

When seeing is not believing: Oxygen on Ag(111), a simple adsorption system?

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A number of recent studies indicate that, under the oxygen rich conditions of oxidation catalysis, some transition metal catalysts may be covered by thin oxide overlayers. Moreover, it has been suggested that such “surface-oxide” layers are catalytically active, possibly more active than the pure metal surfaces as was traditionally assumed. This contemporary picture can be traced back to Ag catalysis, where over 30 years ago it was suggested that the top layer of Ag(111) reconstructed to an epitaxial Ag₂O like overlayer upon exposure to oxygen [Rovida *et al.*, Surf. Sci. **43**, 230 (1974)]. Extensive experimental work, including scanning tunneling microscopy studies in which the oxide was apparently imaged with atomic resolution, as well as density-functional theory calculations, largely confirmed this interpretation. However, a review of published experimental data and new density-functional theory results presented here indicate that previous conclusions are significantly incomplete and that the structure of this original surface oxide must be reconsidered.
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I. INTRODUCTION

“Solving” atomic structures is a common activity for the natural scientist. A structure, whether of relevance to molecular biology, chemical physics, catalysis, or another area, is considered solved when an atom-by-atom structural understanding of the molecular or solid state systems involved has been obtained. Such detailed understanding not only satisfies a natural desire for fundamental insight, but is often a necessary prerequisite for the development or advancement of technologies and devices. In surface science such efforts are mostly directed at clean and adsorbate covered single-crystal surfaces, that are, e.g., of relevance in the context of heterogeneous catalysis or the semiconductor industries. After some 50 years of surface science, many such surface structures have now been “solved,” including many cases with highly complex, large surface unit-cell reconstructions.¹ However, one seemingly simple structure evades solution, namely oxygen on Ag(111), despite having been intensively examined since the early 1970s.

There are many reasons for the interest in oxygen interaction with Ag(111). First, it comprises a diatomic molecule and a close packed fcc(111) surface and so is a prototype for a seemingly “simple” model adsorption system. Further, Ag is an efficient (partial) oxidation catalyst. In particular, Ag is the catalyst of choice for two important oxidation reactions: methanol to formaldehyde and ethylene to ethylene epoxide. The epoxidation reaction is an interesting scientific process as it is one of the few reactions catalyzed by a noble metal and the simplest example of a kinetically controlled selective

oxidation: carbon dioxide and water are the thermodynamically most stable products of the reaction of ethylene and oxygen, yet ethylene-epoxide is the main product. This has led to countless studies of oxygen on Ag in general, and on Ag(111), in particular. Also, as will become clear, exposure of oxygen to Ag(111) is believed to yield an ultrathin two-dimensional (2D) oxide adlayer. Such “surface oxides” are now repeatedly being identified, characterized, and their relevance to heterogeneous catalysis highlighted.²⁻⁵ Indeed there is increasing awareness that 2D surface oxides, such as those discussed here on Ag, could actually be the active phases of many transition metal oxidation catalysts at high-pressure conditions representative of technological applications.⁶⁻⁸

The first aim of this article is to provide a concise review of the work carried out on oxygen on Ag(111) that over 30 years led to a unique structural model for a characteristic $p(4 \times 4)$ overlayer that forms upon exposure to oxygen. The second aim is to note our concerns with this model in light of new density-functional theory (DFT) results, which question its validity. Although this is a review of oxygen adsorption on Ag we will not at any stage discuss the catalytic activity of Ag, nor shall we enter into the (sometimes contentious) debate of what the nature of the “active” form of oxygen is in the Ag catalyzed ethylene epoxidation reaction. Discussion concerning these issues can be found in many of the excellent papers from the groups of Barteau,^{9,10} Stoltz,¹¹ Schlögl,^{12,13} and others.¹⁴⁻¹⁶ Instead, we will focus almost exclusively on only one specific Ag orientation and on one adsorbate overlayer, namely the $p(4 \times 4)$ -O/Ag(111) structure. Despite the apparently narrow focus this article will

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potentially be of interest to anyone involved in surface science research, as the history of this system is very much a history of modern surface science. The lesson to us all of the history of this system is that even a model described as “compelling,”¹⁷ “convincing,”¹⁸ apparently imaged with atomic resolution by scanning tunneling microscopy (STM),^{19,20} and found in two separate DFT studies^{21,22} to be stable or metastable, may still be wrong or significantly incomplete.

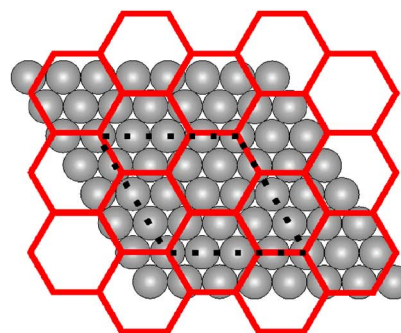
II. A BRIEF HISTORY OF OXYGEN ON AG(111)

A. 1970s

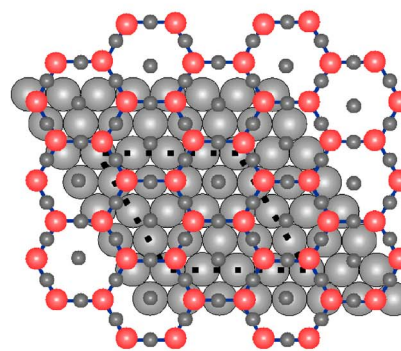
A history of the $p(4 \times 4)$ -O/Ag(111) overlayer [to which we shall from now on refer to simply as the “ (4×4) overlayer”] must begin with the brief communication published in the forerunner of the present journal, the *Journal of Vacuum Science and Technology*, by Rovida *et al.* in 1972.²³ In this article the results of O₂ adsorption studies on the (100), (110), and (111) surfaces of Ag were reported in the pressure range 10⁻³–1 Torr ($\sim 10^{-3}$ –10⁻⁶ atm.). Such high pressures were needed to obtain an appreciable coverage of O atoms on Ag, due to the by now well established low sticking probability on the order of 10⁻⁶–10⁻³.^{24,25} On exposure of O₂ (approximately 1 Torr or 10⁻³ atm) to Ag(111) a (4×4) superstructure was observed with low energy electron diffraction (LEED). This was the only ordered structure identified on any of the three Ag surfaces examined and it remained stable upon heating in vacuum until about 500–600 K. In this article the (4×4) superstructure was then actually attributed to adsorption of intact O₂ molecules, while dissociative adsorption of O₂ was ruled out. However, in a subsequent more substantive article, published 2 years later by the same authors in *Surface Science*, the molecular O₂ interpretation of the (4×4) overlayer was dismissed. This was to be the first of many times that the structure of the (4×4) overlayer would be revisited!

