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Additive-enhanced coarsening and smoothening of metal films: Complex mass-flow dynamics underlying nanostructure evolution

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Abstract

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Keywords

metal, oxygen, diffusion, dissociation, dynamics, energy transfer, film, flow, low temperature, mass, nanoparticle

Disciplines

Mathematics | Physical Chemistry

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Additive-enhanced coarsening and smoothening of metal films: Complex mass-flow dynamics underlying nanostructure evolution

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Exposure of Ag/Ag(100) thin films to molecular oxygen (O_2) at 220–250 K is shown to *activate* low-temperature coarsening of submonolayer island distributions, and a smoothening of multilayer films with “mounded” morphologies. Dissociation of O_2 at kink sites populates step edges with atomic oxygen (O), modifying the step-edge energetics, and facilitating Ostwald ripening of film nanostructures. We propose that ripening occurs by “easy” detachment and terrace diffusion of an Ag_nO species. Cluster diffusion does not play a significant role, contrasting with the O-free system.

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Many of the phenomena that we see in everyday life, whenever a liquid interacts with a solid, can also occur when a solid interacts with another solid, at least when one of the two solids is in the form of a very thin film. In such a case, the thin film can wet the other solid or not; the film can redistribute itself spatially with time—e.g., its droplets (clusters) can merge; and both behaviors can be affected by “third parties,” i.e., additives. The effect of additives, particularly additives that act as surfactants, has been investigated and exploited extensively in the growth of thin solid films. However, the effect of additives on mass redistribution and relaxation after growth has been much less examined for thin solid films. Both are important topics, since they relate to the formation and temporal stabilities of solid nanostructures.

One example of considerable technological significance is the use of surfactants to control the growth mode in semiconductor heteroepitaxy, e.g., converting Stranski-Krastanov growth of Ge on Si(100) to quasi-layer-by-layer growth.¹ In other words, the surfactant increases the propensity of the Ge to spread over the Si substrate. Surfactants can also produce smoother interfaces in the fabrication of superlattice heterostructures (e.g., spin valves) in thin metal films.² Naturally, there have also been many theoretical proposals for detailed mechanisms of surfactant action,³ assisted by experimental studies of simple model systems. The simplicity of the latter often springs from the fact that film and substrate are chosen to be chemically identical (homoepitaxial growth),^{4–8} which is also true in the present study.

Much less studied, but just as critical, is an assessment of the effect of adsorbates on the *stability and evolution of thin-film nanostructures* after deposition. This impacts the operation of nanostructure devices in nonpristine environments. One early, notable study showed that rough, multilayer Au/Au(111) films in *air* relax (smoothen) quickly, but are quite stable in ultrahigh vacuum.⁹ In this study, we consider one component of air, oxygen, and its effect on Ag nanostructures. (The interaction of oxygen with Ag nanoparticles is also of considerable technological importance in catalytic epoxidation of ethylene.) The substrate is chosen to be Ag(100), which has a low reactivity to oxygen,^{11,12} thus allowing a controlled analysis of the effect of a weak adsorbate [unlike the Ag(110) surface, which is highly reactive to oxygen¹⁰]. Despite the low reactivity, our previous diffrac-

tion study showed that the presence of oxygen accelerates nanostructure relaxation.¹² The present microscopy study provides a detailed real-space picture of coarsening, demonstrating that oxygen actually changes the kinetic pathway for relaxation, and allowing us to make deductions about how that occurs.

It is essential to first review the behavior of the Ag/Ag(100) system without oxygen. For deposition between 190 K and room temperature, distributions of compact two-dimensional (2D) islands form effectively irreversibly in the low submonolayer regime (0.1–0.4 ML), whereas arrays of 3D “mounds” (stacks of islands) develop in the multilayer regime.¹³ Both these morphologies are nonequilibrium structures. Hence, after deposition, submonolayer films relax (coarsen, ripen) at room temperature, small islands disappearing and large islands growing. This occurs via a mechanism termed Smoluchowski ripening (SR),¹⁴ which is diffusion and coalescence of large 2D islands, analogous to classic coagulation.¹⁵ The alternative mechanism, Ostwald ripening (OR), which is diffusive mass transfer from smaller to larger islands, does not take place because, for pure Ag/Ag(100), as SR has an energetic advantage over OR.¹⁶ After deposition, multilayer films also relax (smoothen) at room temperature.¹⁷ All these relaxation processes are driven by the tendency to minimize the free energy associated with step edges.

