Revisiting the Structure of the $p(4 \times 4)$ Surface Oxide on Ag(111)

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Scanning tunneling microscopy (STM) and density-functional theory are used to reexamine the structure of the renowned $p(4 \times 4)$-O/Ag(111) surface oxide. The accepted structural model [C. I. Carlisle *et al.*, Phys. Rev. Lett. **84**, 3899 (2000)] is incompatible with the enhanced resolution of the current STM measurements. An "Ag_6 model" is proposed that is more stable than its predecessor and accounts for the coexistence of the $p(4 \times 4)$ and a novel $c(3 \times 5\sqrt{3})$rect phase. This coexistence is an indication of the dynamic complexity of the system that until now has not been appreciated.

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Under ambient and oxygen-rich conditions, ultrathin oxide films may form on the surfaces of transition metals [1–7]. Such nanoscale surface oxides are not only relevant to corrosion and corrosion resistant materials, but they may also be the active phases of transition metal oxidation catalysts, as has been demonstrated by recent theoretical and experimental studies [1–7]. The surface oxide that has perhaps received the most attention is a $p(4 \times 4)$ phase that forms on Ag(111) [6]. This is in some respects the "original" surface oxide since it was the first to be identified in the 1970s [8,9], and indeed ever since it has been a key challenge of surface science to achieve an atomic-scale characterization of its structure [6]. In fact, for some years it was believed that the structure of this surface oxide had been "solved" by means of the scanning tunneling microscopy (STM) experiments of Carlisle *et al.* [10,11]. The unique structural model that emerged from this work and which was supported by subsequent density-functional theory (DFT) studies [12–14] was an Ag_2O-like oxide adlayer with a stoichiometry of $Ag_{1.83}O$. Through some of the first *ab initio* (T, p) phase diagrams, the $Ag_{1.83}O$ overlayer was predicted to be the thermodynamically most stable phase of those identified at ambient oxygen pressures, and was then credited with being of importance to one of the top ten industrial catalytic processes, namely, the Ag catalyzed partial oxidation of ethene to ethene epoxide [12–15]. However, this interpretation and the correctness of the $Ag_{1.83}O$ model was challenged recently by a literature review supplemented with a new DFT study [6] and by a surface x-ray diffraction investigation [16].

Here we show through a combination of STM and DFT that the existing model for the $p(4 \times 4)$ overlayer is indeed incorrect and propose an alternative comprised of Ag_6 motifs, which bears little or no resemblance to its predecessor. Of broader significance, however, is our characterization of a second phase, a $c(3 \times 5\sqrt{3})$rect overlayer, built from the same Ag_6 motifs as the $p(4 \times 4)$, and the realization that the O/Ag(111) system is much more complex than hitherto anticipated. With DFT a wealth of structures, all with comparable energetic stability, are identified, and with STM we see that the oxide overlayer(s) which form depend sensitively upon the preparation conditions of temperature, pressure, and oxidant. More often than not, the substrate is shrouded in a coexistence of many phases rather than a single well-formed $p(4 \times 4)$ overlayer. A clear implication of the present results is that at the temperatures and pressures characteristic of industrial epoxidation catalysis this Ag surface is likely to comprise a complex coexistence or mix of oxide overlayers.

Figure 1(a) shows a typical image obtained with our home-built Aarhus STM [17] after oxidizing the Ag(111) surface by exposing it to atomic oxygen [18]. Although there are well-ordered domains with $p(4 \times 4)$ symmetry on the surface, they coexist with equally well-ordered domains of different symmetry. Apart from a $p(4 \times 5\sqrt{3})$rect phase discussed already by Carlisle *et al.* [11], there is a $c(3 \times 5\sqrt{3})$rect phase identified here for the first time [19]. Notably, the bright features exhibited by this and the $p(4 \times 4)$ phase are exceedingly similar. Both the line scan taken along the dashed line in Fig. 1(a) and the superposition of peaks from each phase, left and right insets, respectively, show that the apparent heights and diameters of the bright features match extremely well. This suggests that the two phases share a common structural element or "building block," with the difference between the phases apparently being how these building blocks are arranged.

