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Adsorbate-enhanced transport of metals on metal surfaces: Oxygen and sulfur on coinage metals

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Coarsening (i.e., ripening) of single-atom-high, metal homoepitaxial islands provides a useful window on the mechanism and kinetics of mass transport at metal surfaces. This article focuses on this type of coarsening on the surfaces of coinage metals (Cu, Ag, Au), both clean and with an adsorbed chalcogen (O, S) present. For the clean surfaces, three aspects are summarized: (1) the balance between the two major mechanisms—Ostwald ripening (the most commonly anticipated mechanism) and Smoluchowski ripening—and how that balance depends on island size; (2) the nature of the mass transport agents, which are metal adatoms in almost all known cases; and (3) the dependence of the ripening kinetics on surface crystallography. Ripening rates are in the order (110) > (111) > (100), a feature that can be rationalized in terms of the energetics of key processes. This discussion of behavior on the clean surfaces establishes a background for understanding why coarsening can be accelerated by adsorbates. Evidence that O and S accelerate mass transport on Ag, Cu, and Au surfaces is then reviewed. The most detailed information is available for two specific systems, S/Ag (111) and S/Cu(111). Here, metal-chalcogen clusters are clearly responsible for accelerated coarsening. This conclusion rests partly on deductive reasoning, partly on calculations of key energetic quantities for the clusters (compared with quantities for the clean surfaces), and partly on direct experimental observations. In these two systems, it appears that the adsorbate, S, must first decorate—and, in fact, saturate—the edges of metal islands and steps, and then build up at least slightly in coverage on the terraces before acceleration begins. Acceleration can occur at coverages as low as a few thousandths to a few hundredths of a monolayer. Despite the significant recent advances in our understanding of these systems, many open questions remain. Among them is the identification of the agents of mass transport on crystallographically different surfaces e.g., 111, 110, and 100. © 2010 American Vacuum Society. [DOI: 10.1116/1.3490017]

I. INTRODUCTION

In everyday practice, one does not think of the surface of a metal as being “alive.” On the nanoscale, however, clean metal surfaces are alive, in the sense that they are typically in constant motion, and subject to rearrangement, even at room temperature. More specifically, some of the atoms on a clean metal surface are diffusing. For a surface that is not in its equilibrium morphology, this self-diffusion can result in net mass transport and morphological changes. Surface adsorbates, or “additives,” can profoundly change both the dynamics of mass transport and the equilibrium morphology. These effects of adsorbates have been revealed by studies of surface faceting and step bunching, film growth, island shapes, reconstruction, coarsening, step fluctuations, and other phenomena.

Mass transport at metal surfaces is not only ubiquitous but it is technologically important. For instance, it is typically used to advantage in surfactant-mediated film growth, an example being the fabrication of giant magnetoresistance hard drives. On the other hand, it is problematic when it destabilizes desired metal structures, for instance, in microelectron-
ics (electromigration), heterogeneous catalysis (sintering), and sensors (instability of Raman-active nanoarrays).

Over a range of different metals and at a given temperature, surface self-diffusion is faster, and the mobile atoms more numerous, in low-melting metals such as Cu, Ag, Au, and Al than in the higher-melting metal—although surface mass transport can occur in all metals at sufficiently high temperature. Given this, studies of surface mass transport on the low-melting metals at experimentally convenient temperatures (say, room temperature or below) can lead to general models that may apply to many transition metals, albeit at higher temperatures. This is one reason to focus on certain low-melting transition metals—the coinage metals, Cu, Ag, and Au—as we do in this article. We also focus on changes in surface mass transport induced by two common adsorbates: oxygen and sulfur, both of which belong to the group known as the chalcogens in the periodic table.

Our approach is to use coarsening as a window on mass transport. Further, the objects selected to undergo coarsening are small, two-dimensional (2D) islands of metal adatoms. These are prepared by physical vapor deposition in ultrahigh vacuum, at sufficiently high fluxes and low temperatures, such that islands nucleate and grow on terraces (as opposed to, say, step flow growth of pre-existing steps on the substrate).

It should be noted that the concept of metal-adsorbate clusters as important conduits of mass transport is by no means, a new one. It seems to have arisen independently in several different communities in the mid-1990s. For instance, catalyst sintering is a major concern in the heterogeneous catalysis community. Already in 1995, PtO$_2$ was proposed as a carrier between Pt nanoclusters dispersed on oxide supports which lead to enhanced sintering. Furthermore, this effect was proposed to occur due to a thermodynamic preference to form the PtO$_2$ complex (relative to metal adatoms) from the nanoclusters. In self-assembled monolayers, thiol-gold complexes were proposed to be responsible for Au transport in 1994. The same authors predicted that formation of mobile adsorbate-metal complexes might be a general phenomenon when electronegative adsorbates interact with “soft” metals. In the late 1990s, researchers in the surface science community identified metal-hydrogen complexes that could diffuse faster than single metal atoms, at least for certain metals. This was called by some a skyhook effect, the basic principle being that in the complex, bonds between the diffusing metal atom and surface were weakened, leading to a smoother potential energy surface and a lower diffusion barrier. In 1999, superfast decay of Cu islands was observed on Cu(111) in the presence of sulfur, and in 2000 it was proposed that Cu$_9$S$_3$ complexes were responsible for this enhanced mass transport. The explanation was the opposite of the skyhook effect: The diffusion barrier of the cluster was relatively high, but this was more than compensated by the high population of these carriers. Enhanced metal transport via metal-oxygen complexes was also proposed (but not confirmed) on Ag(100) in 2001 and 2002. In more recent years, there have been a number of ultrahigh vacuum studies reporting mobile complexes; those which concern coinage metal-chalcogen couples will be described in the text.

In the current review, as necessary background, Sec. II provides a brief description of the mechanisms by which such islands coarsen without adsorbates, on low-index surfaces of Cu and Ag. Section III reviews evidence that O and S can accelerate coarsening on these surfaces. Section IV presents evidence that metal-chalcogenide clusters are the mass carriers in accelerated coarsening. Possible mechanisms for formation of metal-chalcogenide clusters are discussed in Sec. V, and Sec. VI is a summary of open questions that could be fruitfully addressed by future work.

II. REVIEW OF COARSENING ON CU AND AG SURFACES WITHOUT ADSORBATES

A. Mechanisms

Two mechanisms of coarsening exist: the well-known Ostwald ripening (OR) and the less-familiar Smoluchowski ripening (SR). In both cases, a system containing droplets (or clusters or islands) of different sizes evolves toward lower droplet density and larger average size. This change is driven thermodynamically by an overall reduction in the three-dimensional (3D) surface energy (for 3D droplets) or 2D line energy (for 2D ones).