The current experiments were performed in an ultrahigh-vacuum chamber—base pressure $< 10^{-10}$ Torr. Evaporative deposition of Ag onto the Ag(100) single-crystal surface was usually performed at $T \leq 250$ K. The surface was also exposed to molecular oxygen (O_2) by back-filling the chamber to $\sim 10^{-8}$ Torr (typically after deposition of Ag). Dissociation of (transient) adsorbed O_2 to more stable atomic oxygen (O) is thermally activated and site specific. It is inefficient on the Ag(100) terraces, occurring only at kink sites along step edges.¹¹ This process populates step and island edges in our deposited films with O above 210 K (although O can likely also leave the step edges¹¹). Nanostructure evolution is monitored with an Omicron variable-temperature scanning tunneling microscope (VTSTM). The variable-temperature capability is crucial: the clearest elucidation of the effects of oxygen comes from experiments below room temperature, where relaxation processes in clean films become negligibly slow (see above).

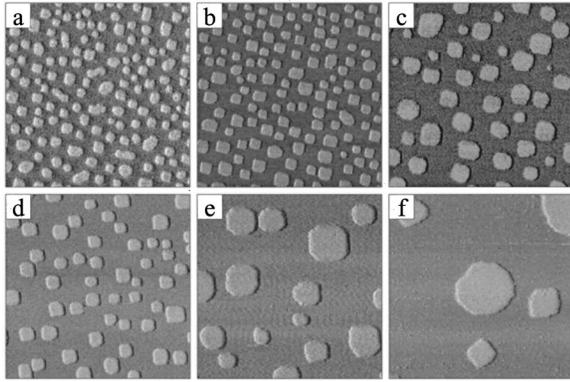


FIG. 1. Evolution of 0.3-ML Ag/Ag(100) films deposited and maintained at 250 K: (a) just after deposition without O; (b) after 160 min without O; (c) after 167 min with 20-L O₂. Evolution of 0.3-ML films deposited at 300 K, then cooled to 250 K and exposed to 20-L O₂, after (d) 44 min, (e) 8 h, and (f) 44 h. STM images are 100×100 nm².

First, the VTSTM data of Figs. 1 and 2 reveal the influence of oxygen on relaxation of submonolayer island distributions. Figure 1(a) shows an island distribution created by deposition of 0.3-ML Ag films on broad terraces of Ag(100) at 250 K. No significant evolution occurs in the absence of oxygen [Fig. 1(b)]. This is consistent with an effective barrier for SR of $E_{SR} \approx 0.75$ eV,¹⁶ implying that coarsening is slower by a factor of 330 than at 300 K (where it occurs over tens of minutes). However, dramatic evolution after exposure to O₂ is apparent in Fig. 1(c) [cf. Fig. 1(a)]. Similar oxygen-induced evolution at 250 K is apparent in Figs. 1(d)–1(f), where islands are initially larger due to deposition at 300 K. Coarsening also occurs down to 220 K, after exposure to O₂. This is consistent with earlier low-energy electron-diffraction studies,¹² which could monitor only mean island separations, and provided no information on island distributions or the coarsening mechanism. Note that large islands coarsened over very long times [Figs. 1(e) and 1(f)] reveal a change in island shape from a near-square configuration with [110] step edges (familiar from the O-free system), to a rounded or even diamond-shaped “equilibrium” configuration with

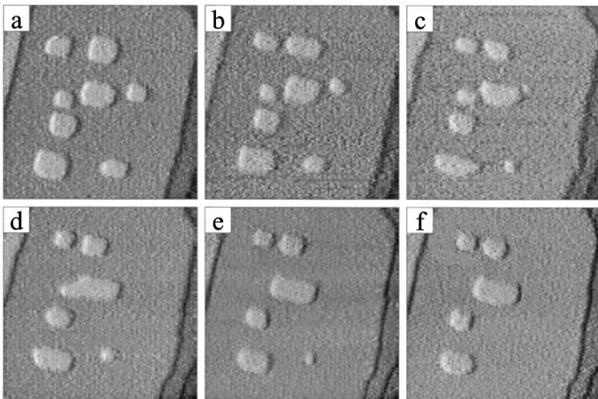


FIG. 2. (a)–(f) Evolution over about 15 min of Ag islands on a narrow terrace at 250 K after exposure to 20-L O₂. Image sizes are 35×35 nm².

