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The effect of common gases on nucleation of metal islands: The role of oxygen in Ag(100) homoepitaxy

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Preexposure to molecular oxygen gas, $O_{2,g}$, can have a strong effect on the nucleation and growth of Ag islands on Ag(100) at 250 K. At this temperature, molecular oxygen dissociates efficiently at kink sites on steps. Subsequent deposition of Ag produces a far lower density of Ag_{ad} islands than without oxygen. There is an associated increase in the Ag flux-scaling exponent, from 0.28 for the oxygen-free surface to 0.9 for the preexposed surface. Two-step deposition experiments show that species containing atomic oxygen diffuse freely across terraces and steps at this temperature and on the time scale of deposition. We hypothesize that the nucleating species contains both Ag and O, and that nucleation of islands is highly reversible (critical size $i \gg 1$). The diffusion of small islands, if it occurs, is not sufficient to explain the data. © *2003 American Institute of Physics.*
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I. INTRODUCTION

As trends in technology advance to ever-smaller scales, the production and control of nanoscale structures becomes increasingly important, and the sensitivity to contamination becomes increasingly critical. Contamination from common background gases can never be eliminated entirely, even in the cleanest environments. However, this disadvantage may also be turned to advantage: If the effects of adsorbed gases are sufficiently understood, they can be used as deliberate tools in controlling nanostructure morphology. Indeed, surfactants have drawn much interest because of their ability to alter the *vertical* atomic-scale morphology of deposited films, i.e., to enhance layer-by-layer growth.[1–10] A related phenomenon is the effect of adsorbates, including surfactants, on the *lateral* (in-plane) morphology that is typically controlled by nucleation and growth of islands during metal deposition.[4,5,10–12] In this paper, we focus specifically on Ag(100) homoepitaxy, since this is a simple model system in which the pure-film characteristics are well understood.[13] Furthermore, we concentrate on the lateral morphology at low coverages of Ag, thereby gaining insights specifically into the nucleation process.

Other studies indicate that the effect of common adsorbed gases on lateral structure in metal homoepitaxy may be a rich topic. For example, the presence of CO_{ad} affects the size, shape, and density of islands formed in deposition of Pt/Pt(111).[14] The presence of O_{ad} on Ni(100) causes the rotation and elongation of Ni islands formed via Ni deposition.[15]

Here, we show that exposing Ag(100) to $O_{2,g}$ prior to Ag deposition interferes with the initial nucleation of Ag islands. As a result, the use of $O_{2,g}$ provides a means to control the size and density of these islands. We also examine the underlying processes by which O_{ad} interacts with the Ag atoms.

Much is known about the interaction of $O_{2,g}$ with the Ag(100) surface from the extensive studies of Valbusa and co-workers. $O_{2,g}$ is quite unreactive to Ag(100), with a sticking probability of 10^{-4} at 300 K.[16] $O_{2,g}$ adsorbs with higher probability and dissociates at kink sites on steps.[17–20] The rate for dissociation of $O_{2,g}$ is, in fact, determined by the population of kink sites. The resultant O_{ad} is very stable on the (100) surface, as it does not recombine and desorb molecularly at higher temperature.[17] We assume that this process—dissociation at kink sites—generates the oxygen-containing species that so strongly affects nucleation on Ag(100), as reported in this study.

Our own studies of relaxation processes in Ag/Ag(100) films after growth[21,22] are highly relevant as well, since some of the atomic-scale processes operative in relaxation are also involved in nucleation and growth. Relaxation occurs because nucleation and growth is a kinetically governed process, producing nonequilibrium features that then evolve with time toward equilibrium. For instance, any ensemble of islands will evolve (coarsen) toward larger average size and lower density. Elsewhere[21,22] we have shown that exposure to $O_{2,g}$ accelerates and changes the mechanism of coarsening of Ag islands on Ag(100) after nucleation and growth, and that dissociation of $O_{2,ad}$ is necessary for this to occur.