In our case, the particles are 2D metal islands on metal surfaces. In OR, mass is transferred by carriers which diffuse between effectively stationary islands, leading to growth of larger islands at the expense of smaller ones. In SR, mass is transferred by diffusion—and subsequent collision and coalescence—of the islands themselves. The rate of both OR and SR depends on the average island size, $R_{av}$, where one typically measures size as a linear dimension or “effective radius.” In the case of OR, the rate depends on size because the chemical potential is a decreasing function of size, $R$, of individual islands, whereas for SR the island diffusion coefficient decreases with $R$. Using scanning tunneling microscopy (STM), one can differentiate between two mechanisms straightforwardly based on observations of the evolution of individual islands. In OR, a small and roughly stationary island becomes progressively smaller and then disappears over time, while in SR, island diffusion and coalescence can be tracked directly. An example of each case is shown in Fig. 1.

B. Competition between the mechanisms

Reasonably extensive coarsening data are available for homoepitaxial Cu and Ag islands on (111) and (100) surfaces. Data for Au are less complete, with only one study each reported for the (110) surface and the (111) surface—perhaps because of the complication added by the Au surface reconstructions. Also, there are not many studies of (110) surfaces in general, although some information is available for Ag(110) and Au(110).

The well-studied surfaces of Cu and Ag exhibit common trends. OR is reported for the (111) faces, but SR for the
Fig. 1. Time-lapse STM images that illustrate ripening mechanisms of 2D Ag islands. (A) A small island, noted by the arrow, diminishes due to OR on Ag(111) at 300 K. 2 min after the last image, the island disappears. Image sizes are 150×120 nm². (B) Islands coalesce due to diffusion (SR) on Ag(100) at 300 K. Image sizes are 110×60 nm². Islands that will merge before a following image are linked by black bars. This analysis is based upon inspection of many sequential images in between the ones shown.

(100) faces, at room temperature. This dependence on surface geometry is illuminated for one pair of surfaces—Ag(111) and Ag(100)—by the graphs in Fig. 2. These show the calculated coarsening rate (K) as a function of average island size, R av, for each mechanism and for each surface. Here, \( K = -\frac{dR_{av}}{dt} \) and \( R_{av} \) is in units of \( a \), the surface lattice constant. The calculations are based on appropriate theoretical formulations for OR (Lifschitz–Slyosov–Wagner theory) and for SR (Smoluchowski coagulation equations with size dependent island diffusivity). These formulations require, as input, fundamental parameters (energy barriers and scaling exponents) which are obtained either from theoretical analysis or from extensive experimental data for both Ag surfaces. Two trends are noteworthy in these graphs. First, SR dominates at small island size, whereas OR dominates at large island size. Second, the rates of the two processes cross over at an island radius of \( 15a - 18a \). In these respects, coarsening on the two Ag surfaces is predicted to be quite similar. Then why is there a difference in the experimental observations?

The wide white arrows show the average island sizes used in the experimental observations on the two surfaces; the arrow in Fig. 2(a) falls below the crossover radius, whereas in Fig. 2(b) it falls above the crossover radius. The different sizes used in the experiments are partly a consequence of the nucleation kinetics: much slower atomic diffusion on Ag(100), coupled with the fact that typical deposition rates do not vary strongly from one laboratory to another, favors smaller islands on Ag(100) at any given \( T \). The difference may also result from the fact that decay rates on the order of \( 10^{-2} \text{a/s} \) to \( 10^{-3} \text{a/s} \) are most amenable to experimental observation, leading to choices of island sizes in specific ranges. The different experimental island sizes may thus explain the different mechanisms observed on Ag(100) and Ag(111). Figure 2 predicts a single coarsening mechanism on both surfaces if island arrays have the same average size, which would be interesting to test.

C. Nature of the transport agents in OR

One of the most intriguing and important challenges in understanding surface OR is to identify the species that mediate mass transfer. Experimentally, it is extremely difficult to observe such carriers directly and to confirm their role unambiguously—at least for the clean surfaces. Indirect experimental evidence, or energetic arguments, must therefore suffice. In principle, two types of carriers are possible on the clean surfaces: adatoms and vacancies. For Ag, adatoms are the predominant carriers on (111) and (110) surfaces since they have significantly lower terrace diffusion barriers. However, there is a close balance between adatoms and vacancies on the (100) surface since both diffusion barriers and formation energies are similar, thus making it difficult to predict which is the main carrier. These conclusions undoubtedly apply to Cu surfaces (see Ref. 54 for the relevant energetics) and may apply to unreconstructed Au surfaces as well. Supporting the extrapolation for Cu, there is indirect evidence of a temperature-dependent transition from SR at 300 K, to vacancy-mediated OR at 350 K for ripening of Cu islands on Cu(100).

D. Dependence of coarsening rates on surface crystallography

It is useful to compare the magnitudes of the relative rates expected on the three low-index faces of a given coinage metal. A strong influence of surface crystallography is already obvious from Fig. 2. There, at any given island size, coarsening is several orders of magnitude faster on Ag(111) than on Ag(100) regardless of the dominant mechanism.

A prediction of the crystallographic effect is reasonably straightforward for OR, and it can be built upon the following background. OR consists of two key steps, either of which can be rate limiting. These are attachment-detachment (AD) of carriers from island edges and terrace diffusion (TD)
of carriers. The effective activation barrier for OR, which also corresponds to the barrier for detachment, has the form

\[ E_{\text{OR}} = E_d + E_{\text{form}} + E_{\text{attach}} \]  

(1)

where \( E_d \) is the terrace diffusion barrier, and \( E_{\text{attach}} \) is any extra barrier (i.e., above the terrace diffusion barrier) to attachment at step edges. \( E_{\text{form}} \) is the energy difference between the island-bound carrier and the free carrier (and is omitted from the calculation of \( E_{\text{OR}} \) if \( E_{\text{form}} < 0 \)).\(^{30}\) See Fig. 3 for an illustration of the potential energy surface. The basic idea behind Eq. (1) is that the coarsening rate \( K \) is given by the product of three factors: (1) the diffusion coefficient for the carrier, controlled by barrier \( E_d \); (2) the equilibrium population of carriers, controlled by the formation energy, \( E_{\text{form}} \); and (3) a penalty factor of \( \exp(-E_{\text{attach}}/kT) \) in the presence of an attachment barrier.

TD- and AD-limited kinetics can be distinguished experimentally with STM. This is done by determining whether the area of a single island decays linearly with time and/or whether its decay rate depends on its environment, e.g., proximity to terrace steps or other islands. A nonlinear decay of the area, and/or a sensitivity to the local environment, are signatures of TD-limited kinetics. Linear decay of the area and an insensitivity to the local environment are signatures of AD-limited decay.