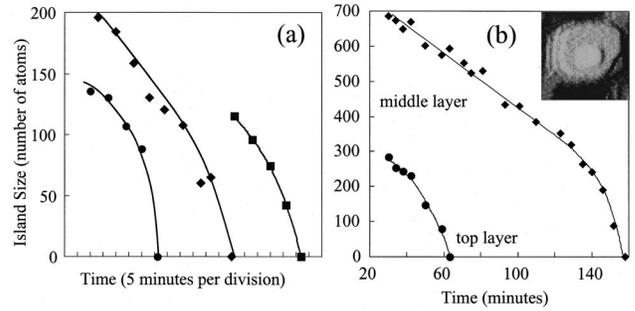


FIG. 3. (a) Decay of areas of islands, created by deposition of 0.05-ML Ag/Ag(100) at 250 K, after exposure to 17-L O₂. (b) Decay of area islands in the top two levels of a three-layer stack (see the inset), created by deposition of 25-ML Ag/Ag(100) at 250 K, after exposure to 17-L O₂. In (a) and (b), the zero-size points are *upper* estimates of the disappearance times. Curves are to guide the eye.

more preference for [100] orientations. Extended step edges bounding broad terraces also adopt a different structure from the O-free system. This is clear evidence of step decoration by O (see below).

Detailed analysis of scanning tunneling microscopy (STM) images reveals no significant island diffusion and coarsening via collision, but rather dissolution of small islands. This is demonstrated clearly by following the evolution of the islands in Figs. 2(a)–2(f), where smaller islands dissolve and larger ones grow. Clearly, this is not Smoluchowski ripening, but rather Ostwald ripening.

It is also appropriate to check if the observed coarsening kinetics on broad terraces is consistent with classic expectations for OR. In fact, we do not see the expected deceleration of coarsening where the mean island separation satisfies $L_{av} \sim L_0(1+t/\tau)^{1/3}$. However, this relation is predicated on the island size distribution having achieved its “selected” long-time shape,¹⁸ a condition which is not met in our experiments initially (where distributions are narrow),¹⁹ but only after 2–3 h of coarsening. A detailed analysis will be reported elsewhere.

Thus, exposure to oxygen not only *activates* coarsening at 250 K, but it actually *changes* the dominant coarsening mechanism. In general, OR can be terrace diffusion limited (expected for clean metal systems) or interface transfer limited (due to an extra barrier for attachment at step edges, possible in the presence of adsorbates). The area A of dissolving islands decays like $A \sim (t_0 - t)^{2/3}$ for the former, and decays linearly ($A \sim A_0 - kt$) for the latter.²⁰ Our experimental observations of nonlinear behavior (Fig. 3) indicate terrace-diffusion-limited behavior, as often seen in adsorbate free metal homoepitaxial systems.²⁰

Second, let us examine the smoothing of films with mounded morphologies. Figure 4(a) illustrates the film roughness W (the rms width of the film height distribution), versus time t at 250 K, after deposition of 25-ML Ag. This reveals that smoothing is negligible without oxygen, but becomes significant after exposure to oxygen, the smoothing rate increasing with exposure. Figure 4(c) shows morphological evolution after an exposure of 17-L O₂. Analysis