The model Rovida *et al.* proposed in their now famous 1974 *Surface Science* paper sprang from the interesting realization that there was a common periodic element between the (111) surfaces of Ag and Ag₂O.²⁶ Specifically, Rovida *et al.* noticed that the diagonal of the unit cell of the (111) surface of Ag₂O (11.59 Å) corresponded to within 0.3% to four times the Ag–Ag distance (11.56 Å) between neighboring Ag atoms on the Ag(111) surface. The close match between the (111) planes of Ag and Ag₂O is sketched in Fig. 1. From this realization Rovida *et al.* were prompted to suggest that the (4×4) “superstructure is due to a coincidence lattice between the (111) Ag plane and a thin layer of atoms of Ag and O positioned in the (111) planes of Ag₂O.” Support for this model was drawn from the essentially identical values reported for the activation energy for Ag₂O decomposition (36 kcal/mol, ~ 1.56 eV)²⁷ and O₂ desorption from Ag (35 kcal/mol, ~ 1.52 eV)¹⁷ and from the overlap between the range of experimental values for the heat of adsorption (11–21 kcal/mol, ~ 0.48 –0.91 eV) and their quoted value for the heat of formation of Ag₂O (14.7 kcal/mol,

(a) Rovida: Ag₂O/Ag(111)



(b) Campbell: Ag₂O/Ag(111)



(c) Carlisle: Ag_{1.83}O/Ag(111)

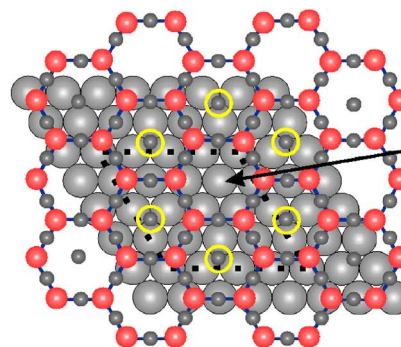


FIG. 1. Schematic illustration of the development of the $p(4 \times 4)$ -O/Ag(111) adsorption model from: (a) the Rovida model, which merely recognized the correspondence between the (111) planes of Ag₂O and Ag; (b) Campbell's trilayer modification; and (c) Carlisle's Ag deficient Ag_{1.83}O model. In (c) the arrow indicates from where an Ag adatom has been removed inside one unit cell, and the Ag adatoms believed to be imaged by STM are circled. Large (small) grey spheres are Ag atoms in the substrate (overlayer) and the red spheres are O atoms.

~ 0.64 eV).²⁸ Although Rovida *et al.* proposed the formation of “an oxide developed only in two dimensions” they did not attempt to establish any details of the structural model although they did suggest that perhaps an oxide adlayer comprised of a plane of O atoms between two planes of Ag atoms was likely. They argued that this may be in better agreement with the slight ($\sim +0.25$ eV) variation of the work function observed upon formation of the (4×4) overlayer.

The range of experimental temperatures and pressures under which the (4×4) LEED pattern was observed—an early day adsorbate–substrate phase diagram—was reported. This range extended from approximately 350 to 500 K and from approximately 10^{-3} to 10^{-5} atm. Following Rovida's papers Czanderna interpreted their isosteric heat of adsorption measurements for oxygen on silver powder as showing evidence for the formation of islands of surface silver oxide and, without actually identifying the (4×4) overlayer, commented on the “very compelling evidence” for oxide formation provided by Rovida.¹⁷ Twice more in the 1970s the (4×4) LEED pattern was observed: first by Albers *et al.*²⁹ and then later by Tibbets *et al.*³⁰ who made the first measurements of the O 1s core levels and valence band spectra of the (4×4) overlayer. However, neither author added to Rovida's model.

B. 1980s

The 1980s saw Lambert apply various surface science techniques to the study of oxygen adsorption and ethylene epoxidation on Ag. LEED, x-ray photoelectron spectroscopy (XPS), ultraviolet photoelectron spectroscopy (UPS), Auger, temperature programmed desorption (TPD), and isotope labeling experiments were employed to study oxygen on several low index Ag surfaces.^{15,18,31,32} Grant and Lambert observed the (4×4) overlayer of O on Ag(111) when dosing at 400–500 K and 1–2 Torr ($\sim 10^{-3}$ atm).¹⁸ With XPS a single O 1s peak at 529.8 ± 0.3 eV below the Fermi level (E_F) was reported; with UPS an adsorbate induced valence band peak at 3.2 eV below E_F was identified; and the TPD desorption temperature was measured to be 580 K for the associative desorption of this state as O₂. This was interpreted as indicating an O₂ desorption energy of ~ 130 kJ/mol (~ 1.35 eV). Despite their endeavors and new data Grant and Lambert were content, however, to conclude that Rovida *et al.* had already “convincingly interpreted” the structural model that lay behind the observed LEED pattern.

The following year Campbell applied a similar array of techniques as Grant and Lambert had, although Campbell was somewhat more circumspect than his predecessors, using his new measurements as a basis to reconsider Rovida's (4×4) model. Indeed Campbell's study provided the first “flesh” to the bones of the skeletal structural model.²⁴ In good agreement with Lambert and others, the characteristic “sharp and bright” (4×4) LEED pattern was identified and found to lead to an O₂ desorption peak at ~ 580 K. A Red-head analysis of this desorption peak with the assumption of first order desorption kinetics and a preexponential of 10^{15} s^{-1} yielded a desorption energy of 40 kcal/mol (~ 1.74 eV).³³ Campbell reasoned that this was essentially equal to the heat of atomic adsorption in the (4×4) adlayer [41 kcal/mol (~ 1.78 eV)]. At oxygen coverages well below saturation the (4×4) LEED pattern was already observed, indicating O nucleation into islands of (4×4) on the surface. Unlike Lambert, however, Campbell measured the O 1s binding energy for the (4×4) overlayer to be at 528.2 eV below E_F . Campbell argued that his value was in good agreement with that reported for atomic O on other Ag surfaces

(for example, 528.1–528.3 eV on Ag(110)^{34,35} or 528.3 eV on Ag foils),³⁶ whereas Grant and Lambert's value was likely to be the result of contamination by surface carbonates which give rise to an O 1s binding energy at ~ 529.9 eV.³⁴ In light of several subsequent measurements^{37,38} of the O 1s level in the (4×4) overlayer at ~ 528.2 –528.3 eV it seems that Campbell's value for the O 1s binding energy is the more reliable one. An estimate of the O coverage in the (4×4) overlayer of 0.41 ± 0.04 (MLs) was made.³⁹ This implied that there should be 6–7 O atoms per (4×4) cell which would be consistent with a single trilayer of Ag₂O on top of Ag(111). Specifically, a trilayer in which a layer of Ag atoms is sandwiched between two O layers was suggested, since this would have an O coverage of 0.375 ML. Thus the Rovida–Campbell trilayer model was born, a schematic of which is shown in Fig. 1(b). Having refined and expanded upon Rovida's 2D oxide adlayer model, Campbell was careful to add a note of caution. Specifically, he pointed out that the “LEED spots for primary scattering off this overlayer were of insufficient intensity for such a structural model” and called for a detailed LEED analysis of this system. This call has not yet been answered.

C. 1990s

A decade later, the structure of the (4×4) overlayer was revisited with a TPD, LEED, XPS, Auger, and nuclear reaction analysis study by Bare *et al.*³⁷ This time the (4×4) overlayer was produced from NO₂ rather than O₂, since studies on other metal surfaces [Pt(111),⁴⁰ Pd(111),⁴¹ Ru(0001)⁴²] had shown that NO₂ was a highly efficient source of atomic O. Bare demonstrated that by adsorbing NO₂ on Ag(111) [and Ag(110)] the problematic low O₂ sticking probability could be circumvented, and that the (4×4) overlayer could be produced on Ag(111) at much lower pressures given a temperature at exposure that is sufficiently high (~ 500 K) to desorb any unwanted NO. Bare *et al.* applied this recipe to produce O adlayers on Ag(110) and Ag(111). Examination of the as prepared overlayers with LEED showed that they had the same periodicity as overlayers produced from O₂. Moreover, when the O 1s spectra for NO₂ produced overlayers were compared to O₂ produced spectra for Ag(110) and Ag(111), they looked the same. Specifically the O 1s level for the (2×1) O adlayer on Ag(110) was 528.5 eV with a full width at half maximum (FWHM) of 1.8 eV for both the NO₂ and O₂ prepared adlayers. For the (4×4) overlayer on Ag(111) the peak was at 528.2 eV with a FWHM of 1.7 eV, in very good agreement with Campbell's values of 528.2 and 1.9 eV FWHM.²⁴ In short, based on this (limited) comparison of features there was no evidence to suggest that the overlayers produced from O₂ and NO₂ were different.