TD-limited coarsening kinetics, for which \( E_{\text{attach}} = 0 \), have been reported experimentally in all cases where clean homoepitaxial islands of Cu, Ag, or Au undergo OR,\(^{17,18,36–50}\) with only one major exception. [This was noted above, i.e., the case of vacancy-mediated AD-OR on Cu(100) above room temperature.\(^{40}\)] Therefore, a comparison of the kinetics of OR on different clean surfaces requires only values of \( E_d \) and \( E_{\text{form}} \) for metal adatoms. These values are summarized in Table I. Using values based on density functional theory (DFT) of \( E_d \) and \( E_{\text{form}} \) for single, isolated Ag atoms, the values of \( E_{\text{OR}} \) for Ag (to one decimal point) are as follows: 0.5 eV for (110), 0.7 eV for (111), and 0.9 eV for (100). For Cu, the trend is the same, but the values are somewhat dif-

### Table I. Values of \( E_{\text{form}} \) and \( E_d \) in eV, for isolated metal atoms on different low-index surfaces. The origin of the values is noted as DFT, effective medium theory (EMT), embedded atom method (EAM), Rosato–Guillope–Legrand (RGL) potential (Refs. 72 and 73), or experiment (EXP).

<table>
<thead>
<tr>
<th>Surface</th>
<th>( E_{\text{form}} )</th>
<th>( E_d )</th>
<th>( E_{\text{form}} + E_d )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag surfaces</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(111)</td>
<td>0.60-DFT(^a)</td>
<td>0.052-DFT(^b)</td>
<td>0.65, 0.71 ± 0.03-EXP (^b)</td>
</tr>
<tr>
<td>(100)</td>
<td>0.42-DFT(^c)</td>
<td>0.44-DFT(^c) 0.40 ± 0.04-EXP (^c)</td>
<td>0.86</td>
</tr>
<tr>
<td>(110)</td>
<td>0.16-EMT(^d) 0.20-RGL(^e)</td>
<td>0.29-EMT(^d) 0.28-RGL(^e)</td>
<td>0.45–0.48</td>
</tr>
<tr>
<td>Cu surfaces</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(111)</td>
<td>0.79-DFT(^f) 0.80-DFT(^f)</td>
<td>0.06-DFT(^f) 0.046-DFT(^f) 0.04 ± 0.01-EXP (^f)</td>
<td>0.85, 0.76 ± 0.04-EXP (^f)</td>
</tr>
<tr>
<td>(100)</td>
<td>0.59-DFT(^f)</td>
<td>0.54-DFT(^f) 0.48-DFT(^f)</td>
<td>1.13</td>
</tr>
<tr>
<td>(110)</td>
<td>0.24-EMT(^d)</td>
<td>0.29-EMT(^d)</td>
<td>0.53</td>
</tr>
<tr>
<td>Au surfaces</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(111)</td>
<td>0.62-DFT(^f)</td>
<td>0.12-DFT(^f)</td>
<td>0.74</td>
</tr>
</tbody>
</table>

\(^a\)Reference 54. 
\(^b\)Reference 43. 
\(^c\)Reference 74. 
\(^d\)Reference 75. 
\(^e\)Reference 72. 
\(^f\)Reference 27. 
\(^g\)Reference 76. 
\(^h\)Reference 38. 
\(^i\)Reference 65.
different: 0.5 eV for (110), 0.9 eV for (111), and 1.1 eV for (100). See Table I. We expect that a similar trend would prevail also for the clean, low-index surfaces of unreconstructed Au. Thus, one expects that for fixed island size and fixed temperature, the rates of OR will vary in the order (110) > (111) > (100).

A test of this prediction is shown in Figs. 4(a) and 4(b). Figure 4(a) shows a comparison of decay rates for \( \text{individual} \) homoepitaxial islands on Ag(110) and Ag(111), at \( T = 225 \) K and an initial island area of \( A = 120 - 140 \) \( \text{nm}^2 \), or about 3000–3500 atoms. This figure shows that a Ag(110) island decays much faster than a Ag(111) island, in accord with the relative rates predicted for that pair of low-index surfaces.

Figure 4(b) compares the rates of coarsening of Ag(111) and Ag(100) homoepitaxial island \( \text{ensembles} \), at \( T = 300 \) K for two different initial average island sizes. Because this is a different type of comparison than in Fig. 4(a)—using ensembles of islands, rather than individual islands—the curves slope upward, reflecting an increase in the average size with time. Noting the different \( y \)-scales for the two data sets, it is clear that the Ag (111) islands coarsen more rapidly than the Ag(100) islands, by about two orders of magnitude. However, this comparison has some complications. One complication is that OR has not been observed experimentally for the (100). Therefore, we show SR data for the (100) surface in Fig. 4(b), because it places the upper bound on the rate of OR [recall Fig. 2(a)]. A second complication is that experimental coarsening data are not available for comparable initial average sizes, for the (111) and (100). If Ag(111) data were available starting from the smaller initial average size of the (100), the (111) curve would be even steeper [recall Fig. 2(b)]. In other words, any measures taken to place the two data sets on a more equal footing would only accentuate the difference between the slopes. Figure 4(b) therefore demonstrates that the coarsening rates of Ag(100) and Ag (111) vary in the predicted order, hence confirming the entire hierarchy of rates, i.e., \((110) > (111) > (100)\).

III. EVIDENCE THAT OXYGEN AND SULFUR ACCELERATE MASS TRANSPORT AND COARSENING ON THE COINAGE METALS

In the 1960s, various authors explored the effect of chalcogens on surface mass transport in the coinage metals.\(^{35-38}\) Oxygen in the gas phase was proven to increase the macroscopic surface self-diffusion coefficient \( (D_s) \) on Cu\(^{35}\) and Ag\(^{37}\) surfaces by moderate amounts—less than an order of magnitude. Sulfur on Ag exhibited a more dramatic effect, increasing \( D_s \) for Ag by factors as high as \( 10^3 \), depending on \( T \), according to Perdereau and Rhead.\(^{56}\) It should be noted that macroscopic diffusion involves detachment and reattachment from steps as well as terrace diffusion, so that \( D_s \) reflects all of these processes. These types of experiments usually started from a flat, polycrystalline surface. The initially flat surfaces traversing the grain boundaries developed grooves over time, at a rate that was limited by the rate of surface diffusion. By monitoring the evolution of the width of the grooves, \( D_s \) could be extracted (using known values of the surface energy). A similar approach can be applied by scratching a surface and monitoring the rate at which the scratch fills in.\(^{55-58}\) As a result of these studies, it was proposed that self-diffusion is accelerated because metal adatoms diffuse “over” the chemisorbed layer, or at least across sites where the corrugation in the potential energy surface of a metal adatom is weakened by the presence of the chemisorbed layer.\(^{56,57}\) It should be noted, however, that in these experiments the gaseous atmospheres and levels of surface contamination were not well controlled by today’s standards.