II. EXPERIMENTAL DETAILS

Our experiments were performed in a ultrahigh vacuum (UHV) chamber with base pressure $<1\times10^{-10}$ Torr, and a typical pressure during experiments of $\approx 1\times10^{-10}$ Torr. The sample was cleaned by repeated cycles of Ar^+ sputtering (20 min, 500 V, $T\approx300$ K) followed by annealing at 700 K. Oxygen treatments [500 langmuir, L ($1\ \mathrm{L}=10^{-6}$ Torr s) 700 K] were performed periodically and were useful in removing the last remnant of contamination from the surface. No re-

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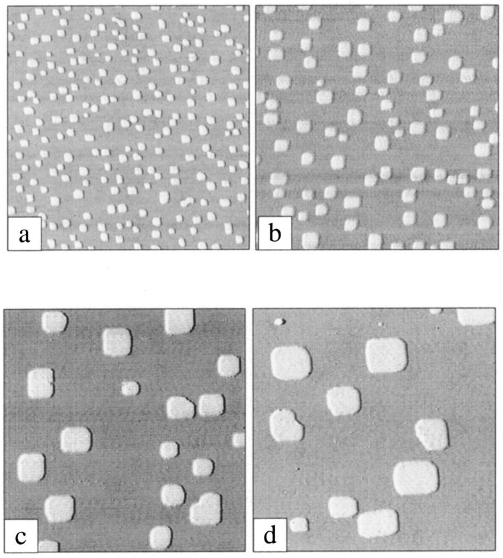

FIG. 1. Ag islands on a Ag(100) surface exposed to various amounts of oxygen prior to deposition at 250 K. Exposures in units of langmuirs (L): (a) 0 L (clean), (b) 5 L, (c) 15 L, (d) 30 L. The deposition flux for all images was 0.002 ML/s. All images span 125×125 nm^2.

sidual oxygen could be detected after these treatments. This was confirmed through the reproduction of known experimental results on the oxygen-free surface. Evaporative deposition of Ag onto the Ag(100) single-crystal surface was usually performed at $T \leqslant 250$ K. The surface was exposed to $O_{2,g}$ by backfilling the chamber to $\sim 10^{-8}$ Torr in continuous flow. Unless noted otherwise, all exposures were conducted at the same temperature as Ag deposition. Temperature variations were minimal, with fluctuations of no more than ±1 K throughout the duration of the experiment. Island evolution was monitored with an Omicron variable-temperature scanning tunneling microscope (VTSTM). Some complementary studies were performed with an Omicron instrument for high-resolution low-energy electron diffraction (HRLEED).

III. RESULTS AND INTERPRETATION

A. Submonolayer deposition

Figure 1 shows a series of scanning tunneling microscope (STM) images from an experiment where clean Ag(100) was exposed to various amounts of $O_{2,g}$ prior to the deposition of 0.2 monolayers (ML) of Ag. The images show that exposure to $O_{2,g}$ prior to Ag deposition affects the nucleation and growth of Ag islands. Increasing the $O_{2,g}$ preexposure results in a decrease in island density (and a corresponding increase in island size).

Based upon work by others, and as mentioned in Sec. I, we infer that exposure to $O_{2,g}$ results in adsorption and dissociation at kink sites along steps. However, if the dissociated oxygen remained trapped at the kink sites, it could not affect nucleation and growth of Ag islands in the centers of broad terraces, in contrast to observations here.[23] Hence, an O_{ad}-containing species must be able to leave the kink sites and diffuse across the terraces, on the time scale of deposition (and the shorter time scale of nucleation) at 250 K. Buatier de Mongeot *et al.* also concluded that O_{ad} does not remain trapped at kink sites after dissociation.[17]

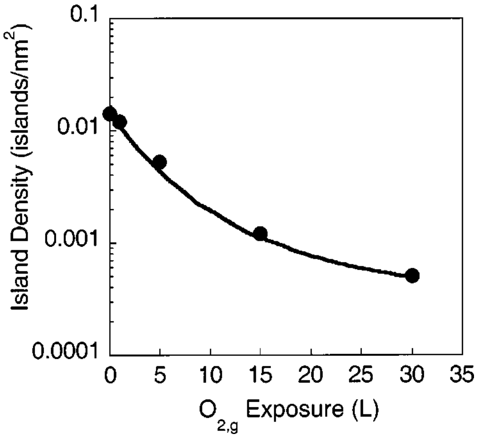

FIG. 2. Variation of average island density, N_{av}, with $O_{2,g}$ preexposure, at fixed temperature (250 K) and fixed flux.

