Structure of Ag(111)-p(4 × 4)-O: No Silver Oxide

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(Received 12 January 2006; published 10 April 2006)

The structure of the oxygen-induced p(4 × 4) reconstruction of Ag(111) is determined by a combination of scanning tunneling microscopy, surface x-ray diffraction, core level spectroscopy, and density functional theory. We demonstrate that all previous models of this surface structure are incorrect and propose a new model which is able to explain all our experimental findings but has no resemblance to bulk silver oxide. We also shed some light on the limitations of current density functional theories and the potential role of van der Waals interactions in the stabilization of oxygen-induced surface reconstructions of noble metals.

Catalysts are not only used for the well-known task of exhaust-gas purification but also employed for synthesis of more than half of all chemical products. For an understanding of the catalytic reaction, it is necessary to know the phases present on the surface and their structure. In recent years, it has been found that ultrathin oxides are often superior to pure-metal catalysts and that some oxidation reactions previously ascribed to catalysis on the pure metals are due to oxide phases on surfaces [1,2]. Whereas these studies were concerning platinum-group metals and their oxides, which act as efficient catalysts for CO oxidation, much less is known for other catalysts and reactions.

An important example is Ag catalysts employed *inter alia* for selective oxidation of ethylene to ethylene oxide (1,2-epoxyethane) as a first step in synthesizing many organic compounds. The first well-ordered structure encountered during oxidation of Ag(111) [3–5], the p(4 × 4) reconstruction, is usually identified with the phase known as "nucleophilic oxygen" or "oxidelike" and made responsible for the reaction [6–8]. More than 30 years ago, its structure has been proposed to be a (111) layer of bulk silver oxide (Ag_2O) [4]. Later on, a slightly modified structure [Fig. 1(a)] was proposed [9], which has hitherto been considered a prototype of a catalytically active surface oxide. However, recent *ab initio* calculations showed that this structure is only metastable [10]. A variety of related structures has been put forward as potential candidates for stable structures at temperature and oxygen pressure values typical for epoxidation catalysis [10,11], among them the structural model of Ref. [9] now with two Ag atoms removed [crosses in Fig. 1(a)], resulting in an Ag_9O_6 overlayer. As we will show below, none of these structures is compatible with our surface x-ray diffraction (SXRD) data, and in view of these results the established concept of the p(4 × 4) phase being related to bulk Ag_2O has to be abandoned. Thus, the structure of this phase,

known since the early 1970s, is one of the great mysteries in surface crystallography [10]. We will present here a new model, which is based on a combined SXRD, scanning tunneling microscopy (STM), density functional theory (DFT), and high-resolution core level spectroscopy (HRCLS) study.

For the current work, clean Ag(111) single crystal surfaces have been prepared by the standard methods of surface physics (sputtering, annealing) and oxidized by either 200 mbar O_2 for 30 min at 490 K (with subsequent cooling to 300 K under O_2 atmosphere and maintaining 5 mbar O_2 pressure during the experiment) or NO_2 (5 × 10^{-6} mbar, 15 min at ≈480 K). In agreement with Ref. [12], our SXRD data showed that the preparations with NO_2 and O_2 produce identical structures; the SXRD data shown were obtained with O_2. We find that all preparation recipes result in a small fraction of the unreconstructed surface. This was taken into account when evaluating the data of SXRD. The SXRD data were measured at the MPI-MF beam line at ANKA [13] with a photon energy of 10.5 keV at grazing incidence (near the
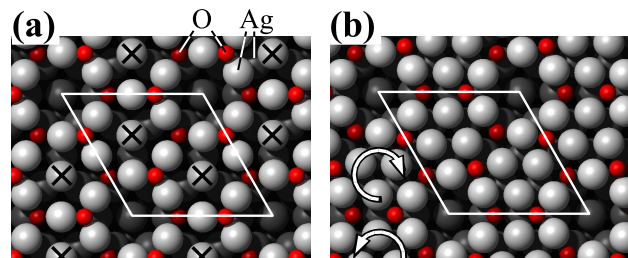

