Thermally Selective Formation of Subsurface Oxygen in Ag(111) and Consequent Surface Structure

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ABSTRACT: A long-standing challenge in the study of heterogeneous catalyzed reactions on silver surfaces has been the determination of what oxygen species are of greatest chemical importance. This is due to the coexistence of several different surface reconstructions on oxidized silver surfaces. A further complication is subsurface oxygen (O_{sub}); O_{sub} are O atoms absorbed into the near surface region of a metal, and are expected to alter the surface in terms of chemistry and structure; however, these effects have yet to be well characterized. We studied oxidized Ag(111) surfaces after exposure to gas-phase O atoms to determine how O_{sub} is formed and how its presence alters the surface structure. Using a combination of surface science techniques to quantify O_{sub} formation and the resultant surface structure, we observed that once 0.1 ML of O_{sub} formed, the surface was dramatically, and uniformly, reconstructed to striped structures at the expense of all other surface structures. Furthermore, O_{sub} formation was hindered at temperatures above 500 K. The thermal dependence for O_{sub} formation suggests that, under the industrial catalytic conditions of 475−500 K for the epoxidation of ethylene to ethylene oxide, O_{sub} would be present and is a factor in the subsequent reactivity of the catalysts. These findings point to the need for the incorporation of O_{sub} into catalytic models, as well as further theoretical investigation of the resultant structure observed in the presence of O_{sub}.

KEYWORDS: Ag(111), surface reconstruction, subsurface oxygen, heterogeneous catalysis, atomic oxygen

INTRODUCTION

It is well-established that subsurface oxygen (O_{sub}) forms in the selvedge region of Ag(111) after exposure to gas-phase atomic oxygen (AO), excess NO_2, or high pressures of O_2. What is far less clear are what factors enhance or disfavor the formation of O_{sub} and furthermore, how the electronic and geometric structure of the surface is altered by O_{sub}. To date, most studies have focused on the formation of surface oxides and their structures; however, quantification of O_{sub} formation, until now, has received far less attention. In this paper, we show that the temperature of the Ag(111) sample is a key parameter in the formation of O_{sub}. Furthermore, over a narrow temperature range (spanning <50 K), O_{sub} formation goes from being highly favorable to completely disfavored. Finally, we show that the surface is rather sensitive to the presence of O_{sub} and once the selvedge of the metal reaches a critical concentration of O_{sub} the surface exhibits a striped structure that is very different from the other surface reconstructions. These findings have direct consequences for our understanding of how the electrophilic oxygen that is reactive toward ethylene epoxidation may be formed and how the structure of a silver catalyst will evolve under conditions of high oxygen coverage.

Oxygen induced reconstructions of Ag(111) surfaces have been widely studied and debated for many years. Ag(111) surfaces exhibit a variety of different surface reconstructions caused by adsorbed oxygen (O_{ad}) along with several other oxygen species. The primary motivation to study the O/Ag(111) system is the importance of silver as an industrial partial oxidation catalyst. Virtually all ethylene oxide (EO), which is an important intermediate in the production of plastics, glycols, and polyester, is produced via the partial oxidation of ethylene to EO over Ag catalysts. The industrial synthesis of formaldehyde by the oxidation of methanol also relies on Ag catalysts. In addition, silver oxide has also shown potential in applications ranging from data storage to antimicrobial coatings. However, a causal link between surface preparation and surface oxide structure(s) remains undeveloped. Furthermore, it is not altogether clear how the various surface structures are tied to the “electrophilic oxygen” species believed to be active in the partial oxidation reactions. Recently, significant progress has been made in these two directions and subsurface oxygen is believed to be critically important, which has motivated the present study.

Silver is readily oxidized at atmospheric and elevated pressures, but preparation of oxidized Ag(111) surfaces is not straightforward under ultra-high vacuum conditions (UHV, P < 1 × 10^{-8} Torr). The sticking probability of O_2 on Ag(111) is very small (∼1 × 10^{-6}); therefore, comparatively high pressures (1 Torr and above) are required to oxidize the surface and then the sample must be returned to UHV conditions for analysis.
To avoid these inconvenient high-pressure exposures, alternative oxidants have been employed in UHV to prepare oxidized Ag(111) surfaces. For example, NO, gas-phase atomic oxygen (AO), will oxidize Ag(111) under conditions conducive for returning the system to UHV conditions. Ozone (O₃) has been used as an oxygen source in a limited number of studies, mostly on polycrystalline Ag. O₃ exposures at 1 atm favored the formation of rough surfaces of the bulk oxide, Ag₂O, as was also observed for high fluxes of AO on Ag(111). Despite the carefully controlled exposure conditions, a complex variety of surface structures and oxygen species have been observed and postulated with these oxidizing techniques. Oxygen species described by various authors have included chemisorbed oxygen, nucleophilic and electrophilic oxygen, oxygen in the bulk, and Osub. Herein, we report the results from a study of Ag(111) oxidized by AO under UHV conditions and show that the surface structure and oxygen species for ethylene epoxidation is still absent.