Figure 2 shows the quantitative variation of average island density, N_{av}, with $O_{2,g}$ preexposure, at fixed temperature (250 K) and fixed flux. N_{av} falls nonlinearly but smoothly from its value at zero exposure to its value at 30 L preexposure. At 30 L, a plateau has not yet been reached but is being approached. We interpret this to mean that increasing exposure to $O_{2,g}$ interferes with (and inhibits) the simple nucleation scenario. It is likely replaced by a more complex pathway characterized by an effective critical size that increases and finally saturates with $O_{2,g}$ exposure (see Sec. IV).

An upper limit on the coverage of oxygen in our experiments is probably given by the work of Rocca *et al.*, wherein the coverage was estimated from vibrational experiments to be about 0.04 ML at 250 K on Ag(100), after an $O_{2,g}$ exposure of 1000 L.[24] The coverage of oxygen on our surface is too low to be detectable with Auger electron spectroscopy.

Classic nucleation theory[25–28] shows that the island density should scale with the experimental parameters of flux F and temperature T according to

$$N_{av} \propto F^{\chi} e^{-E/kT}. \tag{1}$$

Examining first the flux dependence, Fig. 3 shows the variation of N_{av} at 250 K, as determined by STM, for (a) zero preexposure to $O_{2,g}$ and (b) 30 L preexposure to $O_{2,g}$. The linear variation of the data are in accord with Eq. (1). From the slopes of the straight lines shown in Fig. 3, the value of χ is 0.28 for the surface with no preexposure to $O_{2,g}$. This is consistent with our previous results for the clean surface.[29] With 30 L preexposure to $O_{2,g}$, however, there is a large increase in the scaling exponent, to about 0.9.

The value of χ depends upon the nucleation mechanism and upon the degree of mobility of very small islands (relative to monomers). The value of 0.28 for the clean surface indicates irreversible island formation (critical size of 1), with no significant mobility of small islands. The larger value of χ for the lower curve in Fig. 3 indicates that the presence of O_{ad} containing species destabilizes very small islands, hence increasing the critical size; it may also induce significant mobility in small Ag islands. Note that in conven-

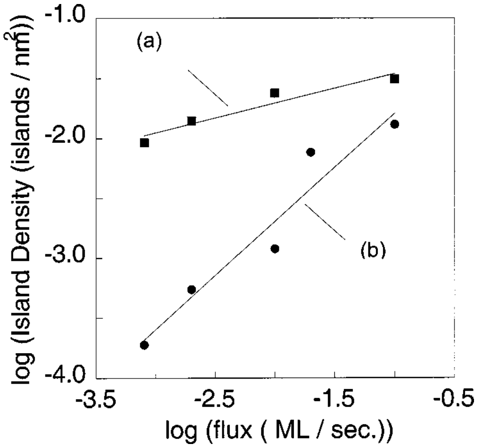

FIG. 3. Island density vs deposition flux for 0.2 ML Ag/Ag(100) at 250 K for (a) O-free surface and (b) surface preexposed to 30 L O_2.

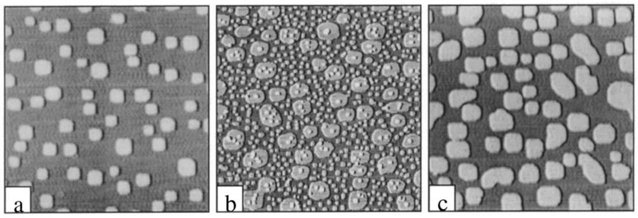

FIG. 5. STM image (a) taken after deposition of 0.2 ML Ag/Ag(100) at 320 K. Image (b) taken after a second deposition of 0.2 ML Ag at 250 K, on the surface shown in (a). Image (c) taken after the surface in (a) was exposed to 30 L O_2, followed by a second deposition of 0.2 ML of Ag at 250 K. The flux for the first and second depositions were 0.002 ML/s and 0.02 ML/s, respectively. All images span $175\times175\ \mathrm{nm}^2$.

tional nucleation theory, χ has a theoretical upper limit of unity for highly reversible island formation,[25,26,30] and higher preexposures of $O_{2,g}$ could presumably have pushed the value of χ even closer to this limit, as implied by Fig. 2.