FIG. 1 (color online). Structural models of the Ag(111)-p(4 × 4)-O structure (a) as proposed in Ref. [9] and (b) the current work. The Ag_9O_6 structure (referred to as "$Ag_{1.33}O$" in Ref. [10]) results from model (a) by removing the Ag adatoms marked by crosses.

critical angle) using an *in situ* high-pressure SXRD chamber for the O_2 preparation and an ultrahigh-vacuum (UHV) SXRD system equipped with LEED for the NO_2 preparation. HRCLS was performed on samples oxidized by NO_2 at the beam line i311 of MAX-lab in Lund, Sweden [14]. STM images were obtained in Vienna with a room-temperature and a low-temperature STM system, both equipped with a separate UHV chamber for sample preparation. For these experiments, we have synthesized NO_2 from NO and O_2 with excess oxygen at $p > 1$ bar. For the DFT calculations, we have used the Vienna *ab initio* simulation package (VASP) [15] employing the projector augmented wave method [16,17] and the generalized gradient approximation (GGA) [18].

After oxidation, STM shows large terraces covered by the $p(4 \times 4)$ structure, without any domain boundaries over hundreds of nanometers. Most STM images [Fig. 2(a)] show the honeycomb structure described in Ref. [9]. At 80 K and similar tunneling conditions, we have sometimes observed protrusions at the positions between the minima in the honeycomb images [Fig. 2(b)]. The only feature present in all images is the "corner hole" appearing up to approximately 2 Å deep. These STM images do not show the features expected for most of the stable models suggested in a recent DFT study [10], such as the Ag_9O_6 model.
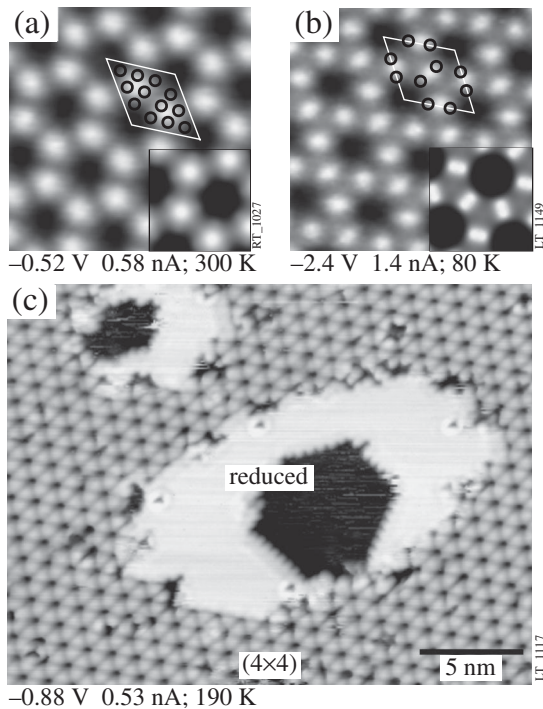

FIG. 2.   STM images of the O-induced $p(4 \times 4)$ structure on Ag(111). The insets show simulated images [25] at $V_{sample} = -1$ V for (a) the time-averaged atomic positions of an MD run and (b) the average density of the two equivalent orientations of the structure at 0 K. Small black circles mark the average positions of the Ag and O atoms, respectively. Frame (c) has been taken during reduction of the structure by CO.

To determine the number of Ag atoms in the unit cell, we have chemically reduced the structure by CO and determined the amount of remaining metallic Ag (see Ref. [19]). At a temperature of 190 K, at which the mobility of the Ag atoms is sufficiently low to avoid diffusion to or from nearby step edges and reduction is still possible, we observe holes in the reduced patches, which do not show any superstructure and are thus pure Ag(111) [Fig. 2(c)]. We find that holes amount to approximately 25% of the area after reduction. Since the reduced Ag(111) surface contains 16 Ag atoms in the area of the $p(4 \times 4)$ cell, the $p(4 \times 4)$ phase contains 12 ± 1 Ag atoms in its unit cell.