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filament was heated to 1750 K by passing a current of 2.8 A at a potential of 1.6 V (AC) through the 0.25-mm-diameter Ir wire in the UHV chamber. The chamber was backfilled with O₂ gas to a pressure of $5 \times 10^{-7}$ Torr. During exposure, the filament was brought within ~0.5 cm from the front face of the Ag(111) crystal, and the sample temperature was held constant at the deposition temperature ($T_{\text{dep}}$). After exposure, only oxygen was observed to accumulate on the surface, as reported previously. Once the AO exposure was completed, the sample was cooled to either room temperature for temperature-programmed desorption (TPD) and LEED analysis, or to 90 K for insertion into the STM chamber. For STM imaging, the manipulator was used to move the chilled sample to the STM chamber, where a wobble stick was used to insert the sample into the STM. Once inserted, the STM was allowed to cool to the imaging temperature of 20 K. During imaging, there was negligible accumulation of background gases, and the oxidized surfaces were not altered, as confirmed by post-imaging TPD measurements. LEED measurements were performed at room temperature, and similarly, TPD spectra were unchanged by the LEED analysis. All TPD measurements were performed with a ramp rate of 3 K s⁻¹.

## RESULTS AND DISCUSSION

Both AO and NO₂ oxidize Ag(111) surfaces. Although AO exposures yield surfaces with both adsorbed oxygen (O₁₈) and O₁₂ subsurface oxygen (O₁₂) results from NO₂ exposures for $T_{\text{dep}} = 500$ K. For these reasons, NO₂ oxidation provides a convenient calibration method for the uptake of oxygen during AO exposures. The Ag(111) sample was exposed to NO₂ from a directed doser at $T_{\text{dep}} = 500$ K. After 60 s of exposure, the TPD spectra showed a single desorption peak at $T = 595$ K, corresponding to the decomposition of the $p(4 \times 4)$ surface reconstruction with a coverage of $\theta_O = 0.375$ ML, and the peak intensity was unchanged by longer exposures, suggesting that the surface was fully covered by the reconstruction under these conditions. LEED analysis of the NO₂ dosed surface showed a sharp ($4 \times 4$) pattern, and STM imaging exclusively found $p(4 \times 4)$ structures on the surface when the NO₂ exposure was performed at 500 K or higher. The integral of this peak was then used to determine the coverages for the AO exposures.

**Surface Temperature Effect on Oxygen Uptake on Ag(111).** Figure 2 shows TPD data after exposing Ag(111) to AO at five different temperatures: (A) $T_{\text{dep}} = 525$ K, (B) $T_{\text{dep}} = 510$ K, (C) $T_{\text{dep}} = 500$ K, (D) $T_{\text{dep}} = 490$ K, and (E) $T_{\text{dep}} = 475$ K. For each spectrum, the Ir filament was at a temperature of 1750 K and the O₂ background pressure was $5.0 \times 10^{-7}$ Torr. The surface reconstruction peak at 595 K saturates after 300 s (blue traces) for all $T_{\text{dep}}$ values, but the lower temperature peak near 550 K increases with exposure time for $T_{\text{dep}} < 500$ K.

Figure 2. TPD spectra after exposure of Ag(111) to AO at five different temperatures: (A) $T_{\text{dep}} = 525$ K, (B) $T_{\text{dep}} = 510$ K, (C) $T_{\text{dep}} = 500$ K, (D) $T_{\text{dep}} = 490$ K, and (E) $T_{\text{dep}} = 475$ K. For each spectrum, the Ir filament was at a temperature of 1750 K and the O₂ background pressure was $5.0 \times 10^{-7}$ Torr. The surface reconstruction peak at 595 K saturates after 300 s (blue traces) for all $T_{\text{dep}}$ values, but the lower temperature peak near 550 K increases with exposure time for $T_{\text{dep}} < 500$ K.