Equation (1) shows that island density should scale with temperature as well as flux, and should thus yield the parameter E. Figure 4 shows the experimental variation in N_{av} after deposition of 0.2 monolayers of Ag. Curve (a) in Fig. 4 corresponds to data collected previously for the clean surface.[31] [However, the values shown in Fig. 4 have been adjusted according to Eq. (1) to allow direct comparison to the new data, since the two data sets were acquired with different fluxes.] Curve (b) in Fig. 4 corresponds to a 30 L preexposure to $O_{2,g}$, for each temperature. It can be seen that curves (a) and (b) are almost parallel between 300 and 210 K, with curve (b) always lying beneath curve (a) in this temperature range. The relative position of the two lines between 300 and 210 K simply means that, at any given temperature, the island density is always lower in the presence of oxygen than in the absence, as expected from the foregoing discussion. According to Eq. (1), the slope can be used to derive an apparent energy, E. In the temperature range of 300–220 K, the slope corresponds to $E=0.10$ eV in curve (b), and $E=0.13$ eV in curve (a). The physical significance of these energies will be discussed in Sec. IV.

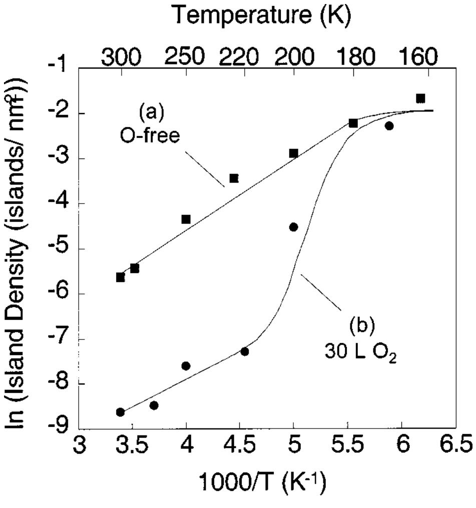

FIG. 4. Arrhenius plot for 0.2 ML Ag/Ag(100) for (a) the O-free surface and (b) surface preexposed to 30 L O_2.

In Fig. 4, curve (b) undergoes a transition, between 210 and 180 K, in which the island density increases rapidly and finally links up with the value for curve (a). At even lower temperatures, island densities match closely for the two curves. Dissociation of molecular oxygen is not active below 180 K. This explains the merger of the two curves below 180 K, and demonstrates again that O_{ad} or something that contains O_{ad} must be the chemical species that interferes with nucleation and growth, rather than $O_{2,ad}$. In other words, $O_{2,ad}$ must dissociate before its effect can be observed.

The requirement of $O_{2,ad}$ dissociation at kinks implies that the density of steps is important. In fact, this is supported by experiments in our laboratory, in which two Ag(100) crystals were compared, albeit with different techniques, as follows. We performed HRLEED experiments on a different crystal than the one used in all of the STM experiments. Like STM, HRLEED provides a measure of average island densities, and in our past work we have shown that HRLEED data are quantitatively comparable to STM data, for clean Ag(100) homoepitaxy.[32] In the new HRLEED experiments, preexposure to oxygen had no measurable effect on subsequent Ag island densities.

We attribute this to the feature that the global average of the step density for the HRLEED sample is much lower than for the STM sample. More specifically, HRLEED profiles indicate a broad terrace with a mean width of about 50 nm, a value which corresponds to a global average over the electron beam diameter of ~1 mm. For the STM sample, all our images and data analysis correspond to a carefully selected broad terrace spanning several tens of nanometers in width. However, such broad terraces are rare. Globally, the STM sample is much rougher than the HRLEED sample, with much higher global step (and kink) density and many regions of rough topography. We believe that this global sample morphology controls the overall oxygen uptake. Thus oxygen must readily adsorb in these rough regions on the STM sample and diffuse to the few broader terraces.

B. Multilayer deposition studies

Figure 5 shows the results from an experiment in which the final surface films are created through two separate Ag deposition steps. The first step is deposition of 0.2 ML of Ag at 320 K, without preexposure to $O_{2,g}$, and at a relatively low flux of 0.002 ML/s. This relatively high temperature and low flux results in large islands, rather homogeneous in shape and size,[33] as shown in Fig. 5(a). The second step is deposition of additional Ag (another 0.2 ML) at a lower temperature, 250 K, and at ten times higher flux, 0.02 ML/s. In the absence of O_{ad}, this produces much smaller islands, on the terrace regions between as well as on top of the previously created large islands, as shown in Fig. 5(b).