Bare's new contribution to the structure of the (4×4) came from two sources. First, a nuclear reaction analysis with a deuteron beam led to a coverage determination of 0.51 ± 0.04 ML. Second, a careful examination of the dependence of the TPD spectra on initial O coverage revealed that two peaks, separated by approximately 10 K, could be resolved in the O₂ desorption feature at ~ 580 K. Using their

value of 0.51 ML for the saturation O coverage approximately 70% (0.37 ML) was found to come from the lower temperature peak and approximately 30% (0.14 ML) from the high temperature minority peak. Since 0.37 ML is precisely the coverage of the Rovida–Campbell trilayer model, Bare *et al.* concluded that the (4×4) overlayer was comprised of an Ag_2O trilayer, plus approximately 0.14 ML randomly adsorbed O atoms.

Less than a year later, Raukema *et al.*²⁵ reported a similar set of TPD experiments to Bare *et al.* for O_2 recombinative desorption from the (4×4) overlayer. By carefully examining the dependence of the TPD peak shape on heating rate it was shown that the double peak nature was only observable for heating rates $\leq 10 \text{ K s}^{-1}$. This explained why the feature had not been observed before Bare's study a year earlier. However, Raukema *et al.* offered another interpretation of their data, suggesting that the twin peaked TPD spectrum was indicative of complex desorption kinetics rather than the presence of two types of O adsorbate. Furthermore, since their measured O coverage for the (4×4) saturated surface of $0.40 \pm 0.02 \text{ ML}$ agreed with Campbell's coverage determination, they did not question or modify the Rovida–Campbell model.

Following this, Bukhtiyarov *et al.* examined O on Ag(111) with TPD, XPS, and angular dependent XPS.³⁸ The (4×4) overlayer was again characterized by an O 1s level at $\sim 582.2 \text{ eV}$ below E_F , desorption by TPD below 600 K (560 K),⁴³ and an O coverage of approximately 0.4 ML ($\sim 0.42 \text{ ML}$). Two key XPS results appeared to support the Ag_2O oxide model. First, an additional Ag 3d component was identified at 367.6 eV below E_F , shifted by $\sim 0.5 \text{ eV}$ from bulk Ag into coincidence with the Ag 3d level in bulk Ag_2O (367.6–367.7^{44,45} eV). Second, the concentration of Ag atoms in the shifted Ag component was estimated to be approximately twice the concentration of adsorbed O which would, of course, be consistent with the stoichiometry of Ag_2O . However, Bukhtiyarov *et al.* concluded that their angular resolved XPS results were not consistent with the Rovida–Campbell model as these indicated that O atoms were located mainly within one layer and that this layer was “possibly located between the topmost and the second silver layers.” Since the individual XPS spectra from which this conclusion was drawn were not presented it is difficult to assess their significance. Indeed the authors did not suggest an alternative model with (4×4) periodicity, but repeated Campbell's call for the application of a diffraction technique to this system. Furthermore, since Rovida's seminal experiments, Binnig and Rohrer had invented the scanning tunneling microscope and so the authors also called for its application to this structure.

D. 2000s

In April, 2000 the anticipated STM experiments of the (4×4) overlayer were reported.¹⁹ Carlisle *et al.* imaged the overlayer, produced from NO_2 following Bare's recipe,³⁷ with apparent atomic resolution. Two typical images of the (4×4) overlayer are shown in Figs. 2(a) and 2(b). In Fig.

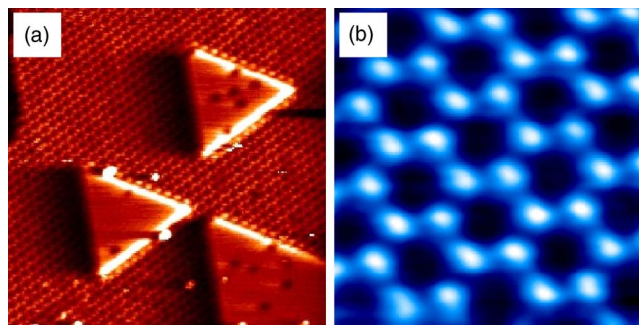


Fig. 2. STM images of the (4×4) overlayer on Ag(111). (a) A constant height image of a $300 \times 300 \text{ \AA}$ region of the surface on which the (4×4) overlayer is in coexistence with triangular islands of Ag(111) (from Ref. 20). (b) Closeup of an approximately $60 \times 60 \text{ \AA}$ region of the (4×4) overlayer, illustrating the clear hexagonal nature of this overlayer (from D.A. King, unpublished). Both images were recorded at 4 K with a $+0.77 \text{ V}$ bias and a 0.7 nA tunneling current. See Ref. 20 for further details.

2(a) the (4×4) overlayer is observed coexisting with triangular islands of Ag(111)⁴⁶ and in Fig. 2(b) a closeup of the (4×4) overlayer is shown, imaged as an hexagonal array of maxima. Simultaneous resolution of the substrate and oxide overlayer at certain bias voltages revealed the registry with the substrate and the distance between the bright maxima to be approximately 6.7 \AA . This, in conjunction with semi-empirical STM simulations of several trial structures,⁴⁷ led to a model that yielded a simulated STM image that closely resembled the measured STM image. Specifically, the model proposed was a “Ag-deficient” version of the Rovida–Campbell trilayer model with an exact stoichiometry of $\text{Ag}_{1.83}\text{O}$ [Fig. 1(c)]. Within this model each protrusion corresponds to a Ag adatom that resides on the Ag(111) surface in the center of the O–Ag–O hexagons.⁴⁸ For a stoichiometric Ag_2O overlayer every hexagon contains one of these Ag adatoms; for the nonstoichiometric model one third of these Ag adatoms are removed. Specifically the Ag adatoms that would in principle be located at on-top sites of the underlying Ag(111) substrate are absent, as indicated by the arrow in Fig. 1(c).