In the 1980s, two techniques emerged which eventually allowed coarsening processes to be monitored in the ultimate controlled environment—ultrahigh vacuum—and with nanoscale precision. These techniques were low-energy electron microscopy (LEEM), and STM. The first study of this era, to our knowledge, was that of Peale \textit{et al.}\(^{58}\) Using STM, they observed that coarsening on Au (111) surfaces occurs much faster in air than in vacuum, although the adsorbate(s) responsible was not identified.
A. Oxygen-enhanced coarsening of Ag/Ag(100)

A series of studies from our laboratory clearly identified oxygen as an accelerator for ripening of Ag islands on Ag(100). Direct evidence of oxygen’s effect in this system can be seen in Fig. 5. Here, 0.3 ML of Ag was deposited at 250 K. Other studies have shown that oxygen on the Ag(100) surface is completely dissociated, well below this temperature. The top three panels show that the clean Ag surface evolves slowly; there is little change in island density over a period of 135 min. The lower panels show that coarsening is strongly accelerated after exposure to 20 L of O2 because the island density decreases much more strongly over a comparable period.

Additionally, oxygen has the following effects on Ag(100) island coarsening: (1) It changes the coarsening mechanism, from SR on the clean surface, to TD-limited OR and (2) it changes the Ag island shapes, from square toward circular and even diamond-shaped (rotated by 45° from the initial orientation), over long coarsening times. The change in island shapes can be attributed to the oxygen atom’s strong binding at kink sites at Ag step edges; complete conversion of an initial step edge into kink sites corresponds to a 45° rotation.

B. Sulfur-enhanced coarsening of Cu/Cu(111)

Turning now to sulfur as the adsorbate, Ling et al. reported very comprehensive evidence in 2004 that S can accelerate island coarsening on Cu(111). Figure 6 is a semilog plot of the scaled decay rate for an island of fixed initial size as a function of S coverage (θS). The decay rate, r, is taken as the reciprocal lifetime of the island, and the scaled rate is defined as the ratio of the decay rate in the presence of S (rS) and in the absence of S (r0), at 490 K. Note that θS on the ordinate ranges from about 0.006 to 0.020 ML, and acceleration already occurs at very small θS, around 0.003 ML. The basic picture presented by Feibelman for accelerated decay is that Cu detaches from the island edge, and forms CuS3 clusters which can potentially enhance mass transport. See Sec. IV for a further discussion.

A more detailed picture of behavior in this system was constructed by Ling et al., exploiting the feature that the experiments actually revealed three distinct regimes of coarsening with coverage ranges: (i) θS < 0.002 ML with TD-like decay and negligible enhancement relative to the clean surface, (ii) 0.002 ML < θS < 0.0065 ML with enhanced AD-like decay, and (iii) 0.0065 ML < θS with enhanced TD-like decay. Ling et al. captured these regimes qualitatively with an elegant linear reaction-diffusion model. The model quantified the ease of converting Cu adatoms into clusters as a function of S coverage, and thus the propensity for mass transport mediated by clusters to enhance decay. This model will be described in more detail in Sec. V.

Ling et al. also observed that during coarsening, island shapes change from hexagonal toward triangular. The distortion from hexagons is only mild at higher temperature of 395 K, but almost complete at lower T of 220 K. This effect is attributed to the stronger affinity of atomic S for the pseudofourfold-hollow sites available on certain step edges than for pseudothreefold sites available on others. These features of island distortion are analogous to those observed later and described above for the O/Ag(100) system.

C. Sulfur-enhanced coarsening of Ag/Ag(111)

Our own work has focused on the destabilizing effect that S exerts on Ag(111) nanoislands. Some of the results are summarized in Fig. 7, which shows a semilog plot of rS/r0 versus θS at 300 K. The horizontal bar at far right is a lower limit; the rate was too fast to be measured accurately, under the given experimental conditions, at this coverage. As for S/Cu(111), the explanation offered for destabilization or enhanced decay was that Ag transport is enhanced by metal-sulfur complexes. These include AgS3, but also other clusters such as AgS2 which could potentially have an even more...
significant effect. These observations prompted more complex and realistic nonlinear reaction-diffusion equation modeling, accounting for the nonlinear multistep reaction kinetics of cluster formation and decomposition. See Sec. V for a more detailed discussion. It can be seen that S accelerates the coarsening process by factors as high as $10^3$ at 300 K, a magnitude similar to that observed on Cu(111) at almost 500 K—see Fig. 6. This implies that the overall kinetics are slower on Cu(111) than on Ag(111) at fixed $T$ and comparable $T_h$.

Significantly, on Ag(111), there is clearly a threshold coverage below which S has no effect on coarsening kinetics at 300 K. See again Fig. 7. Actually, a threshold coverage might also be inferred for Cu(111) at 490 K, from Fig. 6. These thresholds are very low—about 0.008–0.010 ML for Ag(111), and perhaps about 0.002 ML for Cu(111). We conclude that these thresholds exist because the first few traces of S selectively adsorb at the strong pseudo-4$f$ and pseudo-3$f$ binding sites at step edges, before S populates the terrace. This, plus metal-sulfur cluster formation on the terraces, is required for enhanced decay. For our experiments on Ag(111), we have checked that the threshold coverage is consistent with the total length or density of step edges on the surface (accounting for the feature that every second step edge site is populated for saturated steps).30

In summary, there is strong evidence that coarsening of homoepitaxial islands is accelerated by O on Ag(100), by S on Ag(111), and by S on Cu(111). In Sec. IV, we turn to the mechanism responsible for this effect.

IV. EVIDENCE THAT CLUSTERS ARE INVOLVED IN COARSENING

In Sec. II, we mentioned that identifying the mass carriers in OR is one of the most interesting and challenging issues in coarsening. On the clean surfaces, transport agents are generally single metal atoms. But what are the carriers when chalcogens accelerate coarsening by three orders of magnitude, as in Fig. 6 or in Fig. 7? Do they remain single metal adatoms, but moving on a highly modified potential energy surface—as was postulated originally by Perdereau and Rhead56—or are they instead metal-additive complexes or clusters, or perhaps instead advacancies?

As already indicated in Sec. III, recent papers have proposed that mass transport is enhanced by the formation of stable metal-additive clusters. The key proponent of this idea in recent studies was Feibelman,27 who also provided an explanation for enhanced mass transport in terms of low formation energy and high population of these carriers (as described below). However, the concept of complex-enhanced mass transport has its origins in earlier literature on catalyst sintering, where the thermodynamic basis for this effect (a low enthalpy cost for cluster versus adatom formation) was also elucidated.21 Evidence for enhanced mass transport due to clusters arises partly from deductive reasoning, partly from calculations of cluster stabilities, and partly from experimental observations. We turn first to deductive reasoning.