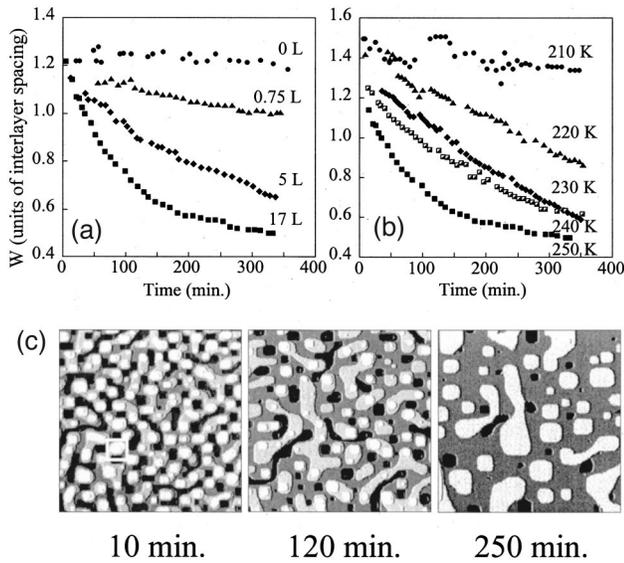


FIG. 4. Smoothing of 25-ML Ag/Ag(100) films. (a) Decay of the roughness W (in units of interlayer spacing) at 250 K with various O_2 exposures (shown). (b) Temperature dependence of the decay of W for a fixed O_2 exposure of 17 L. (c) STM images ($154 \times 154 \text{ nm}^2$) of the smoothing of 25-ML Ag/Ag(100) films at 250 K after exposure to 17-L O_2 . The island stack in Fig. 3(b) is identified by a white square in the left frame.

of the STM images reveals that the mechanism underlying smoothing is a multilayer version of OR. Further, a more detailed analysis of the decay of individual island stacks [Fig. 2(b)] reveals a nonlinear disappearance of the areas of islands in individual levels (cf. Ref. 21). This is analogous to submonolayer island decay behavior, and is again consistent with terrace-diffusion-limited OR.

More generally, for a fixed oxygen exposure of 17 L, a significant smoothing of 25-ML Ag films persists down to 220 K, often with a roughly linear decay of W vs t ; see Fig. 4(b). Akin to theories for submonolayer OR kinetics, there exist some treatments of smoothing kinetics. One thermodynamic formulation (based on line tension reduction for curved steps), as well as simulations of the smoothing of a bi-periodic array of mounds, predict a roughly *linear* decay of the mound height.²² This theory may describe the initial stages of decay, at least for 220–240 K. A more precise description must account for the details of the mound distribution, system-specific aspects of the kinetics of decay of individual island stacks, and the feature that W cannot vanish for nonintegral ML films (as is likely reflected in the 250-K data).

Finally, consider the mechanism underlying film evolution via terrace-diffusion-limited OR. We propose that the dominant mass-transport pathway involves the detachment from step edges of an Ag_nO adspecies, with $n=1$ or 2 (i.e., Ag_2O or AgO) rather than Ag, thus explaining the departure from SR in the O-free system; see Fig. 5(a). Supporting arguments follow.

(i) The effective activation barrier for OR has the form $E_{OR} = E_d + \delta E$, where E_d is the diffusion barrier, and δE is the energy difference between the detached configuration and

