_{eq} = \theta_{eq}$.

Here, one has $J_{MTOT}/(D_M S_j/L_{eq})$, but this regime may not be realized for increasing $S$ given that both $L_{eq}$ and $R_{M}/M_{3S_3}$ decrease.

$E_{eff}/Cu_3S_3$ is the sum of $E_{form}/Cu_3S_3$ = $0.28\text{ eV}$ and $E_d/Cu_3S_3$ = $0.05\text{ eV}$.

$E_{eff}/Cu$ is the sum of $E_{form}/Cu$ = $0.79\text{ eV}$ and $E_d/Cu$ = 0.05 eV.

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