A. Deductive reasoning: Process of elimination

Let us assume, for the sake of argument, that the carriers in the presence of chalcogens are single metal atoms. Then the acceleration must come from a reduction in $E_{OR}$, which is given by Eq. (1). Could the diffusion barrier, $E_d$, be affected (i.e., reduced) by adsorbed S or O? This was essentially the argument advanced by Perdereau and Rhead.56 However, the coverages necessary for acceleration are very small—hundredths or thousandths of a monolayer, as shown in Figs. 6 and 7. In fact, we argue that at these low coverages, much of the adsorbed chalcogen is bound at step edges. We therefore regard this argument as implausible.

Next, consider the formation energy, $E_{form}$. This is not an energy barrier, but rather the energy difference between a metal atom fully embedded within a 2D metal island or terrace and an isolated adatom at a terrace site (see Fig. 3). To calculate this quantity, within a very reasonable nearest-neighbor pairwise interaction model, one counts the number of nearest-neighbor bonds for each adatom within the island and then divides by 2 since these bonds are all shared with other adatoms. The result is the same as the energy cost to remove an atom from a kink site on a step edge. Within the framework of this approximation, Fig. 8 illustrates, in a simple way, the configurations that need to be considered. The (100) surface is chosen as an example, but the argu-

![Fig. 7. Semilog plot of the ratio of decay rates (inverse lifetimes) for 300 nm² Ag islands on Ag(111) in the presence and absence of sulfur, as a function of $T_h$. At $T_h \sim 0.035$, decay is so rapid that a quantitative analysis is not possible, and the horizontal bar represents the lower limit. Adapted from Ref. 30 with permission.](image1)

![Fig. 8. Illustration of the formation of a Ag adatom (labeled Ag) on a terrace, starting from (A) a kink site at a clean step edge and (B) a kink site at a step edge decorated with an adsorbed sulfur or oxygen atom (black circle).](image2)
ments extend to the other two low-index surfaces. On the clean surface, Fig. 8(a), the labeled Ag atom at a terrace site (right side) is less stable than at a kink site at the edge of an island (left side) by an energy corresponding to two nearest-neighbor Ag–Ag bonds for Ag(100). On the surface where a chalcogen (oxygen, for the sake of argument) decorates island edges, the energy difference between the two Ag atom configurations is identical, as illustrated in Fig. 8(b). Note also that changes in quantities such as the Ag atom diffusion barrier close to the step edge would not affect the energetic difference between the two Ag configurations.

Finally, consider the effect of a (possible) attachment energy, $E_{\text{attach}}$. In Sec. II, it was established that kinetics are usually TD-limited in the absence of chalcogens, so $E_{\text{attach}} = 0$ in this case. Thus, the presence of chalcogens could only increase—not decrease—the value of $E_{\text{attach}}$ for metal adatoms, which would have the effect of inhibiting rather than enhancing coarsening (in contrast to observations).

Experimental evidence for these arguments for S/Ag(111) follows from the existence of a threshold coverage described in Sec. III. The fact that S does not affect coarsening kinetics as it decorates step edges supports the claim that a chalcogen in Sec. III. The fact that S does not affect coarsening kinetics follows from the existence of a threshold coverage described in Sec. III. The fact that S does not affect coarsening kinetics as it decorates step edges supports the claim that a chalcogen

B. Cluster stabilities and mass transport propensities

Based on the results from density functional theory (DFT), in 2000 Feibelman proposed Cu$_3$S$_3$ as the carrier that expedites Cu island coarsening on Cu(111) exposed to trace amount of S. Later, using DFT, Shen et al. proposed Ag$_3$S$_3$ as one possible accelerator of Ag island coarsening on Ag(111).

The Ag$_3$S$_3$ cluster is illustrated on the right side of Fig. 9 (and the configuration for Cu$_3$S$_3$ is analogous). The three Ag atoms form a triangle in the center, where each Ag is at a threefold (3f) hollow fcc site and the triangle’s center is above an on-top site. (We call this an fcc-t cluster, after the notation of Chang et al.) Each edge of the Ag triangle comprises a pseudofourfold-hollow site that is decorated by S. Sulfur is known to form a particularly strong adsorption bond at fourfold (4f)-hollow sites on fcc surfaces.

The reason for the energetic viability of clusters such as $M_3S_3$ ($M = Ag, Cu$) as mass transfer agents is based more in thermodynamics than kinetics, as clearly elucidated by Feibelman. Specifically, this viability derives from the feature that the clusters have low $E_{\text{form}}$. In fact, for clusters, it is possible to have $E_{\text{form}} < 0$. Then in the expression Eq. (1) for $E_{\text{OR}}$, it is appropriate to delete $E_{\text{form}}$ [Eq. (30)] and so $E_{\text{OR}} = E_d$ in the case of TD-limited kinetics.] Thus, even though the barrier for cluster diffusion, $E_d$, may be higher than for single metal atoms, the overall barrier $E_{\text{OR}}$ may be lower. In other words, the clusters move more slowly but are far more abundant than metal adatoms. (A slight advantage also derives from the fact that each carrier contains 3, not 1, $M$ atom.) Calculated values of $E_{\text{form}}$ and $E_d$ for Ag$_3$S$_3$ and Cu$_3$S$_3$ are listed in Table II. Note that $E_{\text{OR}}$ is significantly higher for Cu$_3$S$_3$ (0.63 eV) than for Ag$_3$S$_3$ (0.30 eV), consistent with the faster coarsening rate on Ag(111) mentioned toward the end of Sec. II.

As noted in the Introduction to this section, earlier literature on catalyst sintering promoted the idea of enhanced mass transport mediated by complexes as well as its thermodynamic origin. The review by Harris discussing enhanced

| Cluster | $E_{\text{form}}$ | $E_d$ | Cluster | $E_{\text{OR}}$ | Metal atom $E_{\text{OR}}$
<table>
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<tbody>
<tr>
<td>Ag$_3$S$_3$, fcc-t</td>
<td>$-0.17 \pm 0.04$</td>
<td>0.30</td>
<td>0.30</td>
<td>0.65</td>
<td></td>
</tr>
<tr>
<td>Ag$_2$</td>
<td>$-0.07 \pm 0.04$</td>
<td>0.1–0.2</td>
<td>0.1–0.2</td>
<td>0.65</td>
<td></td>
</tr>
<tr>
<td>Cu$_3$S$_3$, fcc-t</td>
<td>$+0.28^{d} +0.30 \pm 0.04$</td>
<td>0.35$^{d} +0.30 \pm 0.04$</td>
<td>0.60–0.63</td>
<td>0.85</td>
<td></td>
</tr>
<tr>
<td>Cu$_2$</td>
<td>$+0.130 \pm 0.006$</td>
<td>Unavailable</td>
<td>&gt;0.13</td>
<td>0.85</td>
<td></td>
</tr>
<tr>
<td>Au$_3$S$_3$, fcc-t</td>
<td>$+1.15 \pm 0.02$</td>
<td>Unavailable</td>
<td>&gt;1.15</td>
<td>0.74</td>
<td></td>
</tr>
<tr>
<td>Au$_2$</td>
<td>$+0.54 \pm 0.02$</td>
<td>Unavailable</td>
<td>&gt;0.54</td>
<td>0.74</td>
<td></td>
</tr>
</tbody>
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$^{a}$This value is a correction to our previously published value of $-0.08$ eV (Ref. 62).