Carlisle's STM experiments appeared to provide the strongest support yet for the Rovida–Campbell trilayer model, albeit with a slightly altered stoichiometry of $\text{Ag}_{1.83}\text{O}$. In a subsequent paper Carlisle *et al.* reported details of the formation and decomposition of the (4×4) overlayer.²⁰ When formed from NO_2 at 500 K, O atoms initially adsorbed randomly on the surface. At coverages as low as 0.05 ML, however, patches of the (4×4) oxide begin to form at surface defect sites (nucleation at a screw dislocation and step edge was identified) before extending across Ag(111) terraces. Prepared under these conditions and imaged with STM, the oxide was practically free from defects, with a visible defect coverage, measured against the underlying Ag(111) substrate, of only $2.5 \times 10^{-4} \text{ ML}$. Upon controlled heating to $\sim 500 \text{ K}$ for several minutes in ultrahigh vacuum (UHV) some new structures were identified. In par-

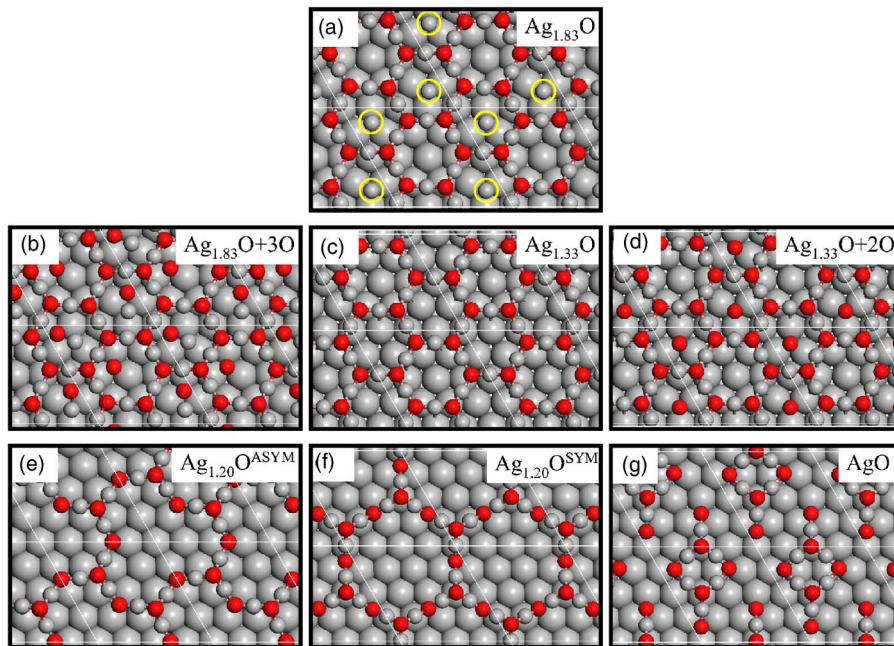


FIG. 3. Selected optimized (4×4) structures for O overlayers on Ag(111). (a) $\text{Ag}_{1.83}\text{O}$ model already shown schematically in Fig. 1(c), and the Ag adatoms believed to be imaged by STM are circled. (b)–(g) Alternative (4×4) models. Large (small) grey spheres are Ag atoms in the substrate (overlayer) and the darker (red) spheres are oxygen atoms. The oxygen coverage in each overlayer is: (a) 0.375 ML; (b) 0.563 ML; (c) 0.375 ML; (d) 0.500 ML; (e) 0.313 ML; (f) 0.313 ML; and (g) 0.375 ML.

ticular, a highly ordered “stripe” structure was identified and a model based on a modification of the $\text{Ag}_{1.83}\text{O}$ model was proposed to explain this structure.

Along with apparent atomic resolution of the (4×4) overlayer, the decade also brought necessary advances in computer algorithms and computational capacity to allow the (4×4) model to be tested with first principles theory. In 2003, Michaelides *et al.*²¹ and Li *et al.*²² reported independent plane wave pseudopotential DFT studies of O adsorption on Ag(111). Michaelides *et al.* examined the adsorption of on-surface and subsurface atomic O, as well as Ag_2O and $\text{Ag}_{1.83}\text{O}$ oxide adlayers. Li *et al.* examined several of the same structures, as well as many others including mixed on-surface and subsurface O layers, compressed Ag_2O -like adlayers, ozone-like structures, and surface substitutional models. Both studies reached the conclusion that the $\text{Ag}_{1.83}\text{O}$ model was energetically favorable, with the lowest O adsorption energy at the O coverages of interest. Both studies also concluded that the $\text{Ag}_{1.83}\text{O}$ model was favored over the unperturbed Ag_2O model by 0.5–0.7 eV/(4×4) cell. By taking temperature T and pressure p into account through the oxygen chemical potential (see below), (T, p) phase diagrams which describe the stable surface phases of O on Ag(111) from UHV to the high pressure conditions representative of real catalysis were determined. Also in this point both studies agreed and predicted that of the phases examined the $\text{Ag}_{1.83}\text{O}$ model would be the most stable phase of O on Ag(111) at the temperatures and pressures characteristic of industrial ethylene epoxidation catalysis (500–600 K; ≥ 1 atm.).¹⁶ Indeed the stability of the (4×4) overlayer was predicted to exceed that of bulk Ag_2O , providing another example of how the properties of materials on the nanoscale can differ from those of the bulk.

Having thus (finally) apparently characterized the (4×4) overlayer, several followup studies investigated aspects of its

reactivity. Notably Bocquet *et al.* revealed that additional O adatoms could readily be coadsorbed along with the $\text{Ag}_{1.83}\text{O}$ adlayer.⁴⁹ Dissociative adsorption of O_2 to yield as many as three extra O adatoms per $p(4 \times 4)$ cell was shown to be exothermic, not lowering the average O adsorption energy by more than a few meV per additional O atom. The integrity of the O–Ag–O trilayer units was retained in these structures, which are most appropriately labeled as $\text{Ag}_{1.83}\text{O}+n\text{O}$ adlayers. An example of one such adlayer with the maximum of three additional oxygen atoms is shown in Fig. 3(b) ($\text{Ag}_{1.83}\text{O}+3\text{O}$). This finding of an oxide adlayer plus additional coadsorbed O atoms is reminiscent of the interpretation reached by Bare *et al.* in the 1990s and seemed to explain their high coverage determination of 0.51 ± 0.04 ML.³⁷ The adsorption of acetaldehyde on the oxide was examined with STM and ethylene adsorption with STM and DFT.^{50,51} In each case an assignment of the preferred adsorption site was made based on the then accepted $\text{Ag}_{1.83}\text{O}$ model for the oxide adlayer. Finally, DFT was also used to determine reaction pathways for the oxidation of ethylene to ethylene-epoxide on the $\text{Ag}_{1.83}\text{O}/\text{Ag}(111)$ surface and for comparison on a low coverage atomic O phase.⁵²

III. LASTING UNDERSTANDING?

So far we have uncritically traced the development of the (4×4) overlayer model, from its inception to the present day. Should we really believe what we have seen? Although the $\text{Ag}_{1.83}\text{O}$ model is derived from Ag_2O [where there exists an almost perfect epitaxial match to the Ag(111) substrate], the model has been observed with apparent atomic resolution in STM, the model yields a simulated STM image which agrees with experiment, and the model is found to be stable according to first principles DFT calculations, our answer is likely to be no. This is mainly because extended DFT studies

TABLE I. Surface adsorption free energies, γ [from Eq. (1)] and adsorption energies per O atom referenced to $1/2\text{O}_2$ in the gas phase, E_{ad} , for various (4×4) overlayers on Ag(111). All calculations are for a three layer Ag(111) slab with the PBE (Ref. 60) exchange correlation functional and with a $4 \times 4 \times 1$ k mesh. Values given in parentheses check on the convergence by varying this computational setup, namely employing (a) a $2 \times 2 \times 1$ k mesh, (b) a $2 \times 2 \times 1$ k mesh, and the PW91 functional (Ref. 62), or (c) a $2 \times 2 \times 1$ k mesh, PW91 and Ag(111) slabs with seven layers.