Figure 5(c) shows a surface that was exposed to 30 L of $O_{2,g}$, at 250 K, between the first and second Ag depositions. The result is that during the second Ag deposition, no additional islands form, either between or on top of the islands generated by the first deposition. With O_{ad}-containing species present, all Ag atoms deposited in the second treatment must have diffused to preexisting step edges; in particular, nucleation on top of islands is eliminated.

IV. DISCUSSION

The main issue to be resolved is the mechanism by which the presence of O_{ad} interferes with the nucleation and growth of Ag islands on Ag(100). Several possibilities emerge. Although we cannot unambiguously determine which of these applies, we discuss one plausible scenario for the saturation regime of 30 L exposure to $O_{2,g}$, and comment on other possibilities. Two key pieces of experimental data which guide our discussion are that the island density, N_{av}, is described by Eq. (1) with a high flux scaling exponent, $\chi=0.9$ (indicating highly reversible island formation), and a low effective energy, $E\approx 0.10$ eV, in the presence of oxygen.

In traditional nucleation theory, a single species with terrace diffusion barrier, E_d, nucleates islands with critical size, i. This means that islands of more than i atoms are effectively stable on the time scale of island growth during deposition, but smaller islands can dissociate; islands of i atoms have a finite binding energy, E_b. Under these conditions, the energy E in Eq. (1) is given by

$$E\approx\chi\left(E_d+\frac{E_b}{i}\right),\quad \text{where}\quad \chi\approx\frac{i}{i+2}. \tag{2}$$

For the clean $Ag_{ad}/Ag(100)$ system, where $i=1$ (so $E_b=0$), $\chi\approx 0.28$ (showing an expected[27,28] slight deviation from the asymptotic theoretical value of 1/3), and $E=0.13$ eV. Thus, one concludes that $E_d(Ag_{ad})=E/\chi=0.45$ eV. This value of $E_d(Ag_{ad})$ is in agreement with the range of previous theoretical and experimental determinations, 0.37 to 0.45 eV.[29,31–35] For the case with 30 L $O_{2,g}$, if Ag_{ad} diffusion were to play a significant role in island nucleation, such a high E_d would be inconsistent with the similar low value of E but much larger χ [assuming that E is determined by some formula such as Eq. (2), even in this more complex case]. This prompts the following model, in which we postulate that a species other than Ag_{ad} plays the key role in island nucleation. This species is likely of the form Ag_mO.

A. Island nucleation mediated by an Ag_mO_{ad} species

As we discuss in Sec. III A and also below, it is clear that an oxygen-containing species can readily detach from step edges, and likely also from far-removed faceted regions of the sample, to populate the terrace of interest. We expect that the population of this species on terraces is determined by an attachment–detachment equilibrium, and that this population is relatively high for 30 L exposure to $O_{2,g}$. Suppose for the moment that this detaching species is O_{ad}. Then, since Ag_{ad} does not play a significant role in island nucleation, we propose that newly deposited Ag_{ad} is quickly captured by O_{ad} to form a diffusing AgO_{ad} species, which mediates island nucleation. Islands thus formed are destabilized by a large population of incorporated O_{ad}. Formation of stable islands requires a sufficiently large number of Ag_{ad} atoms (large i), and expulsion of a sufficient amount of O_{ad}. In this picture, one has $Ag_mO_{ad}=AgO_{ad}$, i.e., $m=1$. Schematically, we write

$$\begin{aligned}
&Ag_{ad}+O_{ad}\xrightarrow{\text{fast}}AgO_{ad},\\
&AgO_{ad}+AgO_{ad}\leftrightarrow Ag_2O_{2,ad}\quad(\text{reversible aggregation}),\\
&AgO_{ad}+Ag_iO_{k,ad}\rightarrow Ag_{i+1}O_{k+1,ad}\\
&\qquad\qquad(\text{irreversible aggregation}),\\
&Ag_jO_{k,ad}\leftrightarrow Ag_jO_{k-1,ad}+O_{ad}\\
&\qquad\qquad(\text{oxygen attachment–detachment}).
\end{aligned}$$