Taking into account the number of Ag atoms, the symmetry and appearance of the STM images, and the fact that the superstructure reflections in both low-energy electron diffraction and SXRD indicate sixfold symmetry of the uppermost layer [in contrast to the threefold symmetry of the fcc(111) substrate], construction of a structure model is straightforward. The necessary free space at the corner hole can be achieved only by packing the 12 Ag atoms more closely together than in the Ag_2O-based structure models. The STM observation of two protrusions per cell [Fig. 2(a)] implies furthermore that we are dealing with two equivalent subunits. Thus we put two triangles of 6 Ag atoms each in fcc sites and in hcp sites of the substrate [Fig. 1(b)], leaving the substrate uncovered in the corner hole. The "furrows" between the Ag_6 triangles are obvious adsorption sites for oxygen, which is also confirmed by the DFT calculations; sites in the corner hole as well as adatom or subsurface sites in the centers of the triangles are energetically unfavorable. The O coverage in this model is 0.375, equal to that of the structure in Ref. [9] and in agreement with all previous photoemission and desorption studies obtaining values between 0.38 [20] and 0.41 [5,21].

Our DFT calculations for this structure indicate that the ground state of the surface structure does not exhibit *p*6*mm* symmetry as in the most simple model conceivable. The symmetry is broken by slightly rotating the Ag_6 triangles clockwise and anticlockwise with respect to the perfect hcp and fcc sites [rotation symbols in Fig. 1(b)], and the two oxygen atoms in the furrows are not in equivalent sites, with significantly different heights of 2.21 and 3.04 Å above the uppermost substrate layer. The energy gained by symmetry breaking is 0.2 eV (at 0 K). At finite temperature, *ab initio* molecular dynamics (MD) shows that the time spent by the O atoms near the upper position decreases, and hence their average height is reduced to 2.32 Å at 700 K. We also find that the structure is very soft. MD at 700 K shows extremely large vibrational amplitudes, especially of the O atoms (0.64 Å). Calculated STM images of the average high-temperature configuration show maxima at the positions of the Ag_6 islands, as observed in the RT images [Fig. 2(a)]. In agreement with the experimental images, these maxima do not appear distinctly triangular. Calculated images for the ground state structure show maxima at the position of the upper oxygen atom; taking flipping between the two symmetry-

equivalent positions into account, these maxima blend into one maximum for each pair of O atoms in a furrow, as observed in some low-temperature images [Fig. 2(b)]. However, the interaction of the tip with the "soft" structure may lead to repulsion or attraction of the O atoms; thus the STM images are compatible with, but do not prove, the symmetry breaking resulting from the DFT calculations.

We find that such a model agrees well with the SXRD data, whereas all the structure models suggested previously [10,11] can be ruled out. Comparing DFT-calculated coordinates without any further optimization, these models yield a χ^2 value approximately twice as high as ours, and attempting to fit the experimental data by these models does not lead to useful results. Since the two Ag_6 triangles (fcc stacked and hcp stacked) in our model are essentially equivalent, we have started by assuming $p3m1$ symmetry for the coordinates of the reconstructed layer and equal probability of both rotational configurations. In the best fit, the rotation of the triangles vanishes, but large vibrational amplitudes are found instead. The oxygen atoms in the furrows sit nearly at the same height. This nicely fits the DFT result of a small energetic barrier between the two rotational configurations. Therefore, in the final fit $p6mm$ symmetry was assumed for the uppermost two layers, reducing the number of independent positional fitting parameters to 13 (thereof 5 in plane). The experimental and calculated structure factors are shown in Fig. 3, and the quality of the fit ($\chi^2 = 2.6$ for the in-plane data, $\chi^2 = 3.7$ including the rods) is reasonable.