“Stoichiometry”	$\gamma(T=0 \text{ K}, p=0)$ (meV/Å ²)	E_{ad} (eV/O)	Figure
Ag _{1.83} O	-20.6	-0.47 (-0.51, ^a -0.46, ^b -0.45) ^c	1(c)/3(a)
Ag _{1.83} O+1O	-23.0	-0.45 (-0.46) ^a	...
Ag _{1.83} O+2O	-25.1	-0.43 (-0.45) ^a	...
Ag _{1.83} O+3O	-26.9	-0.41 (-0.47, ^a -0.44) ^b	3(b)
Ag _{1.33} O	-23.7	-0.54 (-0.57, ^a -0.50, ^b -0.50) ^c	3(c)
Ag _{1.33} O+1O	-25.6	-0.50 (-0.55) ^a	...
Ag _{1.33} O+2O	-26.3	-0.45 (-0.52) ^a	3(d)
Ag _{1.33} O+3O	-26.3	-0.40 (-0.47, ^a -0.43) ^b	...
Ag _{1.2} O ^{ASYM}	-20.4	-0.56 (-0.63, ^a -0.58, ^b -0.56) ^c	3(e)
Ag _{1.2} O ^{ASYM} +1O	-20.6	-0.47 (-0.55) ^a	...
Ag _{1.2} O ^{ASYM} +3O	-19.3	-0.33 (-0.41, ^a -0.38) ^b	...
Ag _{1.2} O ^{SYM}	-15.3	-0.42 (-0.50) ^a	3(f)
Ag _{1.2} O ^{sym} +1O	-17.1	-0.39 (-0.49) ^a	...
AgO	-17.5	-0.40 (-0.48) ^a	3(g)

indicate that this system is much more complex than anticipated, with several structures of comparable or even better stability than the Ag_{1.83}O structure having already been identified. In addition, recent STM⁷² and surface x-ray diffraction⁷³ experiments do not appear to support the Ag_{1.83}O model.

Let us first briefly mention how we shall compare the stability of the different oxide adlayers examined. The thermodynamic stability of adsorbed phases can be compared through the surface free energy or, as we prefer here, through the surface free adsorption energy $\gamma(T, p)$.⁵³ In this case we have

$$\gamma(T, p) = (G_{\text{O/Ag}(111)}^{\text{slab}} - G_{\text{Ag}(111)}^{\text{slab}} - N_{\text{Ag}}\mu_{\text{Ag}} - N_{\text{O}}\mu_{\text{O}})/A, \quad (1)$$

where $G_{\text{O/Ag}(111)}^{\text{slab}}$ and $G_{\text{Ag}(111)}^{\text{slab}}$ are the free energies of the O/Ag surface under consideration and that of the clean Ag(111) reference system, respectively. A is the surface area. N_{Ag} and N_{O} are the numbers of O and Ag atoms in the adlayer [i.e., those in addition to the clean Ag(111) reference system] and μ_{Ag} and μ_{O} are the Ag and oxygen chemical potentials. The oxygen chemical potential is given by

$$\begin{aligned} \mu_{\text{O}}(T, p) &= 1/2E_{\text{O}_2}^{\text{total}} + \Delta\mu_{\text{O}}(T, p) \\ &= 1/2 \left[E_{\text{O}_2}^{\text{total}} + \tilde{\mu}_{\text{O}_2}(T, p^0) + k_B T \ln \left(\frac{p_{\text{O}_2}}{p^0} \right) \right], \quad (2) \end{aligned}$$

where $E_{\text{O}_2}^{\text{total}}$ is the computed DFT total energy of an O₂ molecule and $\Delta\mu_{\text{O}}(T, p)$ thus incorporates the temperature and pressure dependence of the oxygen chemical potential, with the contribution from rotations and vibrations of the molecule, as well as the ideal-gas entropy at $p^0=1$ atm incorporated in $\tilde{\mu}_{\text{O}_2}(T, p^0)$. T and k_B are, of course, temperature and Boltzmann's constant, respectively. $\tilde{\mu}_{\text{O}_2}(T, p^0)$ can be computed from first principles, yielding results that are, at all

temperatures and pressures of interest to us here, virtually indistinguishable from the experimental values listed in the thermodynamic tables.⁵⁴ To make computations of $\gamma(T, p)$ practical, we approximate the chemical potential of Ag by the total energy of a Ag atom in bulk fcc silver and likewise we approximate the difference of the free energies [$G_{\text{O/Ag}(111)}^{\text{slab}} - G_{\text{Ag}(111)}^{\text{slab}}$] by the difference in their total energies. Justification for the use of these approximations for this specific system can be found in Li *et al.*²² and Michaelides *et al.*²¹ We mention in passing that this general approach of combining *ab initio* DFT energetics and thermodynamics, now often termed *ab initio* thermodynamics, is a valuable technique for extending the predictive power of first-principles simulations beyond zero-temperature, zero-pressure conditions to more realistic and often more interesting finite temperature and pressure regimes. Such *ab initio* thermodynamics concepts were introduced in the 1980s for semiconductor surfaces⁵⁵⁻⁵⁷ and are now experiencing somewhat of a renaissance in the area of surface oxides.⁵⁸

The surface free adsorption energy, as defined above, is equivalent to an “adsorption energy per surface area” which is easily related to the more commonly used adsorption energy (E_{ad}) per $1/2\text{O}_2$ by multiplying $\gamma(T=0 \text{ K}, p=0)$ by A/N_{O} . In Table I we list both $\gamma(T=0 \text{ K}, p=0)$ and E_{ad} for several (4×4) structures. We shall now discuss our results presented in Table I and Fig. 3, which form the basis of our doubts on the existing Ag_{1.83}O model. Details of the computational setup used in the DFT calculations reported here are given in Ref. 59.

A. Lower energy Ag₂O like structures have been identified

As we know, the DFT studies of Michaelides *et al.*²¹ and Li *et al.*²² support the Ag_{1.83}O model, having found it to be

TABLE II. Total energy gain, ΔE , for the removal of the two Ag adatoms in the $\text{Ag}_{1.83}\text{O}$ model to yield an $\text{Ag}_{1.33}\text{O}$ model ($\Delta E = E[\text{Ag}_{1.83}\text{O}/\text{Ag}(111)] - E[\text{Ag}_{1.33}\text{O}/\text{Ag}(111)] - 2E[\text{Ag bulk}]$) for several different GGA exchange correlation functionals, namely PBE (Ref. 60), RPBE (Ref. 61), and PW91 (Ref. 62).

Functional	k mesh	Ag layers	ΔE [eV/(4×4)]
PBE	4×4×1	3	0.38
PBE	2×2×1	3	0.32
RPBE	2×2×1	3	0.40
PW91	2×2×1	3	0.28
PW91	2×2×1	7	0.33

the “most stable” structure identified at the appropriate coverage regime of ~ 0.4 ML. However, due to the vastness of configuration space in this system exhaustive structural searches are still prohibitive, and “most stable” refers to the lowest energy structure within the set of trial structures tested. By significantly expanding the set of structural models tested, we have now identified several structures lower in energy than the $\text{Ag}_{1.83}\text{O}$ model.