Here, → and ↔ denote irreversible and reversible steps, respectively. If the species readily detaching from step edges were actually AgO_{ad} rather than O_{ad}, then the above would be replaced by $Ag_mO_{ad}=Ag_2O_{ad}$, i.e., $m=2$, and schematically

$$\begin{aligned}
&Ag_{ad}+AgO_{ad}\xrightarrow{\text{fast}}Ag_2O_{ad},\\
&Ag_2O_{ad}+Ag_2O_{ad}\leftrightarrow Ag_4O_{2,ad}\\
&\qquad\qquad(\text{reversible aggregation}),
\end{aligned}$$

etc.

Returning to the experimental results, and adopting the standard formula (2), one concludes that $i\approx 20$, and that an upper bound on the terrace diffusion barrier, E_d, for Ag_mO_{ad} is provided by $E/\chi=0.10/0.9=0.11$ eV, which is far below $E_d(Ag_{ad})=0.45$ eV. Of course, one should be cautious regarding the use of Eq. (2) for the complex island formation process above. Furthermore, in reality, there is not a single critical size, since presumably Ag islands with less O_{ad} will be stable at smaller sizes, reaching $i=1$ in the limit of no O_{ad}. Thus, the critical size above should be regarded as an effective or average value.

B. Alternative scenarios

(i) One might consider that the rate of terrace diffusion for Ag_{ad} could be enhanced by the presence of an oxygen-containing adsorbate, without direct bonding between Ag_{ad} and the other adsorbate. However, it seems unlikely that such interactions could reduce the terrace diffusion barrier by a factor of 4 or more, to 0.1 eV or below, which would be required for a model in which island nucleation was mediated by diffusion of Ag_{ad}. This is particularly true in light of the low oxygen coverage.

(ii) Equation (2) actually applies only in situations where stable nuclei are relatively immobile. If this condition is not met, χ can increase to a maximum value of 0.5 for irreversible formation ($i=1$) of mobile nuclei.[36–40] Hence, while mobility of small nuclei cannot be ruled out—and is made somewhat plausible by a recent postulate of adsorbate-enhanced mobility for Cu trimers decorated by sulfur on the Cu(111) surface,[41,42]—this effect alone could not explain the experimental value of $\chi=0.9$. Reversibility in island formation is necessary (as well as nucleation mediated by a rapidly diffusing species).

(iii) The picture of newly deposited Ag_{ad} being efficiently captured by O_{ad} (or AgO_{ad}) is an oversimplification. This is certainly the case for exposures of $O_{2,g}$ below 30 L or for low T, where the equilibrium population of O_{ad} (or AgO_{ad}) on the terraces is lower. Equivalently, in the low-exposure or low-T regimes, one can say that the concentration of O_{ad} is not high enough to drive the reaction $Ag_{ad}+O_{ad}\xrightarrow{\text{fast}}AgO_{ad}$ entirely to the right, either for kinetic or thermodynamic reasons. In these regimes, eventually one must cross over to the picture for island nucleation in the clean Ag/Ag(100) system.

C. Interterrace diffusion of Ag_mO

Another issue is whether the O_{ad}-containing species can move freely between terraces, on the time scale of our experiments. This is clarified by the experiments of Fig. 5. The lack of island nucleation on the large islands, after $O_{2,g}$ preexposure and the second deposition of Ag [Fig. 5(c)], shows that the O_{ad}-containing species must be able to move to the tops of these islands, which is equivalent to moving from a lower terrace to an upper terrace on the extended surface. The nucleating species must also be able to get off the island tops again, or else it would nucleate there. Getting off an island is equivalent to moving from an upper terrace to a lower terrace on the extended surface.