The characteristic honeycomb arrangement of the bright features in the $p(4 \times 4)$ phase, apparent in Fig. 1(a), was also observed in the original STM study by Carlisle *et al.* [10]. Interpreting each bright feature as a single Ag adatom led to the $Ag_{1.83}O$ model shown in Fig. 1(b), which finds its roots in the Ag_2O epitaxial overlayer models originally proposed by Rovida *et al.* [9] and Campbell [20]. However, higher resolution images of the $p(4 \times 4)$ obtained with the current STM setup, and at a lower bias than the image in (a), contradict this interpretation. An example of one such higher resolution image of the $p(4 \times 4)$ phase is shown in Fig. 1(c). Clearly the $p(4 \times 4)$ looks significantly different from the region of $p(4 \times 4)$ in (a), and its appear-

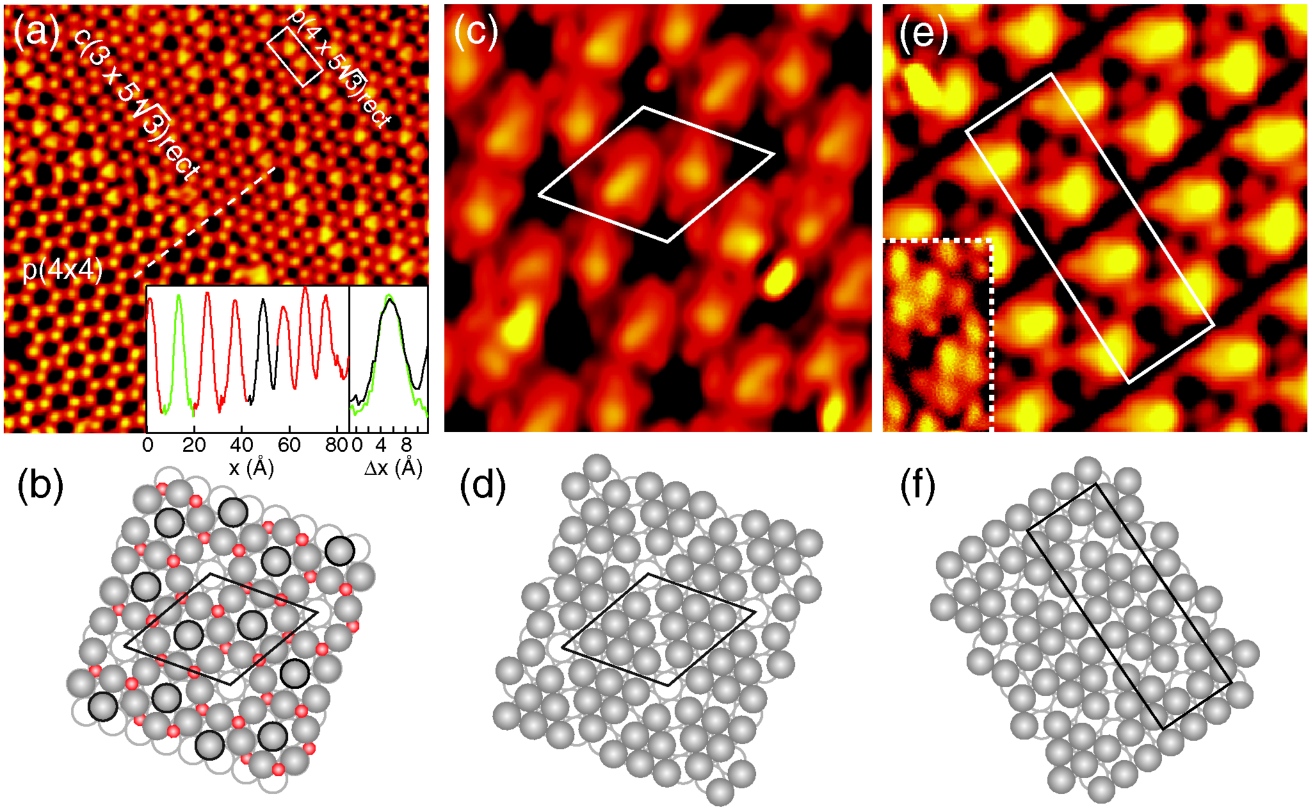

FIG. 1 (color online). STM images and partial structural models of the $p(4 \times 4)$ and $c(3 \times 5\sqrt{3})$rect overlayers. (a) A 200 Å^2 patch of Ag(111) covered by the $p(4 \times 4)$ and $c(3 \times 5\sqrt{3})$rect overlayers with inclusions of isolated $p(4 \times 5\sqrt{3})$rect units (box), measured at -0.51 nA and -131.5 mV. The inset displays a line scan along the dashed line (left) and the superposition of a $p(4 \times 4)$ (green or light gray) with a $c(3 \times 5\sqrt{3})$rect (black) feature (right). (b) The $Ag_{1.83}O$ model for the $p(4 \times 4)$ proposed by Carlisle *et al.* [10]. Solid (open) large gray balls represent the overlayer (substrate) Ag atoms, small (red) balls the oxygen atoms. (c),(e) STM images of 35 Å^2 patches of the $p(4 \times 4)$ and $c(3 \times 5\sqrt{3})$rect overlayers, respectively. (c) is at -0.42 nA and -21.7 mV, and (e) is at -0.40 nA and -34.2 mV. The inset in (e) (dotted lines) displays the six-atom structural element of the $c(3 \times 5\sqrt{3})$rect phase measured with a tip state that allowed resolution of the central parts of the proposed Ag_6 triangles (-0.42 nA, -21.7 mV). (d),(f) The distribution of the overlayer Ag atoms in the $p(4 \times 4)$ and $c(3 \times 5\sqrt{3})$rect phases, respectively, proposed here.