By comparing the mean atomic positions of the two DFT rotational configurations for $T = 0$ K with the best-fit positions from SXRD, we find good agreement between experiment and DFT (in-plane positions of Ag and O agree better than 0.06 and 0.2 Å, respectively, Ag z positions better than 0.18 Å). Bearing in mind that we are dealing with a rather soft structure and the fact that the SXRD data were obtained at 300 K whereas the DFT results are at 0 K, this agreement strongly supports our model. We also note that the Ag atoms in the tips of the Ag_6 triangles show in-plane vibrational amplitudes twice as large as the Ag atoms in the cores of the triangles, in agreement with the notion that the Ag_6 triangles easily flip between clockwise and counterclockwise rotation. Since oxygen is a weak scatterer for x rays, the O coordinates found by SXRD have comparably low accuracy and the observed differences between DFT and the x-ray experiment are within the error bars.

Further confirmation of our model comes from the comparison of experimental and calculated core levels. According to the DFT calculations, the O $1s$ peak of the $p(4 \times 4)$ structure has a binding energy (BE) shift of -0.02 eV with respect to the (2×1) "added-row" structure of O on Ag(110), the only O-on-Ag phase with a well-known structure. This agrees well with the difference of experimental O $1s$ BEs of -0.1 eV determined by Campbell [5,22]. Since the calculated splitting of the O $1s$ peak due to the different heights of the O atoms is only
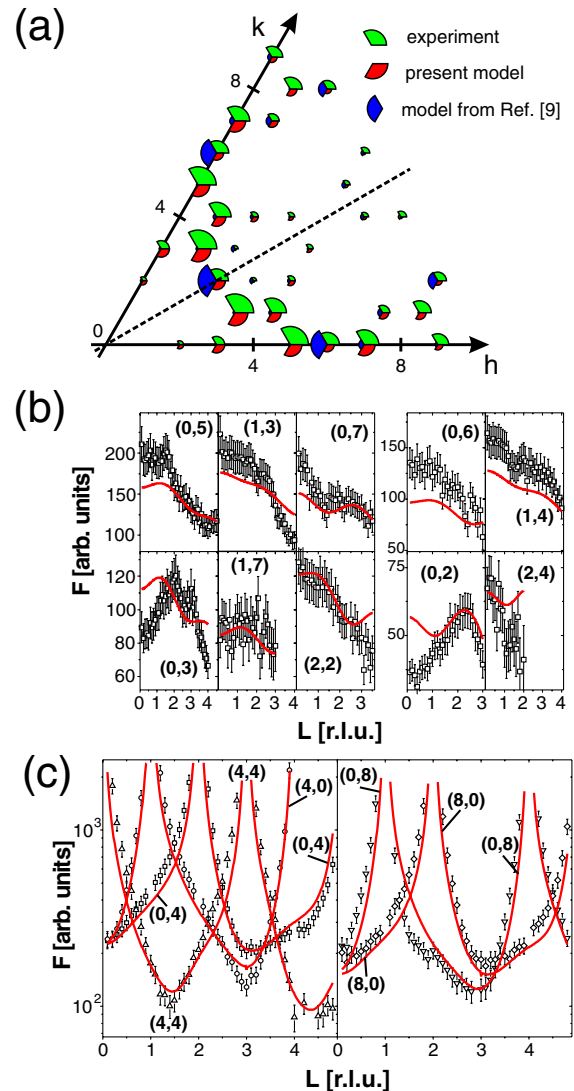

FIG. 3 (color online). (a) In-plane structure factors, (b) superstructure rods, and (c) crystal truncation rods of Ag(111)-$p(4 \times 4)$-O. The error bars in (b) and (c) represent the combined statistical and systematical error. L is given in reciprocal lattice units of an Ag(111) cell containing three atomic layers.