$^{b}$Reference 65.

$^{c}$Reference 62.

$^{d}$Reference 27.
degradation of supported Pt catalyst nanoparticles via PtO2-mediated mass transport notes that “in oxidizing atmospheres, the escape of Pt from a particle in the form of an oxide is much more thermodynamically favorable than the escape of Pt atoms,” and also gives associated enthalpy changes to support this hypothesis.

The appropriate calculation of $E_{\text{form}}$ itself requires an important physical assumption, namely, the nature of the species from which the clusters form. These $M_3S_3$ clusters are only viable, energetically, if the source of S is isolated S atoms on terraces—not S atoms bound at step edges (see the left side of Fig. 9). This is true because the $M_3S_3$ clusters are largely stabilized by the energy decrease of 0.4 eV per S atom when they move from 3f terrace sites to pseudo-4f sites. This contribution to $E_{\text{form}}$ would obviously be (nearly) zero if the S atoms originated, instead, at pseudo-4f sites at an extended M step. For Ag3S3, for example, $E_{\text{form}}$ is small but negative $[-0.17 \text{ eV}, \text{refining an earlier published value of } -0.08 \text{ eV}]^{32}$; meaning that the cluster should form spontaneously in the presence of Ag step edges and S atoms on terraces.

Experimentally, this choice of $E_{\text{form}}$ is supported by the existence of a threshold coverage. The above arguments imply that clusters would form (and coarsening would accelerate) only from S adsorbed on terraces. This means that S must first saturate the strong binding sites at existing step edges, which is corroborated by the observed threshold.

DFT shows that other clusters can have low $E_{\text{form}}$, and may also contribute to or even dominate OR.\(^{30}\) One such is an Ag3S3 cluster with Ag atoms in hcp sites and the triangle’s center over a top site (a “hcp-t” cluster), with three S atoms on the edges at pseudo-4f sites. This is nearly identical, both structurally and energetically, to the fcc-t cluster introduced earlier.\(^{30}\) More significantly, a AgS2 cluster is also viable, with $E_{\text{form}}=-0.04 \text{ eV}$ and a low $E_d$ (see Table II and Fig. 10). Similarly, a CuS2 cluster is found to be particularly stable on Cu(111). The AgS2 cluster is not an intuitively obvious candidate, and its stability was discovered fortuitously in our work, which probably explains why CuS2 was not revealed by previous DFT investigations as a candidate for Cu(111).\(^{27}\) It is possible that other stable clusters also await future discovery.

An analog to $MS_2$ has been discovered by Yates and co-workers on Au(111), where each S atom is replaced by a sulfur-hydrocarbon complex (thiol ligand) which bonds to the Au through the S atom.\(^{35-37}\) Those authors have found that this complex plays an important role in the chemistry and self-assembly of alkanethiol monolayers on Au(111).

Finally, note that the calculations described thus far concern only (111) surfaces of Cu and Ag. The $M_3S_3$ cluster shown in Fig. 9 has an obvious relationship to the substrate geometry, and hence would not be expected on a crystallographically different surface. A major challenge is to determine whether metal-chalcogenide clusters accelerate coarsening on other low-index surfaces. It is clear that oxygen accelerates coarsening on Ag(100), for instance, but the agent of mass transfer has not been identified. Using DFT, we have found that geometrical analogs of Ag3S3 are not reasonable candidates on the (100).\(^{65}\) Further discussion of this point is deferred until Sec. VI.

**C. Experimental evidence for clusters in S/Cu(111)**

In the case of Cu3S3, clear evidence for the cluster has not been reported in STM studies despite searches motivated by Feibelman’s proposal. This is perhaps because the formation energy is slightly positive, as shown in Table II. Wahlström et al.\(^{77}\) reported various ordered extended structures on terraces at temperatures below 230 K. Furthermore, they postulate that structures are formed by condensation of clusters which are mobile at room temperature, with the lack of change of S 2p core level spectra upon condensation indicating that the same clusters exist at both temperatures. As evidence for the existence of clusters at room temperature, they also cite an important study by Ruan et al.\(^{78}\) of etching of steps on Cu(111) exposed to S at room temperature, where it was found that Cu is removed from steps by incorporation into clusters including S and Cu which then form a disordered overlayer. However, a key observation of Wallden et al. is that “none of the extended structures...have features that suggest Cu2S3 as building units.” Instead, all of these structures are noted to have a striking resemblance to atomic order in the (0001) cleavage plane of CuS (covellite). There are protrusions in STM images of this structure suggested by Foss et al.\(^{79}\) as corresponding to S atoms coordinated to four in-plane Cu atoms to form a Cu2S cluster.

Wahlström et al.\(^{77}\) did note that “it seems plausible that the chains and more complex structures” found at step edge and near defects “are built from Cu2S3 clusters.” However, the model for enhanced coarsening requires that these clusters exist on terraces, not just near steps or defects.

In the work of Ling et al.,\(^{34}\) the role of the Cu2S3 cluster in coarsening was inferred from kinetics. In a simple approach, the rate depends on $(k_b)^N$, where $N=3$ if there are three S atoms per cluster. The measured value is $N=2.8–3$.  

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**Fig. 10. Schematic of an AgS2 cluster on Ag(111). The Ag atom is in a 2f bridge site, and the S atoms are in 3f hollow sites. Reproduced from Ref. 30 with permission. Copyright 2009 American Institute of Physics.**
However, these are complex systems and the simple third-order dependence was not tested by modeling. This would be a good problem for future work.

A more recent study by Rousseau et al.,80 following on the work of Feibelman and Ling et al., proposed that disordered S/Cu(111) overlayers at room temperature consist of a disordered, equilibrated mixture of sulfur adatoms and Cu$_3$S$_3$ clusters. This conclusion was based on normal incidence x-ray standing wave absorption data. However, their model for adlayer structure also required that the ratio of terrace S to terrace Cu$_3$S$_3$ populations remains constant over a rather broad range of S coverage from 0.13–0.33 ML, whereas a simple equilibrium analysis suggests that the ratio should increase strongly with increasing S coverage.

### D. Experimental evidence for clusters in S/Ag(111)

In the case of Ag(111), there is solid experimental evidence that the Ag$_3$S$_3$ clusters can be observed directly, and that they serve as mass transfer agents in OER. This does not preclude the participation of other clusters, but the Ag$_3$S$_3$ cluster is the only one for which experimental evidence exists thus far.