ance in (c) indicates that each of the bright features in (a) contains a detailed substructure. Indeed, the somewhat triangular appearance in (c), with clearly separable corner atoms and a bright protrusion in the middle of each triangle, is clear evidence that the prevailing $Ag_{1.83}O$ model is incorrect. As shown in Fig. 1(e), we obtain an even better resolved image of the related $c(3 \times 5\sqrt{3})$rect phase. Apart from the already identified corner atoms, which we anticipate are Ag atoms since O atoms tend to image as depressions when adsorbed on Ag(111) [11], this image suggests that the bright protrusion in the middle of the triangles is composed of another three Ag atoms. This is also confirmed by the image in the inset of Fig. 1(e), where an even higher resolution could be obtained. We therefore arrive at the conclusion that the common building block of the $p(4 \times 4)$ and the $c(3 \times 5\sqrt{3})$rect phases is a triangular arrangement of six Ag atoms, not just a single Ag atom as in the $Ag_{1.83}O$ model. This provides the foundation of the alternative "Ag_6 model" that we now propose for the $p(4 \times 4)$ phase, in which there are two six-atom Ag triangles facing each other as shown in Fig. 1(d).

Taking this embryonic model provided by STM, we turn to DFT to determine if a stable $p(4 \times 4)$ model consistent with the new STM data can be identified. And if so, how many oxygen atoms does it contain and what is the registry of this oxide with the substrate? To this end we performed an extensive series of DFT calculations [21]. The $p(4 \times 4)$ model that emerges from these calculations is shown in Fig. 2(a). In addition to the 12 Ag atoms of the two Ag_6 triangles, there are six O atoms, two located in each "trough" between the Ag_6 triangles. The 12 overlayer Ag atoms are located approximately above the threefold sites of the underlying Ag(111) substrate, six close to hcp sites and six close to fcc sites [22]. While the stoichiometry of this new model is formally Ag_2O, it does not resemble the former Ag_2O-derived models, of which the $Ag_{1.83}O$ model was one. These models resemble the structure of bulk Ag_2O, being comprised of a trilayer of Ag_2O cut along the (111) plane and epitaxed upon Ag(111) [9,20]. In contrast, the new Ag_6 model is not related to the bulk oxide. Instead it is better understood in terms of an arrangement of O atoms embedded between separate six-atom