The most likely explanation for the lower temperature desorption peak near 550 K in Figures 2C–E is O₁₂. Previous reports showed that bulk oxygen desorbs from Ag in a broad peak from 600 K to >800 K. However, O₁₂, which are dissolved O atoms in the selvedge of the metal, has been shown to desorb from Ag at temperatures of ~580 K, below that of the surface reconstruction at 595 K. As observed both in a previous report and in the present study, Rehren et al. found that the lower-temperature TPD peak corresponding to desorption of O₁₂ did not saturate with exposure, whereas the surface peak did. O₁₂ desorbs at a lower temperature, because it is thermodynamically unstable with respect to surface adsorbed oxygen. Calculations show that the several surface oxides and reconstructions have similar surface free energies, and they are more stable than O₁₂ at ~600 K; therefore, O₁₂ desorbs before decomposition of the surface reconstruction. This behavior is qualitatively similar to subsurface H (H₁₂) on Ni(111), where because H₁₂ is metastable with respect to surface H, it desorbs at temperatures ~100 K lower.

Figure 3A shows TPD spectra for 300 s AO exposures at five different deposition temperatures, along with desorption spectra after saturation dosing with NO₂ yielding $\theta_O = 0.375$ ML. Figure 3A clearly shows that substantially more than $\theta_O =$
K. As Figure 3B shows, with extended dosing at lower assignment of the peak to Osub is supported by the apparent top of the surface structures, similar to O on Pd.52 Again, Osub known or predicted surface structures, which suggests that observed. Such high coverages are not consistent with any Oad or other emergent O atoms. This analysis is further pseudo-zero-order peaks has been reported for other species,56 which can then di

Figure 3. (A) TPD spectra after 300 s AO exposures at various Tdep. The black trace is for \( \theta_O = 0.375 \) ML from a saturation NO2 exposure and shows that the peak at 595 K corresponds to the decomposition of the surface reconstruction. The O2 desorption peak below 575 K increases with decreasing temperature and is caused by the emergence and recombinative desorption of Osub to O2. (B) Plot of the total amount of O (Oad and Osub, \( \theta_O \)) versus AO exposure time for several Tdep. For Tdep > 500 K, only surface-bound O was observed (\( \theta_O \leq 0.375 \) ML, dashed line); however, for lower Tdep \( \theta_O \) exceeded what was present in the surface reconstruction.

0.375 ML of O2 desorbed after dosing for 300 s at Tdep \( \leq 500 \) K. As Figure 3B shows, with extended dosing at lower temperatures, the desorption of more than 1.0 ML of O2 was observed. Such high coverages are not consistent with any known or predicted surface structures, which suggests that oxygen is desorbing from the subsurface or from adsorption on top of the surface structures, similar to O on Pd.52 Again, Osub is the most plausible explanation. In addition to the fact that more than the equivalent of 1.0 ML of O2 desorbs, the assignment of the peak to Osub is supported by the apparent zero-order shape of the peak. A common leading edge with the peak maximum shifting to higher temperatures, as shown in Figures 2C–E and 3A, is characteristic of zero-order desorption kinetics.53 Because oxygen desorbs from Ag(111) as a molecule rather than an atomic species, recombination must occur prior to desorption; therefore, true zero-order desorption is not possible. However, recombinative desorption leading to pseudo-zero-order peaks has been reported for other surfaces.56,54,55 The shape of the lower-temperature desorption peak was most likely due to the surface coverage-independent emergence of oxygen from the subsurface in a zero-order process. Emergent O atoms from the subsurface transiently adsorb onto unstable surface sites before rapidly reacting with Oad or other emergent O atoms. This analysis is further supported by a closer examination of the peaks in Figure 3A. When the lower temperature peak was present, the surface oxygen desorption peak was slightly larger than the saturated NO2 surface desorption peak. This is consistent with some O atoms emerging from the subsurface and replacing the O atoms desorbed from surface reconstruction.