0.12 eV, it cannot be detected experimentally and our spectra show only a single nonbroadened peak. For Ag $3d_{5/2}$, deconvolution of the experimental spectra shows three peaks with lower BE than the bulk; the strongest ones at approximately -0.60 and -0.23 eV (Fig. 4; exact values and the strength of the -0.23 eV component depend on the details of the fitting procedure). The DFT-calculated shifts (including final state effects) are -0.53 and -0.46 eV for Ag in the Ag_6 triangles (corners and sides, respectively; not separated in experiment) and -0.26 eV (Ag atoms at the bottom of the furrow, below lower O), all in reasonable agreement with the strong peaks observed in experiment. Since we have also observed weak O $1s$ peaks typical for impurities, we attribute the small Ag component at ≈ -0.9 eV to impurities, probably on residual unreconstructed patches of the surface.
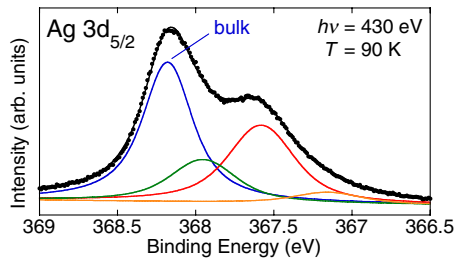
FIG. 4 (color online). Photoemission spectrum of the Ag $3d_{5/2}$ level. The decomposition into different components is explained in the text.

In spite of the clear-cut experimental evidence for our model of the $p(4 \times 4)$ phase, it does not have the lowest energy of all models in well-converged DFT calculations (6 layers, 6×6 k points, 400 eV cutoff). The ground state energy [per $p(4 \times 4)$ cell] of our structure is 0.24 eV higher than that of the Ag_9O_6 model [cf. Fig. 1(a)], the lowest-energy structure with the same O coverage found by DFT [10]. Neither inclusion of zero point vibrations nor vibrational entropy effects in the harmonic approximation or anharmonic effects (evaluated at 700 K using thermodynamic integration) makes our model more favorable than Ag_9O_6. The rather small energy difference, equivalent to 0.015 eV per Ag surface unit cell, is a typical error of today's DFT functionals. It is most likely related to neglecting the van der Waals–like interactions between the $4d$ shells of Ag. Note that the comparison of the calculated Ag fcc atomization energy with the experimental value shows that GGA functionals [18] underestimate the Ag-Ag nearest-neighbor bond strength in bulk Ag by 0.07 eV, which matches the neglected van der Waals interaction [23]. Using the usual asymptotic behavior of van der Waals forces ($1/r^6$) we can extrapolate that DFT underestimates the stability of our $Ag_{12}O_6$ model by 0.8 eV compared to the Ag_9O_6 model [24].

Upon oxygen exposure the Ag atoms form compact metallic Ag_6 islands, and therefore the structure is very different from Ag_2O-based models which exhibit an Ag-Ag distance expanded by $\approx 20\%$ with respect to metallic Ag. With its metallic bond lengths, the $p(4 \times 4)$ structure is similar to the O-induced reconstructions of the other low-index Ag surfaces [missing-row and added-row structures on Ag(100) and Ag(110), respectively]. Also in these structures, the Ag atoms are in lattice sites of metallic Ag. Such a restructuring transforms the surface into a hybrid state between metal and oxide, thereby creating catalytically active sites neither present on the clean metal surface nor on a fully oxidized surface.

In summary, we have presented an extensive experimental and theoretical study of the oxygen-induced $p(4 \times 4)$ reconstruction of the Ag(111) surface, which has been discussed in the literature for many decades. We unambiguously demonstrate that all hitherto proposed models of this structure are incorrect and propose a new model which is in very good agreement with all experimental findings.

The present work also highlights the limits of today's density functionals. Since van der Waals–like interactions between closed d shells play an important role at the end of the 3d, 4d, and 5d series, binding in metal-like clusters is underestimated, resulting in an overestimation of the relative stability of structures with lower coordination of the metal atoms.

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