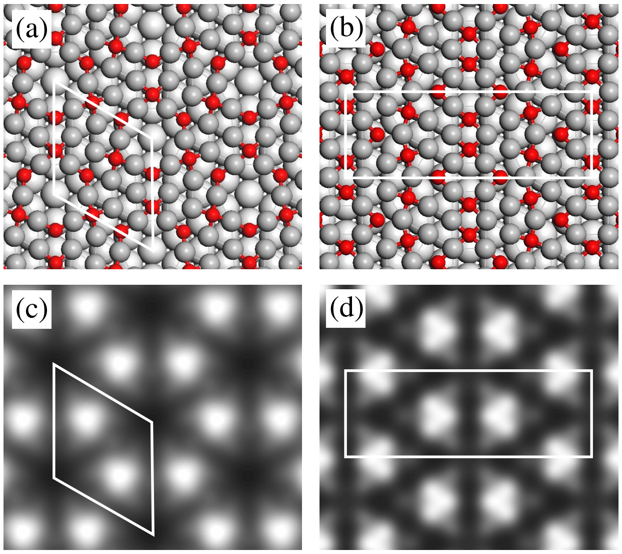

FIG. 2 (color online). Structural models and Tersoff-Hamann simulated STM images for (a),(c) the $p(4 \times 4)$ and (b),(d) the $c(3 \times 5\sqrt{3})$rect phase. The dark (light) gray balls are Ag atoms in the overlayer (substrate), and the small dark (red) balls are O atoms. In all four images a circa 30 Å^2 region of the surface is displayed.

patches of fcc- and hcp-like Ag(111). Slightly rearranging the Ag_6 building blocks with respect to each other leads to the equivalent model for the $c(3 \times 5\sqrt{3})$rect phase displayed in Fig. 2(b). Thus, whether it remains appropriate to describe the overlayer models proposed here as surface oxides is somewhat unclear. However, since the physical differences between overlayers variously described as ‘‘surface oxides,’’ ‘‘oxygen adsorbate phases,’’ or ‘‘oxygen actuated reconstructions’’ are often difficult, if not impossible, to define, this issue is little more than one of semantics. This is particularly true for the models proposed here which exhibit elements characteristic of a local oxidic structure and of an adsorbate induced metal-surface reconstruction.

Within the current computational setup, the new $p(4 \times 4)$ and the $c(3 \times 5\sqrt{3})$rect models have comparable energetic stability. Furthermore, they are both more stable than the prevailing $Ag_{1.83}O$ model for the $p(4 \times 4)$, by circa 0.09 eV/O and circa 0.05 eV/O, respectively. Additional support for the models proposed here comes from the Tersoff-Hamann STM simulations shown in Figs. 2(c) and 2(d) [23]. Clearly the agreement with the experimental images is good. In fact, by slightly modifying the tip height and bias conditions in the STM simulations we are able to reproduce not only the triangular appearance of the building blocks shown in Figs. 2(c) and 2(d), but also the more spherical appearance of the bright features observed in Fig. 1(a) [23]. Furthermore, we verified that the simulated O 1s x-ray photoemission spectrum for the $p(4 \times 4)$ agrees with the published experimental data [20,24].

While the specific Ag_6 models proposed here for the $p(4 \times 4)$ and $c(3 \times 5\sqrt{3})$rect phases are consistent with the present STM and DFT data, the DFT calculations provide additional, more general insight that broadens the discussion to the relevance of these phases to oxidation catalysis. In the search for structural models with DFT, we identified a wealth of structures of similar energetic stability, some of which were already discussed in Ref. [6]. Considering the uncertainty (to a lesser extent) due to the finite basis set and (to a larger extent) due to the approximate exchange-correlation functional, it is not possible to give preference to one or the other of these models. Hunting for ‘‘the most stable’’ structure may not even be particularly useful, especially when taking the vibrational and configurational free energy contributions at the elevated temperatures of epoxidation catalysis into account. In fact, within the current computational setup the energy difference between the new $p(4 \times 4)$ model and some of those discussed in Ref. [6] is less than $k_B T$ per oxygen adatom. In light of these results, this system appears much more complex than previously recognized, and at the high temperatures of oxidation catalysis there is no reason why only the ordered $p(4 \times 4)$ surface oxide should prevail. Indeed, from the present STM experiments it is clear that the overlayer which forms depends sensitively on the precise preparation conditions of temperature, pressure, and oxidant (O_2, atomic oxygen, or NO_2). For any of the employed oxidants, conditions can be found under which a well-ordered $p(4 \times 4)$ overlayer covers the entire surface. However, it was much more common to observe a coexistence of several structures such as those depicted in Fig. 1(a) [25]. This is, in particular, valid for O_2, which is a more common oxidant than atomic oxygen or NO_2 and which is used in industrial Ag catalysis, too.