It is clear from Figure 3B that, for Tdep \( \geq 500 \) K, the uptake of O on the Ag(111) surface reached a limiting coverage. This was likely because the surface reconstruction grew until it extended across the entire surface, and Osub was unstable. However, for Tdep \( < 500 \) K, O continued to stick, even after the surface reconstruction peak saturated, and the sticking was favored at lower temperatures. As discussed, this lower temperature peak (Figure 3A) was caused by the emergence of Osub and the subsequent recombinative desorption of O2.1,47 Because of the pronounced temperature dependence of the peak intensity, Osub formation was clearly hindered for exposure temperatures above 500 K. In contrast, for Tdep \( < 500 \) K, uptake continued, suggesting that Osub was stable at 475 K, although slightly less so at 490 K. The decrease in oxygen desorption cannot be explained by desorption because of the elevated Tdep alone. For example, a 600 s AO exposure at Tdep = 475 K yielded 1.2 ML O. When Tdep was increased to 500 K, the O uptake was 0.42 ML, and the desorption spectra was dominated by surface O with a small lower temperature peak corresponding to Osub. From the TPD data, at 500 K, dO2/dt = \( 1.8 \times 10^{-3} \) ML s\(^{-1}\), so only a 0.015 ML decrease in O desorption would be anticipated, rather than the nearly 0.8 ML decrease that has been observed. This confirms that desorption due to elevated Tdep is insufficient to explain the reduction in O uptake. For all experiments, after the exposure was completed, the crystal was immediately cooled to room temperature or below.

Note that the Osub observed here is a different species than the “strongly bound” subsurface oxygen, or bulk oxygen, formed at exposure temperatures of >650 K.2 It turns out that the barrier for diffusion from the subsurface to the bulk is greater than the barrier for diffusion from the subsurface to the surface,2 thereby requiring elevated temperatures to activate the penetration of O into the bulk. In the present study, we observed that, under modest fluxes of incident O atoms, dissolved O formation was hindered at temperatures above 500 K; thus, correspondingly, the higher dosing temperatures required to form bulk oxygen in earlier TPD studies preclude the presence of Osub. When an Ag surface is exposed to gas-phase O atoms, the selvedge is likely populated with Osub during exposure; because of the modest temperature, the Osub atoms lack the energy to diffuse into the bulk, and remain trapped in the near-surface region. Alternatively, when Ag surfaces are exposed to O2 under high-temperature, high-pressure conditions, dissolved O forms directly from surface species,56 which can then diffuse into the bulk.

Evolution of Surface Structure with Osub Abundance. The surface structures for varying total coverages of O were determined using LEED and STM. These methods are considered complementary, in that LEED provides a diffraction pattern that shows an average structure, while STM provides an atomic-scale image map of the local surface structure. Interpretation of the LEED pattern is facilitated by comparison to STM images obtained at several different positions across the surface (separated by a few micrometers). In the case where a single, clean LEED pattern is observed, and the STM images also show little structural variation, it is reasonable to infer that the surface is covered with the structure corresponding to that LEED pattern. Alternatively, a complicated LEED pattern and STM images showing the coexistence of different surface structures indicates that the surface is inhomogeneous, and there is no single representative surface structure. In this study of the surface structure of Ag(111) after AO oxidation, we found that prolonged exposure often results in a single, dominant phase, but intermediate exposures result in several phases coexisting on the surface. We also saw that high concentrations (\( \theta_{Osub} \geq 0.1 \) ML) of subsurface oxygen induce a new surface structure that covers the entire surface in a single domain.

Figure 4 shows representative LEED patterns taken after exposing the Ag(111) sample to AO for 30 or 600 s, at either
increasing exposure. On the other hand, at the entire surface became covered in that single structure with patches of a single surface reconstruction formed initially, and pattern from the underlying Ag(111) faded, which suggests that previously for NO2 and O2 oxidation.6,37

Figure 4. Photographs of the LEED patterns (all at 52 eV) showing evolution of the surface structure after 30 and 600 s AO exposures for (A, B) T_{dep} = 525 K and (C, D) T_{dep} = 490 K. After 30 s of exposure, the patterns were very similar for both temperatures (panels (A) and (C)), but faint rows appeared for T_{dep} = 490 K (panel (C)). Panel (B) shows that, after 600 s of exposure, the pattern was very similar for T_{dep} = 525 K; however, in panel (D), for T_{dep} = 490 K, only rows of spots were observed.