Recall that the protrusions imaged by STM are believed to be the Ag adatoms that sit inside two thirds of the O–Ag–O hexagons, the silvers marked in Fig. 1(c). These Ag atoms are, however, unstable compared to a thermodynamic reservoir of bulk Ag by ~ 0.2 eV/Ag. Thus approximately 0.4 eV per (4×4) cell can be gained, simply by removing them from the $\text{Ag}_{1.83}\text{O}$ model to yield a new $\text{Ag}_{1.33}\text{O}$ model. To put this another way, the $\text{Ag}_{1.33}\text{O}$ model has a lower surface energy, $\gamma(T=0, p=0)$, than the $\text{Ag}_{1.83}\text{O}$ model (by approximately 3 meV/Å²). As can be seen in Table II this result holds with three different exchange correlation functionals (“PBE,”⁶⁰ “RPBE,”⁶¹ and “PW91”⁶²), or if the thickness of the Ag(111) slab employed in the calculations is increased to seven Ag layers.

Bearing in mind the results of Bocquet *et al.*,⁴⁹ which showed that extra O adatoms could be coadsorbed within the $\text{Ag}_{1.83}\text{O}$ model, O adatoms were also coadsorbed within the $\text{Ag}_{1.33}\text{O}$ model. Indeed, an exhaustive search of possible $\text{Ag}_{1.33}\text{O}+n\text{O}$ and $\text{Ag}_{1.83}\text{O}+n\text{O}$ models was performed, with n between 0 and 3. The most stable structure at each “stoichiometry” is listed in Table I. These calculations reinforce the finding that the $\text{Ag}_{1.83}\text{O}$ model is clearly not the most stable structure, and reveal that generally energy is gained by removing the Ag adatoms, whether or not this is in the presence of coadsorbed O atoms. Since the Ag adatoms are thought to be the bright protrusions imaged in STM, and are indeed the key feature that made the $\text{Ag}_{1.83}\text{O}$ model compatible with STM, this finding indicates that the prevailing $\text{Ag}_{1.83}\text{O}$ model is just a metastable structure. This makes it hardly imaginable that this structure exists under realistic conditions in large areas and/or without a significant number of defects.

B. Lower energy non Ag_2O like structures have been identified

So far we have only discussed structures that essentially amount to small modifications of the Rovida–Campbell

trilayer model, in which Ag adatoms have been removed and/or O adatoms added, while the O–Ag–O oxide-like hexagons have remained effectively unperturbed. Essentially this is a single class of structures that resemble to a greater or lesser extent adlayers of Ag_2O -(111), as originally proposed by Rovida on the basis that the epitaxial mismatch between the (111) surfaces of Ag_2O and Ag is almost zero. However, here we are considering subnanometer Ag_2O like films. Since it is well known that the properties of materials on the nanoscale often differ from those in the bulk, it is not clear if such an optimal lattice match does in fact exist between a single Ag_2O like trilayer film and Ag(111). To test this we have calculated the energy of a free standing 2D film as a function of area, yielding an effective 2D “lattice constant” of the free standing film.⁶³ We find that this is 12% less than the calculated lattice constant of bulk Ag_2O , which would give rise to a theoretical mismatch between an Ag_2O like trilayer and Ag(111) of 13%, compared to a theoretical mismatch between bulk Ag_2O and Ag(111) of $<1\%$. Of course, a gas phase trilayer is not the same as an adsorbed one. Nonetheless the simple realization that a trilayer need not necessarily possess the same lattice constant as bulk Ag_2O causes one to question the initial basis that an Ag_2O like overlayer is desirable *per se* and leads us to extend the search for possible structural models for the (4×4) overlayer beyond Ag_2O like overlayers.

On this basis, other models have been explored. This search, of more than 100 trial (4×4) structures, with varying stoichiometries and adlayer configurations yielded several new models that are equally stable to or more stable than the $\text{Ag}_{1.83}\text{O}$ overlayer. Since the experimental oxygen coverage estimates in the (4×4) overlayer are 0.4 ML²⁴ or 0.5 ML,³⁷ only models with an oxygen coverage within 20% of either of these estimates will be discussed here, which restricts the discussion of plausible models to ones that contain 5–9 oxygen atoms per $p(4\times 4)$ unit cell. Three examples are shown in Figs. 3(e)–3(g) and their energies are listed in Table I. From Table I it can be seen that the average O adsorption energy in these structures is similar to or greater than in the $\text{Ag}_{1.83}\text{O}$ model. These three structures have been selected in particular to illustrate an interesting observation. Several low energy overlayers identified so far, including the Ag_2O like models discussed above, share a common structural element, namely an Ag_3O_4 pyramidal unit. The main difference between each structure shown is simply how these Ag_3O_4 “building blocks” are arranged.⁶⁴ In particular some of the various models identified can be distinguished by the coordination of the basal O atoms in each Ag_3O_4 pyramid. In the Ag_2O like models every basal O is threefold coordinated to Ag atoms in adjacent pyramids, with the result being a single trilayer. In the other structures shown in Fig. 3 the basal oxygen atoms are either twofold coordinated—from which the asymmetric and symmetric $\text{Ag}_{1.2}\text{O}$ overlayers are produced [Figs. 3(e) and 3(f)]—or are a mixture of twofold and onefold coordinated yielding, for example, the isolated AgO clusters shown in Fig. 3(g).⁶⁵ Some of the different ways of arranging the Ag_3O_4 building blocks are shown schemati-

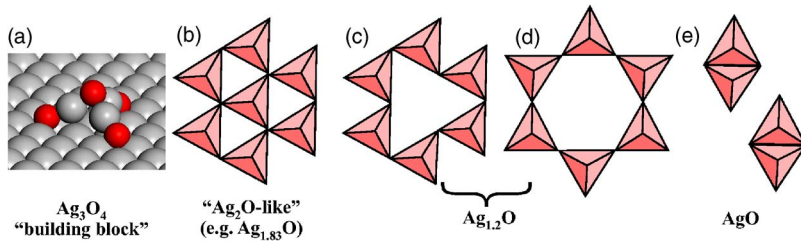


FIG. 4. Schematic representation of some of the ways the pyramidal Ag₃O₄ unit shown in (a) can be arranged to yield some of the low energy structures identified. Each triangular based pyramid in (b)–(e) represents one of the Ag₃O₄ units shown in (a). For clarity the Ag(111) substrate and any additional oxygen atoms which may be present are not shown. In (a) the oxygen atoms are the darker (red) spheres.

cally in Fig. 4. In addition to the Ag₃O₄ motif, we find a second distinct type of building block which yields stable structures that appear to be consistent with recent STM experiments.⁷⁴ Indeed, our ongoing calculations indicate that it is more informative and appropriate to discuss the structure of oxide-like overlayers on Ag(111) in terms of small Ag_xO_y units, rather than making a connection to the lattice match between the (111) planes of Ag₂O and Ag.

C. Extension to finite temperatures and pressures

With several (4×4) structures identified, we now extend the discussion to look at how the relative stability of each phase varies with temperature and pressure. In Fig. 5 the variation of the surface free adsorption energy, γ , with oxygen chemical potential, $\Delta\mu_{\text{O}}$, is plotted for many of the different phases examined. Through Eq. (2), $\Delta\mu_{\text{O}}$ can readily be equated to temperature and pressure and this is illustrated with two additional axes in Fig. 5, showing the resulting temperature scales for two given pressures (1 and 10⁻¹² atm). Only the three stable phases and the Ag_{1.83}O phase are highlighted, while the other less stable (4×4) models are shaded in grey. From Fig. 5 one can see that outside the calculated stability region of bulk Ag₂O, $\Delta\mu_{\text{O}} \leq -0.3$ eV,⁶⁶ 2–3 oxide phases enjoy the lowest energy at some values of $\Delta\mu_{\text{O}}$. First, an Ag_{1.33}O+2O adlayer [Fig. 3(d)] is stable down to $\Delta\mu_{\text{O}} \sim -0.42$ eV (~ 450 K at 1 atm), then, for only some tens of meV, an Ag_{1.33}O adlayer [Fig. 3(c)], and then an Ag_{1.2}O adlayer [the “asymmetric” Ag_{1.2}O structure shown in Fig. 3(e)]. At $\Delta\mu_{\text{O}} \leq -0.57$ eV (~ 550 K at 1 atm) the clean Ag(111) surface is predicted to be stable. Again we note that the stability of several of the subnanoscale oxide overlayers identified extends well beyond the stability of bulk Ag₂O.