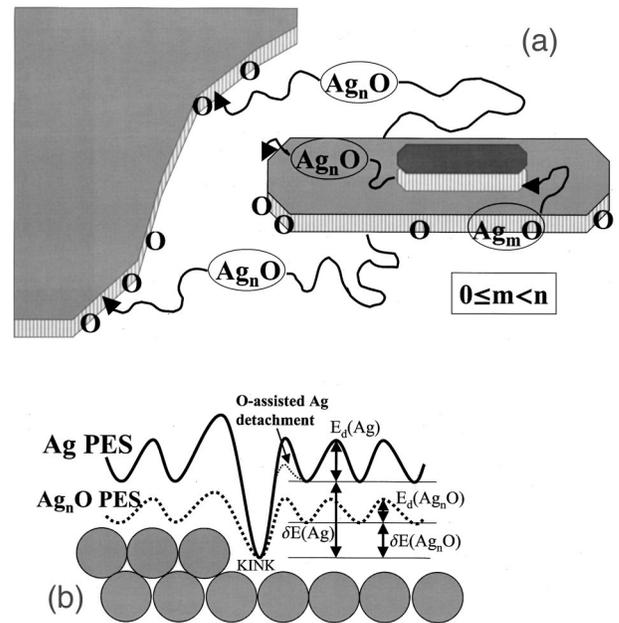


FIG. 5. Schematics for (a) the atomistic mechanism of coarsening and smoothing. (b) Potential-energy surface for an adspecies detaching from a typical (kink) site at the step edge for Ag in an O-free system (solid curve), Ag with detachment assisted by O at the step edge (thin dotted curve), and an Ag_nO adspecies (thick dotted curve).

typical attached configurations (at kink sites) of the diffusing species. If mass transport involved just Ag atoms, then E_d and δE (and E_{OR}) would be unchanged from the O-free system [see Fig. 5(b)], so coarsening would not be enhanced. (One exception is if sufficient O exists on or below the terrace to influence E_d for diffusing Ag. Conditions of very high O_2 exposure and low temperature needed for such high O coverages²³ are not met in our study.)

(ii) One might imagine that the presence of O at step edges could simply reduce the barrier for the first hop away from the step by detaching Ag (thus perhaps enhancing coarsening by Ag mass transport). But then the barrier for the reverse attachment hop would also be reduced (due to detailed balance). Consequently, the overall or effective rate for complete detachment would actually be unchanged from the O-free system, as would the effective barrier E_{OR} . See Fig. 5(b).

(iii) We conclude that an Ag_nO species must detach with effective detachment barrier lower than for Ag due to a lower δE or lower E_d (or both). A lower δE seems consistent with strong Ag-O bonding. We note that mobile $M-O$ -units are believed to mediate formation of domains of oxygen-induced reconstructions on $M(110)$ surfaces, where $M = Ag, Cu,$ and Ni .²⁴

(iv) Strong Ag-O bonding would likely be reflected in a reduced step edge energy of open or kinked [100]-type step edges (relative to close-packed [110] step edges), as the former are preferentially decorated by O at kinks. Exactly this feature is seen in Fig. 1.

(v) The proposed role of Ag_nO in coarsening is consistent with the strong dependence of coarsening rate on O_2 expo-

sure: the process is limited by the amount of O at the step edge.

To summarize, the addition of oxygen to the system introduces an adspecies (Ag_nO) which can transport Ag between islands more easily than Ag adatoms. This is due to a lower effective detachment barrier from step edges (due in turn to weaker binding or faster terrace diffusion). This explains the change in mechanism for coarsening relative to the O-free system.

There is one potential problem with the above picture. It is possible, particularly for low O_2 exposure, that a small island could be depleted of O before completely dissolving, either in submonolayer or multilayer experiments, thus “freezing out” further evolution. However, we see no evidence of this effect in STM images. Thus we argue that O (or perhaps AgO , if the Ag transporting species is Ag_2O) can also detach from step edges, and diffuse across terraces and steps to repopulate O depleted islands in the same or higher layers, facilitating further decay via Ag_nO detachment. To at least partially test this claim, we pre-exposed an $\text{Ag}(100)$ surface to 20-L O_2 , and found that during subsequent deposition of Ag at low T , the nucleation of Ag islands is greatly

inhibited both on terraces *and* on top of a pre-existing island. The latter requires an upward transport of some O-containing species, which interferes with nucleation.

In conclusion, exposure to O_2 of Ag films on the unreactive $\text{Ag}(100)$ surface is shown to activate coarsening and smoothing processes at low temperature via an enhanced mass transport due to formation of a complex including Ag and O. This type of complex formation facilitating mass transport has in fact been seen in other systems.²⁵ Our STM analysis cannot resolve the various participating adspecies. However, based on a consideration of effective detachment energies, and extensive observations of film coarsening and smoothing dynamics, we propose the following picture. Film evolution is primarily due to step-edge detachment and diffusion of an Ag-rich species, Ag_nO with $n=1$ or 2, facilitating Ag mass transport. It likely also involves transport of O (or perhaps AgO , if $n=2$) facilitating repopulation of islands depleted of O.

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