First, the clusters can be imaged with STM. Figure 11 shows a series of images after adsorption and dissociation of S$_2$ from an S$_2$ electrochemical source, on Ag(111) at 200 K. At very low coverage, the S first adsorbs at terrace step edges and causes faceting. As coverage increases, the dominant motifs—shown in Fig. 11—are rows of dots.63 The dimensions of individual dots match reasonably well with the dimensions predicted from a Tersoff–Hamann treatment of DFT.62

Second, the clusters seem to be very dynamic. In Fig. 11(a), at $\theta_S = 0.03$, many streaks can be observed, which suggests that clusters are moving, or forming and dissolving, on the timescale of the STM line scan (2.5 Hz). Figure 12 shows another example at higher coverage, $\theta_S = 0.10$, and $T = 200$ K. Here, the three panels show continuous successive images, at 200 s per image. Many of the dot-rows rearrange between images, most spectacularly the extended rows in the lower center, which flip orientation by 60°. It should be noted that the changes in Fig. 12 are not part of an approach to an equilibrium configuration; the surface had been allowed to equilibrate prior to this set of images, by heating to room temperature and recooling.62 (The dots disappear reversibly upon heating to room temperature.) Instead, the changes in Fig. 12 are random, thermal fluctuations. These fluctuations disappear as $\theta_S$ increases, at 200 K. The dynamic nature of the dots, at least in certain ranges of $T$ and $\theta_S$, suggests that they can participate in coarsening.

Third, the acceleration of coarsening is related to the dots in the following way. In Fig. 13(a),31 an ensemble of clean Ag islands was prepared. Conditions were tailored to make the islands small and ramified. Figure 13(b), taken 2 h later, shows that the clean islands are quite stable at 200 K. However, after adsorption of 0.1 ML of S at 200 K, Fig. 13(c) shows that massive coarsening has occurred. At the same time, $\theta_S$ has increased and the dot-row structure has formed.
as shown by the higher-magnification image in Fig. 13(d). Remarkably, the Ag islands do not coarsen further at 200 K—they are locked in place. This is shown by Fig. 13(e), taken 45 min after Figs. 13(c) and 13(d). In other words, coarsening accelerates at some intermediate S coverage but shuts down again when S coverage becomes too high.\textsuperscript{31} When a surface such as Figs. 13(c) and 13(d) is heated to room temperature, the dots disappear (reversibly) and the Ag islands do too (irreversibly). The overall picture that develops is this: The dots become somewhat “locked into” the dot-row structure at relatively high $\theta_S$ or low $T$, and at the same time coarsening is inhibited. It follows that the dots—Ag$_3$S$_3$ clusters—play an integral role in Ag mass transport.

Additional support for inhibited mass transport at high $\theta_S$ comes from the fact that pits appear on the Ag(111) surface with increasing $\theta_S$ at 200 K. At low $\theta_S$, pits are nonexistent [Fig. 11(a)]. As $\theta_S$ increases and the density of dots increases, pits are small and transient [one small pit can be seen in Fig. 11(b), at $\theta_S=0.1$]. By $\theta_S=0.3$, the pits are large and stable [Fig. 11(c)]. The interpretation is as follows. The dots incorporate Ag atoms. At low $\theta_S$, the source of Ag is the edges of terraces. At higher $\theta_S$, the source is the middle of terraces. Since the latter source is energetically more costly, the observation of these pits—and the fact that they are stable over time—is evidence of inhibited Ag mass transport.\textsuperscript{62} The model is shown schematically in Fig. 14.

### E. Clusters and adlayer structures in other systems

Interestingly, S adsorption induces terrace pitting, island formation, and step serration on Au(111). The details of these phenomenon have led Friend \textit{et al.}\textsuperscript{66–68} to conclude that S enhances Au mass transport at 300 K and above, by forming a mobile Au–S complex (of indeterminate stoichiometry) which ultimately assists the formation of a 2D AuS phase. Low coverages of S, $\theta_S \leq 0.1$, lift the herringbone reconstruction and hence allow the Au surface to be treated as a bulk-terminated (1×1).\textsuperscript{66–68} Similar to S, adsorbed O is also associated with surface pitting and other evidence of adsorbate-induced mass transport on O/Au(111), although oxygen is less effective than sulfur at lifting the Au reconstruction.\textsuperscript{67,69} Returning to S, it would be tempting to speculate that a Au$_3$S$_3$ cluster could be the agent of mass transport, except that Table II shows that this is unlikely—the cluster’s formation energy alone is significantly higher than the sum $E_{\text{form}} + E_d$ of Au atoms on Au(111). Instead, AuS$_2$ is a better candidate for accelerating mass transport in this case.

Finally, there are two examples where clusters of $M_3S_3$ or similar type have been identified firmly on other close-packed surfaces. On Ni(111), Ni$_3$S$_3$ clusters have been observed with STM.\textsuperscript{70} Both the hcp-$t$ and fcc-$t$ configuration were identified at 300 K, but the populations are not equal. The Ni$_3$S$_3$ clusters tend to form multicluster units like those shown in Fig. 15(a).\textsuperscript{70} The second case is clusters of Co$_3$S$_4$ on Au(111) and Ag (111).\textsuperscript{33,32} These clusters expedite Co mass transfer in the transformation of Co nanoparticles to a cobalt sulfide phase at 300 K.\textsuperscript{33} The structure of the Co$_3$S$_4$ cluster is shown in Fig. 15(b). It is similar to the Ag$_3$S$_3$ cluster in Fig. 9 except for the presence of an extra S atom atop the center of the Co triangle, making the cluster three dimensional. Together, these observations suggest that clusters analogous to, or resembling, $M_3S_3$ may be ubiquitous on hexagonal metal surfaces. A common driving force is presumably the strong adsorption bond formed by S at pseudo-4$f$ sites.

### V. MECHANISMS FOR METAL-CHALCOGEN CLUSTER FORMATION AND ENHANCED COARSENING

Two mechanisms have been suggested for formation of $M$-$X$ clusters ($M=$Cu, Ag and $X=O, S$) on (111) surfaces and associated enhanced coarsening. They mainly differ in whether the clusters form at the step edges, or on the terraces.

#### A. First mechanism

In this mechanism [Fig. 16(a)], an intact cluster detaches from a step edge and diffuses across a terrace, reattaching...
when it encounters another step edge. The chemical potential of this species is higher at smaller islands, and thus the associated equilibrium density at the step edge is also higher. Differences in these densities for islands of different size drive coarsening. In this scenario, it is unlikely that metal-chalcogen bonding can significantly reduce the cluster formation energy, since the X atom is already bonded at the step edge. Furthermore, the cluster formation energy could be significantly increased (relative to that of a metal adatom) if the cluster contains multiple M which must all be detached from the step edge. Thus, this scenario is most viable for cluster compositions containing just one metal atom, i.e., $MX_n$ where one might anticipate that $n = 1$ or $2$.