T_{dep} = 525 or 490 K. After the 30 s exposures, the patterns were similar for both T_{dep} = 525 and 490 K. As the exposure increased, the evolution of the LEED patterns for the two T_{dep} diverged. At T_{dep} = 525 K, the LEED pattern for the 600 s exposure did not appear to change significantly from the 30 s exposure. The pattern appeared to sharpen and the (1 × 1) pattern from the underlying Ag(111) faded, which suggests that patches of a single surface reconstruction formed initially, and the entire surface became covered in that single structure with increasing exposure. On the other hand, at T_{dep} = 490 K, the LEED pattern changed with increasing AO exposure, and for 300 s and longer exposures, a striped pattern, shown in Figure 4D, became predominant. At exposures between 30 and 300 s, the LEED pattern was complex, indicating several structures were present on the surface. It is interesting to note that the p(4 × 4) pattern was not predominant at any exposure. In complicated LEED patterns (e.g., Figure 4C), faint (4 × 4) patterns were seen, but they were never particularly bright. When the Ag(111) crystal was exposed to NO2 to oxidize the surface, only the (4 × 4) pattern was observed, as reported previously for NO2 and O2 oxidation.6,37

Although we are presently unable to provide a detailed analysis of the LEED pattern obtained for higher O sub concentrations (Figure 4D), some qualitative properties are useful to highlight. The stripes retain the 60° angle characteristic of commensurate structures on face-centered cubic (FCC) (111) surfaces. Moreover, the spacing between the spots in the stripes is significantly less than the separation between the stripes. There appears to be a repeating unit of either 6 or 12 spots, somewhat regularly spaced, between the stripes. This data suggests that the surface features giving the diffraction pattern have a single nearest neighbor spacing (reciprocal of stripe spacing), while the longer-range structure (reciprocal of the spot separation) is less regular.

The oxidized Ag(111) surfaces were imaged using STM for different combinations of T_{dep} and AO exposure times to determine the structures formed under each set of conditions. The LEED patterns were used as guides for interpretation of the STM images. With NO2 oxidation, only the p(4 × 4) surface reconstruction was observed for T_{dep} ≥ 500 K, and the surface was uniformly covered with this structure. With the single LEED pattern, this confirmed the use of the TPD integral as the standard for 0.375 ML O on the Ag(111) surface.

At higher AO deposition temperatures, specifically at T_{dep} = 525 K, a single surface reconstruction structure, p(4 × 5√3), was observed to uniformly cover the Ag(111) surface over the course of time. STM images after AO dosing at T_{dep} = 525 K are shown in Figure 5. After dosing for less than 60 s, the

Figure 5. STM images of Ag(111) after exposure to AO at T_{dep} = 525 K. Exposure duration is labeled in the upper left corner of each image (exposure times of (A, B) 30 s, (C) 300 s, and (D) 600 s), and a 5 nm scale bar is provided in the lower right corner of each panel. The p(4 × 5√3) domain was evident in all images. After brief (<120 s) exposures (panels (A) and (B)), areas of clean Ag(111) with isolated O adatoms were observed as black depressions. Imaging conditions for each image were i = 300 pA and V = 900 mV, except for panel (B), which was obtained at V = 1.1 V.

surface has sizable domains of p(4 × 5√3) (Figure 5A) and large areas of bare Ag with chemisorbed O, which appear as randomly scattered dark spots (Figure 5B). The presence of bare Ag(111) with scattered chemisorbed O interspersed with ordered domains of p(4 × 5√3) is consistent with the LEED patterns seen in Figure 4. The Ag(111) displayed the characteristic hexagonal diffraction pattern, while the p(4 × 5√3) structure resulted in the faint additional decorations in the LEED image, which were suggestive of the introduction of a long-range ordered surface structure. As the AO exposure increased over time, the entire surface was covered with the surface reconstruction. The principal structure was the p(4 × 5√3) reconstruction, but areas of the c(3 × 5√3) structure were also found. However, eventually the surface was predominantly covered by c(3 × 5√3) structures with bands.
of $p(4 \times 5\sqrt{3})$ structures, as shown by the 600 s exposure image (Figure 5D). The oxygen coverages for the two structures were very close, 0.375 ML for $p(4 \times 5\sqrt{3})$ versus 0.4 ML for $c(3 \times 5\sqrt{3})$, and either case indicates that the surface was saturated with oxygen. The TPD data support this statement, because the peak intensity did not increase from 300 s to 600 s. Furthermore, despite the principal surface structure shifting from $p(4 \times 5\sqrt{3})$ to $c(3 \times 5\sqrt{3})$, there were very little changes in the observed LEED pattern. Taken together, this demonstrates that at 525 K, subsurface oxygen formation was eliminated, and large homogeneous domains of a single surface reconstruction were formed.