It could be argued that, in the experiments of Fig. 5, the O_{ad}-containing species does not cross upward at all, but rather helps Ag_{ad} move downward. That is to say, the O_{ad}-containing species might lower the step-edge barrier for downward transport of Ag_{ad} that lands on top of islands in the second deposition. For clean Ag(100) homoepitaxy, there is a small extra barrier of ≈70 meV to downward diffusion of Ag_{ad} on the close-packed ⟨110⟩-type steps.[43,44] is zero on the most open ⟨001⟩-type steps. However, this argument is not viable because the experimental conditions in Fig. 5(c) (high flux, large preexisting islands, and low temperature) are such that second layer nucleation would still be expected, even if the step-edge barrier for Ag_{ad} were zero everywhere (as confirmed by simulations).[45] Hence, the species that detach from the steps and that combine with Ag_{ad} to mediate nucleation must be able to ascend and descend steps freely at these temperatures and on the time scale of deposition.

D. Steps as dissociation sites for $O_{2,g}$

Comparing the results for two different samples, one with higher step density than the other, shows that steps are extremely important in providing sites where the active species are generated (Sec. III A), and that step densities can affect the reproducibility of results from sample to sample. This probably also accounts for the fact that, in previous work, we reported that $O_{2,g}$ had no effect on nucleation and growth in Ag(100) homoepitaxy.[21] Those experiments were done under somewhat different conditions, i.e., *simultaneous* $O_{2,g}$ exposure and Ag deposition, and the impact on nucleation was measured with HRLEED. This was done using the same HRLEED (lower-step-density) crystal mentioned in Sec. III A. Presumably, a negligible amount of O_{ad} had accumulated at early times, when island nucleation was occurring.

E. Comparison with other systems

Let us compare the effect that O_{ad} exerts on nucleation in this system, to the effect exerted by other surfactants in other simple, homoepitaxial systems. [Elsewhere, we present evidence that O_{ad} is a good surfactant on Ag(100), and so this is a relevant context.] One observation is clear: Other surfactants affect the value of N_{av} strongly but differently. Thus, Sb_{ad} on Ag(111) and Ag(100),[4,10] and O_{ad} on Pt(111),[11] all cause N_{av} to *increase*, while O_{ad} on Ag(100) causes N_{av} to *decrease*. The two metal (111) systems have been studied in most detail. There, the interpretation is that the surfactant exerts two effects simultaneously: it impedes diffusion of metal atoms across the terraces (i.e., it raises the terrace diffusion barrier), *and* it lowers the step-edge barrier.[4,10] The first half of this explanation cannot apply in our system, because quantitative evaluation of N_{av} vs F [Fig. 3 and Eq. (2)] and N_{av} vs T (Fig. 4) reveals that the activation barrier to diffusion of the diffusing species *must* be *lower* in the presence of O_{ad} than in its absence. The second part is only tangentially relevant, since we do not believe that the step-edge barrier for Ag_{ad} is important, but rather the step-edge barrier for a different species.

In short, the model for our system differs fundamentally from those proposed in other systems because in our model, *the surfactant changes the nature of the diffusing and nucleating species*, rather than simply modifying energetic barriers within a preexisting mechanism of metal–adatom nucleation. This is consistent with the fact that the fundamental effect of the surfactant in our system is also different; it causes N_{av} to decrease, relative to the clean surface, whereas in the other three systems cited above it causes N_{av} to increase.

V. CONCLUSIONS

Island nucleation on Ag(100) at 250 K is impeded by preexposure to $O_{2,g}$. In order for this to occur, the $O_{2,g}$ must adsorb and dissociate. $O_{2,ad}$ dissociates at kink sites at steps. Hence, step density is important in determining the extent of the effect of $O_{2,g}$ preexposure.

The effect of oxygen is to decrease the average island density. Analysis of average island density as a function of Ag flux reveals a threefold increase in the flux exponent (χ)

from $O_{2,g}$ preexposure. The temperature dependence of island density, with preexposure to $O_{2,g}$, gives an apparent energy (E) of 0.10 eV in the range 300–220 K.

We hypothesize that Ag_mO_{ad} is the nucleating species, and its nucleation is highly reversible (critical size $i \gg 1$). Small aggregates of this species may also be mobile. Its activation energy for terrace diffusion (E_d) is $\leqslant$0.11 eV, much lower than the value of 0.45 eV for Ag_{ad} on clean Ag(100). Two-step deposition experiments indicate that the oxygen-containing species that is generated at step edges, as well as the Ag_mO_{ad} species that mediates nucleation, diffuse freely across terrace steps, as well as across terraces.

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