Over time, the net accumulation of these clusters at larger islands leads to coarsening. However, not only M atoms accumulate at larger islands, but also X atoms. At some point, the smaller islands could run out of X and thus terminate enhanced coarsening—contrary to observation. Therefore, if this mechanism applies, we deduce that a second species with a lower $M:X$ ratio must also be able to attach/detach and diffuse. The constituents of such a “shuttle pair” could, for instance, be $MX_2$ and X. This type of cluster-based model is illustrated in Fig. 16(a). Such a model was originally proposed for O/Ag(100), partly because O interacts very strongly with step edges, even changing the step orientation—but it seems unlikely now, in light of the inability to identify a viable candidate Ag–O cluster using DFT. See Secs. IV B and VI.

### B. Second mechanism

In this mechanism, proposed by Ling et al., single metal atoms detach from step edges, but efficiently form $M$-$X$ clusters close to the step edge, using excess X which is on the terrace. The clusters can diffuse across terraces, and are continually dissociating and reforming. Subsequent to dissociation close to a step edge, they may contribute $M$ atoms back to the step. This mechanism is illustrated in Fig. 16(b). Interestingly, this mechanism requires that clusters are sufficiently stable to have a significant population on terraces, but not so stable as to be unable to dissociate (in which case they would be passive by-standers in the mass transport process).

Behavior of this model was also analyzed by Ling et al., assuming linear kinetics for the “direct formation” of clusters from adatoms. This assumption resulted in a coupled linear set of reaction-diffusion equations for the densities of adatoms and clusters. Boundary conditions imposed on these equations are consistent with the above model description: the adatom density matches its equilibrium value at island edges (being higher at smaller islands), and there is a zero-flux boundary condition on the cluster density. Analysis of these equations revealed three distinct regimes (i)–(iii) of behavior with increasing S coverage. These regimes will now be described in more detail.

For regime (i), the S coverage is so low that the “reaction length”—the distance within which a detaching and diffusing Cu atom typically forms a cluster—exceeds the typical island separation. Thus, most mass transport between islands occurs via Cu adatoms, and one finds TD-limited decay as for the S-free system, with negligible enhancement. In regime (ii), the reaction length has decreased significantly below the island separation. Thus, Cu adatoms form clusters within a “short” distance of the island edge and these produce enhanced mass transport. However, the conversion is not so facile as to produce complete equilibration of adatom and cluster densities, and the adatom density is roughly uniform on terraces away from island edges. The result is AD-like decay kinetics. Finally, in regime (iii), conversion between adatoms and clusters is so facile that the associated densities are fully equilibrated, and thus both vary smoothly across terraces between higher values at small islands and lower values at large islands. Thus, one again recovers TD-like decay kinetics. The success of the model is reflected in the feature that these three regimes match qualitatively the behavior described in Sec. III B for the S/Cu(111) system.

Later refinement of the model for application to the S/Ag(111) system incorporated two key features required for quantitative predictive capability. These refinements should also produce a quantitative description for the S/Cu(111). First, we account for a threshold coverage, $\theta_C$, for S to saturate existing step edges on the surface. This means that the key variable is the excess S coverage, $N_s = \theta_s - \theta_C$, which then effectively replaces the absolute S coverage in the formulation of Ling et al. Second, one must realistically account for the complex multistep mechanism leading to the formation of such species as $M_3X_3$. Such species will not be formed by the simultaneous collision of three $M$ and three S. Rather, one can imagine a multistep pathway such as: $M + X \rightarrow MX, MX + X \rightarrow MX_2, \ldots, M_2X_3 + M \rightarrow M_3X_3$. The formation of “bimolecular reaction” kinetics of any of these
cluster species is necessarily nonlinear. Thus, the appropriate formulation is in terms of a coupled set of nonlinear reaction-diffusion equations. However, the boundary conditions remain as they were in the formulation of Ling et al.\textsuperscript{34} Approximate but effective analysis of these equations is achieved by linearization about the spatially uniform equilibrium values of cluster densities, noting that coarsening is driven by small differences in chemical potentials and thus in adspecies densities induced by differences in island sizes. Analysis of these linearized equations can recover the type of scenarios described above for the simple linear model.

C. Other mechanisms

Finally, we should mention the possibility of other scenarios for enhanced coarsening. For example, if mass transport is dominated by the species $M_3X_3$, then as noted by Ling et al.,\textsuperscript{34} one does not expect direct detachment of this species from step edges. However, it is plausible that a smaller cluster such as $MX$ or $M_X$ does detach directly. In this case, one must change the boundary condition in the nonlinear reaction-diffusion equations to reflect the detachment of these clusters (thereby incorporating differences in their chemical potentials and equilibrium densities at the edges of islands of different sizes). There is perhaps no energetic advantage to this mechanism relative to detachment of $M$. However, there is a potential kinetic advantage since for enhanced mass transport, there must be sufficiently strong coupling between the detaching species and the cluster dominating mass transport. The coupling would be enhanced by a more direct pathway for formation of the key cluster. Another example would be if mass transport is dominated by $MX_2$. Then this species could be formed fairly directly by detachment of $MX$ together with the reaction $MX+X\rightarrow MX_2$.

VI. SUMMARY AND FUTURE CHALLENGES

Chalcogens accelerate coarsening of homoepitaxial metal islands, and hence accelerate mass transport, on coinage metal surfaces. This sweeping statement must be tempered by several caveats, each of which represents a large challenge. For instance, oxygen accelerates coarsening on Ag(100), but DFT analysis has not identified suitable Ag–O clusters. A possible alternative mechanism has been suggested recently,\textsuperscript{17} based on an interesting observation for coarsening in clean metal(100) homoepitaxial systems. For these surfaces, vacancies rather than adatoms in some respects provide the most natural carrier for mass transport. This is because vacancies have both lower $E_V$ and lower $E_{\text{form}}$\textsuperscript{7}. However, typically they do not control coarsening since $E_{\text{attach}}$ is prohibitively high. (Note that exceptions exist.) However, there is the possibility that an adsorbate, particularly one that prefers adsorption at step edges, could reduce $E_{\text{attach}}$ for vacancies, thus opening a new dominant pathway for mass transport. This scenario might be described as coarsening “catalyzed” by the presence of an adsorbate, since the adsorbate just reduces a rate-controlling kinetic barrier but does not directly participate in mass transport. Yet another possibility can be envisioned under conditions where there is significant adsorbate coverage on terraces. Here, some adsorbate is always in the vicinity of metal adatoms (or metal vacancies) on terraces and thus could modify their formation energy relative to the clean system. The presence of adsorbate could also modify diffusion barriers as suggested in early work.

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\textsuperscript{1}E. Williams and N. C. Bartelt, Ultramicroscopy 31, 36 (1989).
\textsuperscript{8}J. A. Venables, Introduction to Surface and Thin Film Processes (Cambridge University Press, Cambridge, 2000).
\textsuperscript{15}P. A. Thiel and P. J. Estrup, in The Handbook of Surface Imaging and