When the Ag(111) sample was exposed to AO at $T_{dep} = 490$ K, the resultant surfaces were initially inhomogeneous; however, after continued exposure, the surfaces became dominated by large homogeneous domains of a striped pattern. Figure 6 shows STM images taken after several AO exposures, and these images demonstrate how the surface structure evolved with increasing AO exposure. Initially, uptake was similar to what was seen at elevated temperature, but at intermediate exposures, the surfaces were markedly different. After 30 s AO exposure (Figure 6A) at 490 K, the surface had patches of the $p(4 \times 5\sqrt{3})$ surface reconstruction, but was largely clean Ag(111) and chemisorbed O atoms. As the AO exposure increased, no single surface structure became predominant. Instead, a few different surface reconstructions were observed to coexist, and interestingly, these domains had different oxygen coverages. For example, after a 120 s AO exposure at $T_{dep} = 490$ K (Figures 6C and 6D), areas of $p(4 \times 4)$, $c(3 \times 5\sqrt{3})$, and $c(4 \times 8)$ were observed. The first two structures have $\theta_O = 0.375$ ML, but the $c(4 \times 8)$ structure corresponds to $\theta_O = 0.5$ ML. Because of the atomic-level spatial resolution that is possible with STM imaging measurements, small domains of varying surface structures were identified. While the TPD spectra averages the total amount of O for the entire Ag(111) surface, STM allows for the very precise, local analysis of the Ag(111) surface. These STM images revealed the coexistence of multiple surface structure domains and, as a result, show local variations in the oxygen surface coverage. The coverage of the $c(4 \times 8)$ structure increased with exposure, but multiple structures were always observed. However, after 300 s AO exposure, the surface structure homogenized to a single, striped surface. For AO exposures with $T_{dep} < 500$ K, and for exposure times longer than 300 s, the entire surface was observed to be covered with a striped pattern (Figures 6E and 6F). Small patches of this pattern were previously reported by Besenbacher’s group,7 but it has not been observed to be particularly common, much less entirely covering the surface. A closer look at the STM images of the surface after a 300 s AO exposure, shown in Figure 6E, reveals an intermixing of thin and thick stripes across the terrace. Presently, we have been unable to further resolve these features, but they qualitatively agree with the LEED images. The key detail from these STM images is that the surface adopts the striped pattern after subsurface oxygen forms, as indicated by the TPD spectra. This indicates that $O_{sub}$ induces the striped pattern, disrupting the previously observed surface reconstructions. The effect occurs once the abundance of $O_{sub}$ exceeds 0.1 ML (total $\theta_O > 0.5$ ML).

### CONCLUSION

Subsurface oxygen distorts the surface structures of oxidized Ag(111) surfaces. This effect is moderated by the temperature of the silver surface during the exposure to atomic oxygen. At exposure temperatures above 500 K, subsurface oxygen formation was hindered, and the oxygen was only found on the surface in well-ordered surface reconstructions. On the other hand, when the Ag(111) surface was oxidized below 500 K, subsurface oxygen was formed, and when the coverage was $\sim 0.1$ ML $O_{sub}$, a striped pattern was observed across the surface. These findings are relevant to the heterogeneously catalyzed transformation of ethylene over silver catalysts. Industrially, these reactions are performed at temperatures close to 500 K, which is right on the dividing line for subsurface oxygen stability; therefore, subsurface oxygen is an important factor in the structural and chemical nature of the surface and must be included in accurate models of silver-catalyzed reactions.

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**Figure 6.** STM images of Ag(111) after exposure to AO at $T_{dep} = 490$ K. Exposure duration is labeled in the upper left corner of each image, and the scale bar is in the lower right corner. Panels (A) and (B) show that the $p(4 \times 5\sqrt{3})$ domain was predominant after brief exposures, as were areas of clean Ag(111) with isolated O adatoms that were observed as black depressions, as shown in panel (B). Panels (C)–(F) show that, with increasing AO exposure, several domains coexisted until the surface became uniformly covered in the striped pattern after 300 and 600 s exposures. Imaging conditions for each image were as follows: (A) $i = 280$ pA, $V = 1.0$ V; (B) $i = 300$ pA, $V = 800$ mV; (C) $i = 260$ pA, $V = 0.400$ mV; (D) $i = 200$ pA, $V = 800$ mV; (E) $i = 300$ pA, $V = 900$ mV; and (F) $i = 260$ pA, $V = 0.970$ mV.
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