In summary, our combined STM and DFT study shows that the presently accepted structural model for the renowned $p(4 \times 4)$ overlayer phase of O on Ag(111) [10] is incorrect. We propose an alternative Ag_6 model that has an O coverage within the experimentally estimated range [6,20], according to DFT is more stable than its predecessor, and yields simulated STM images that agree with experiment. However, before the case can be closed on this ‘‘evolving oxide structure’’ [26], further experimental support will be needed for a full and final structure determination. Aside from the atomic-scale characterization of this complex reconstructed surface, it is intriguing how sensitively the O overlayers that form depend on the precise preparation conditions of temperature, pressure, and oxidant. While previous studies focused almost exclusively on the $p(4 \times 4)$ phase, we find here that the Ag(111) substrate is almost always cloaked in a complex coexistence of surface structures, among which the $p(4 \times 4)$ and the novel $c(3 \times 5\sqrt{3})$rect phase are prominent examples. In our DFT calculations, the proposed Ag_6 models for both the $p(4 \times 4)$ and $c(3 \times 5\sqrt{3})$rect phases have comparable energetic stability, as have a host of other structural models. Instead of focusing on a single well-ordered surface structure corresponding somehow to an epitaxial overlayer of a bulk oxide phase, it is thus clearly more appropriate to expect a complex coexistence of oxide overlayers to form under the reactive conditions of industrial ethene epoxidation catalysis. The present work, however, suggests that it is useful to rationalize the complexity of the superstructures that form through the concept of a common building block. It remains to be seen if this way of thinking proves enlightening to other catalytic systems, too.

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[18] The STM is mounted on a UHV chamber (base pressure 1×10^{-10} torr) with facilities for sample cleaning and preparation. The sample was cleaned by Ar sputtering and annealing cycles, and the oxide was prepared by exposing the heated sample (500 K, 20 to 40 min) to atomic oxygen produced using a thermal gas cracker (1×10^{-7} torr O + O_2 pressure, cracking efficiency 30%). The images were taken at room temperature, with the exception of the inset of Fig. 1(e), which was recorded at $-140\,^{\circ}$C.

[19] The primitive surface unit cell of the conventional $c(3 \times 5\sqrt{3})$rect overlayer is a

$$\begin{pmatrix} 3 & 0 \\ -1 & 5 \end{pmatrix}$$

cell with edge lengths 3 and $\sqrt{21}$ in terms of the Ag(111) nearest-neighbor distance.

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[21] All calculations were carried out with the Perdew-Burke-Ernzerhof generalized gradient approximation [J. P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. **77**, 3865 (1996)] in periodic supercells within the plane-wave pseudopotential formalism as implemented in the CASTEP code [M. D. Segall *et al.*, J. Phys. Condens. Matter **14**, 2717 (2002)]. A $p(4 \times 4)$ surface unit cell was used with a five layer Ag(111) slab and a fine $6 \times 6 \times 1$ Monkhorst-Pack $\boldsymbol{k}$-point mesh. During structure optimizations the top layer of Ag atoms as well as the oxide overlayer atoms were allowed to relax, while the bottom four layers of Ag were held fixed. Calculations were also performed for the $c(3 \times 5\sqrt{3})$rect phase in its primitive

$$\begin{pmatrix} 3 & 0 \\ -1 & 5 \end{pmatrix}$$

surface unit cell with an equivalent computational setup to that used for the $p(4 \times 4)$.

[22] There is a noticeable asymmetry in the overlayer with the two Ag_6 triangles rotated slightly about the surface normal with respect to each other. Thus the Ag atoms do not reside precisely above the three-fold sites of Ag(111), being displaced by 0.15 Å on average. In addition the two O atoms in each trough are not equivalent: one type, those depicted as being fourfold coordinated to the overlayer Ag atoms in Fig. 2(a), reside circa 0.85 Å above the other. However, it is important to recognize that this overlayer exhibits considerable structural flexibility with several very similar structures close in energy, particularly with regard to the relative height of the O atoms.

[23] STM simulations were performed within the Tersoff-Hamann approximation [J. Tersoff and D. R. Hamann, Phys. Rev. B **31**, 805 (1985)] at a tip height of 2.5 Å above the highest atom in each overlayer for occupied states within 2 eV of the Fermi level. By simply increasing the height of the tip to 3.5–4.0 Å above the highest atom in each overlayer, the spherical appearance of the bright features becomes more apparent.

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