The main conclusion we draw from Fig. 5 is that at no values of $\Delta\mu_{\text{O}}$, and hence at no particular temperature and pressure, is the Ag_{1.83}O model the most stable phase. Although this conclusion is clear, it is less clear what the alternative phase is at any value of $\Delta\mu_{\text{O}}$, since outside the stability region of bulk Ag₂O the three lowest energy phases—the Ag_{1.33}O [Fig. 3(c)], the Ag_{1.33}O+2O [Fig. 3(d)], and the asymmetric Ag_{1.2}O [Fig. 3(e)] structures—are always within only 2–3 meV/Å² of each other,⁶⁷ which is within the margin of error of our DFT calculations. Indeed such similar energies for several low energy structures could readily lead to a coexistence of oxide structures at the high temperatures and pressures characteristic of epoxidation catalysis.

D. Compatibility of the model(s) with existing XPS spectra

Bearing in mind that it is not possible to know whether we can distinguish between the (4×4) models based on energy, we turn to the calculation of some experimental observables. Aside from STM, XPS measurements of O 1s and Ag 3d surface core-level shifts (SCLSs) have been interpreted as lending support to a model consisting of an Ag₂O like overlayer.⁶⁸ Since the binding energy of core electrons depends on the local environment, typically the local coordination of the atom, core level spectroscopy is often a sensitive structural probe. This is particularly true in the area of oxygen adsorption and oxide formation where XPS and XPS in conjunction with DFT have been used to successfully characterize the structure of several “surface-oxide” covered transition metal surfaces.^{3–5} Here the O 1s and Ag 3d SCLS have been calculated for all low energy structures shown in Fig. 3. These calculations, which include both “initial” and “final” state effects, were carried out with O and Ag pseudopotentials that contain O 1s and Ag 3d core holes, respectively.^{69,70} The results of these calculations for the Ag_{1.83}O overlayer, the two Ag_{1.2}O overlayers, and the AgO overlayer are shown in Fig. 6. On the left hand side the O 1s shifts are plotted relative to O in bulk Ag₂O, while on the right hand side the Ag 3d shifts relative to Ag in bulk Ag are

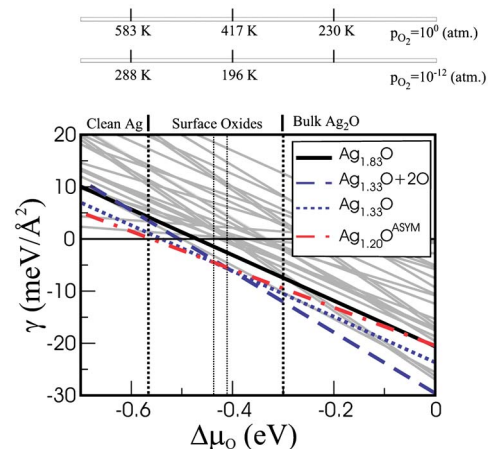


FIG. 5. Surface free adsorption energy, γ , as a function of oxygen chemical potential, $\Delta\mu_{\text{O}}$, for a selection of the $p(4 \times 4)$ -O/Ag(111) overlayer structures computed within this study. Only the three stable phases and the Ag_{1.83}O model are highlighted, while the other less stable (4×4) models are shaded in grey. Temperature scales at two pressures (1 and 10⁻¹² atm) are also given.

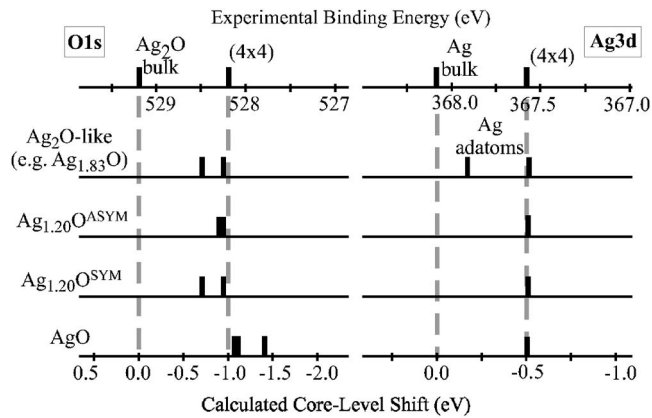


FIG. 6. Comparison between experimental O $1s$ (left) and Ag $3d$ (right) core level shifts for the (4×4) overlayer, with the data computed for several (4×4) models considered here. The theoretical O $1s$ energy zero corresponds to O in Ag_2O , and the theoretical Ag $3d$ energy zero corresponds to Ag in bulk. For comparison with experiment these O and Ag theoretical energy zeros have been aligned to the O $1s$ energy in bulk Ag_2O and the Ag $3d$ energy in bulk Ag. A vertical stick is shown for each different type of O or Ag in a given overlayer. Sticks often overlap and/or appear thicker when two different types of O in an overlayer are shifted by almost identical amounts. The experimental data have been taken from Refs. 24, 25, 45, and 71.

given. To facilitate comparison with the experimental data (shown schematically in the upper part of Fig. 6) the theoretical O and Ag reference states in Fig. 6 have been aligned to their respective experimental values.

This extensive set of calculations does not, however, allow us to draw firm conclusions on which, if any, of the models under consideration is the “correct” one. This is because all models, except possibly for the AgO overlayer model, are largely consistent with the existing experimental data. Let’s first consider the Ag $3d$ core level, which in the experiment appears at $\sim 0.5 \text{ eV}$ ³⁸ lower binding energy (closer to E_F) than in bulk silver (368.1–368.0 eV).^{38,71} We find that the calculated Ag $3d$ SCLS for *all* the different types of Ag overlayer atoms in the four overlayers shown are extremely close in energy. Each Ag atom in the four overlayers (with one exception) is shifted by $-0.50 \pm 0.02 \text{ eV}$, which is in agreement with experiment. The exception is the Ag adatom(s) in the $\text{Ag}_{1.83}\text{O}$ model [the silvers circled in Figs. 1(c) and 3(a)], which appear at -0.2 eV . However, since there are only two of these Ag adatoms per (4×4) cell (1/8 ML), it is plausible that they would not be resolved in the experiment from the bulk Ag peak, implying that the absence of a feature at -0.2 eV in the experimental spectra cannot be taken as evidence against the $\text{Ag}_{1.83}\text{O}$ model.

Turning now to the O $1s$ level, which in experiment shows up as a single peak at 582.2 eV,^{24,37,38} at 1 eV lower there is lower binding energy than O in Ag_2O (529.2 eV).⁴⁵ In the $\text{Ag}_{1.83}\text{O}$ overlayer two O $1s$ levels are predicted, one for the low lying (-0.75 eV) and one for the high lying (-0.90 eV) sets of oxygen in the trilayer. The calculated shifts for the two types of O in the $\text{Ag}_{1.83}\text{O}$ overlayer are in reasonable agreement with experiment and although two peaks are predicted, whereas only one is observed, the reso-

lution in the reported spectra is not sufficiently high to exclude the possibility that two peaks are indeed contained within the single one observed. We must therefore refrain from definitively ruling out the $\text{Ag}_{1.83}\text{O}$ model based on these results. The same conclusion must be drawn from the calculated O $1s$ SCLS for the two $\text{Ag}_{1.2}\text{O}$ overlayers shown in Fig. 6. Neither is sufficiently different from experiment to be definitively ruled out as possible models for the (4×4) overlayer. However, oxygen adatoms in, for example, the $\text{Ag}_{1.33}\text{O} + 2\text{O}$ model (corresponding to 1/8 ML of O adatoms) are predicted to show up at approximately -1.7 eV . Thus large concentrations of adsorbed O atoms should be detectable and can thus be excluded. To close this section, the main conclusion we draw is that the existing XPS data can neither be used to support nor to undermine the $\text{Ag}_{1.83}\text{O}$ model.

IV. CONCLUDING REMARKS

The development of a model for the $p(4 \times 4)$ -O/Ag(111) structure from what was little more than an interesting observation in the 1970s to an accepted reality in recent years has been traced. Essentially five ingredients went into the $\text{Ag}_{1.83}\text{O}$ model that emerged: (i) the almost zero epitaxial mismatch between the (111) planes of Ag_2O and Ag; (ii) an O coverage of $\sim 0.4 \text{ ML}$; (iii) the measured O $1s$ and Ag $3d$ levels; (iv) the STM experiments; and (v) the DFT energetics. From our calculations summarized here, it should now be clear that each element, which originally seemed to favor the $\text{Ag}_{1.83}\text{O}$ model, may also be used against it or can at least be described as ambiguous with regard to alternatives. Specifically we find that: (i) there is no *a priori* need to have an oxide-like overlayer that resembles the (111) trilayer of Ag_2O and that a good lattice match between bulk Ag_2O and Ag(111) may be irrelevant; (ii) several stable structures within the appropriate O coverage range are possible; (iii) several structures in addition to the $\text{Ag}_{1.83}\text{O}$ model are consistent with existing O $1s$ and Ag $3d$ core level spectroscopy; (iv) the Ag adatoms believed to be imaged in STM are unstable with respect to bulk Ag atoms; and (v) several structures equally stable to or more stable than the $\text{Ag}_{1.83}\text{O}$ model have been identified.

Our main conclusion is that the existing $\text{Ag}_{1.83}\text{O}$ overlayer model is either incorrect or is a metastable structure. Given that several other structures equally stable to or more stable than the $\text{Ag}_{1.83}\text{O}$ model have now been identified it is unclear why a single almost defect free (4×4) overlayer is apparently observed under UHV conditions. Perhaps entropy (vibrational and/or configurational entropy) stabilizes one overlayer more than the others, or perhaps the observed structure is determined by the nucleation of the very first O-Ag element and from this nucleation center onwards the formation of the adlayer is then determined by kinetics. Or perhaps there remains one uniquely stable but as yet unidentified (4×4) structure. It remains to be seen. A clear implication of the present results, however, is that this system is likely to be much more complex than anticipated and, in particular, at the high temperatures and high pressures characteristic of indus-

trial epoxidation catalysis the Ag surface is likely to comprise a complex coexistence of related subnanoscale oxide overlayers, or, in other words, should oxide-like overlayers play a role in epoxidation catalysis on Ag, it is unlikely that just one such overlayer will be present. Given the doubts we have raised against the $\text{Ag}_{1.83}\text{O}$ overlayer model we reinitiate the calls for further experiments to be performed. In particular the application of diffraction techniques, additional STM experiments, and/or spectroscopic techniques (vibrational spectroscopy, for example) may finally lead to a truly convincing structural model; a model that we do believe when we see it.

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Monkhorst–Pack k -point mesh. Unless otherwise stated, energies reported refer to adsorption on three layer Ag(111) slabs. Several test calculations with seven layer thick Ag (111) slabs indicate that none of the conclusions reached are altered by our use of such thin Ag slabs (see Tables I and II). During structure optimizations the top layer of Ag atoms as well as the oxide overlayer atoms were allowed to fully relax while the bottom two (or six) layers were fixed.

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⁶³These calculations were done in unit cells similar to the (4×4) cell used for the adsorption calculations. The structure of a free-standing trilayer film was optimized as a function of unit cell area by varying together both unit cell vectors from -20% to $+20\%$ of their value in the (4×4) adsorption cell.

⁶⁴The O–Ag distances within the triangular building blocks of each overlayer are all 2.07 ± 0.05 Å. The Ag–Ag distances differ by as much as 0.6 Å, specifically the Ag–Ag distances representing the base of each pyramid are 3.30 ± 0.30 Å. This reflects, however, large variations in Ag–Ag distances within individual overlayers, in particular within the Ag₂O like models, rather than an inherent difference between the various overlayer structures themselves.

⁶⁵We notice that the coordination of the basal oxygen atoms to Ag atoms in the overlayer also affects the registry of the oxide-like overlayer with the Ag(111) substrate. Stable structures with onefold coordinated O atoms invariably have their Ag–O bonds of these “undercoordinated” basal O atoms directed toward atop sites of the underlying substrate. Structures with twofold coordinated O atoms tend to have these oxygens located at bridge sites on the underlying Ag(111) substrate. For the structures in which all oxygen atoms are threefold coordinated, i.e., the Ag₂O like overlayers, a strong preference for the location of the basal oxygen atoms has not been observed.

⁶⁶With the current computational setup we calculate the heat of formation of bulk Ag₂O ($T=0$ K, $P=0$) to be 0.30 eV. The experimental value for the standard enthalpy of formation of Ag₂O is 0.32 eV [*Handbook of Chemistry and Physics*, 76th ed., edited by D. R. Lide (CRC Press, Boca Raton, FL, 1995)].

⁶⁷We add a (somewhat obvious) word of caution concerning the interpretation of Fig. 5 and indeed plots like this in general. Only phases which we have calculated will appear on it. Thus there may always exist a lower energy structure which we have not yet identified. Of course, however, nature does not always find the lowest energy structures either, diamonds and nanotubes are metastable yet long lived forms of carbon!

⁶⁸Some valence band photoemission experiments have also been reported for the (4×4) overlayer (Refs. 18 and 30). However, they do not agree on the location of the O adsorbate induced resonances. Moreover, when we calculate the total and partial densities of states for the various low energy (4×4) structures under consideration here we find them to be essentially indistinguishable.

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⁷⁰Following the procedure introduced in Ref. 69, the core level shifts for each atom were computed by comparing the total energy of the ground-state to calculations with an “impurity” atom. The impurity atom was an atom with a core hole in its pseudopotential. For the Ag pseudopotential, where a valuable comparison to experiment can be made, we calculate a difference of 0.5 eV between the Ag $3d$ binding energies in bulk Ag and bulk Ag₂O in agreement with experiment. A detailed discussion on this approach for calculating core level shifts and its successful application to the adsorption of CO on Rh(111) can be found in: M. Birgersson, C.-O. Almbladh, M. Borg, and J. N. Andersen, *Phys. Rev. B* **67**, 045402 (2003).

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