Two-Dimensional Oxide on Pd(111)

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(Received 21 February 2002; published 3 June 2002)

The oxidation of Pd(111) leads to an incommensurate surface oxide, which was studied by the use of scanning tunneling microscopy, surface x-ray diffraction, high resolution core level spectroscopy, and density functional calculations. A combination of these methods reveals a two-dimensional structure having no resemblance to bulk oxides of Pd. Our study also demonstrates how the atomic arrangement of a nontrivial incommensurate surface can be solved by molecular dynamics in a case where experimental techniques alone give no solution.

DOI: 10.1103/PhysRevLett.88.246103 PACS numbers: 68.47.Gh, 68.37.Ef, 68.43.Bc, 68.43.Fg

The formation of oxides on metal surfaces has recently received much attention. Apart from the fundamental importance of oxidation processes, the interest is driven by the observation that oxides can play an important role in catalysis, even in cases where the catalytic properties were previously attributed to the metal surface [1,2]. The formation of an oxide on a metal changes not only the surface properties in a profound way but also serves as a source or sink of oxygen in oxidation/reduction reactions [1]. Since the oxides of the more noble metals form only at rather high oxygen partial pressures and elevated temperatures, they are often neglected when surfaces are studied in ultrahigh vacuum, but they are of importance under realistic catalytic conditions. Previously, it was assumed that oxygen on metal surfaces forms either overlayers, sometimes causing simple rearrangements of the metal atoms such as vacancies [3] or additional metal atoms [4] at lattice sites, or causes the formation of oxides, which were believed to be identical or closely related to the corresponding bulk oxides [5]. We will show in this Letter that this simple view is incorrect and that oxidation of a metal surface can also lead to a two-dimensional oxide which is neither related to the metal structure nor to any bulk oxide.

One problem in this context is that many oxide structures and, in particular, surface oxides exhibit an atomic arrangement which is difficult to resolve with traditional experimental techniques [8,9]. The reasons for these difficulties may vary, but part of the problem lies in large unit cells or incommensurate structures, strong buckling of the surface layer, and difficulties in detecting the exact location and the coverage of the oxygen atoms. Using traditional diffraction techniques such as low energy electron diffraction (LEED) and surface x-ray diffraction (SXRD), difficulties with extensive trial and error fit procedures and low cross section for scattering from the oxygen atoms are certain to arise in such complicated structures. Using scanning probe techniques such as scanning tunneling microscopy (STM), the electronic structure of the oxidic surface is probed rather than the atomic arrangement, leading to difficulties in the interpretation of the images obtained. In this report, we present a solution to this problem: extensive finite temperature molecular dynamics based on density functional theory (DFT).

The exposure of Pd(111) to oxygen above room temperature results in three ordered surface structures [10–14]: a $p(2 \times 2)$ overlayer with a coverage of 0.25 ML [monolayers; 1 ML equals the number of Pd atoms in a Pd(111) plane], at higher coverage a metastable structure [13] not discussed here, and a complex structure, which will be the topic of this Letter. We will confirm previous studies of this complex structure pointing towards the formation of a surface oxide and therefore refer to it as "surface oxide." It has been suggested that the structure could be due to (001) planes of PdO stacked on the (111) planes of the Pd surface, exhibiting a $(\sqrt{5} \times \sqrt{5})$ ordered vacancy structure [13], a conjecture not supported by our results.

In our experimental study, we have used three Pd(111) single crystals, cleaned by cycles of Ar^+ sputtering, annealing and oxygen treatments keeping the sample at 600 °C in an oxygen pressure of 2×10^{-8} mbar followed by flashes to 1100 °C. As judged by Auger electron spectroscopy (AES) and/or photoelectron spectroscopy, the surface was free from contaminants such as C, O, and S. The surface oxide was formed by exposing the Pd(111) surface to molecular oxygen at a temperature of 300 °C and an oxygen pressure of 5×10^{-6} mbar for 600 s. In the work of Zheng and Altman [13], nitrogen dioxide, (NO_2), was used, but, despite the differences in preparation, a comparison of the LEED patterns and STM images obtained in the present study with those of Ref. [13] shows that both preparations yield an identical ordered structure. All crystals used gave identical diffraction patterns (LEED or SXRD).

The STM measurements were done in Vienna in a UHV chamber with a base pressure below 5×10^{-11} mbar. Images were obtained in constant current mode with the sample negative. The high resolution core level spectroscopy (HRCLS) measurements were conducted at the beam line I311 [15] at MAXII in Lund, Sweden. The photon energies for the measurements of the Pd $3d$ and O $1s$ core levels were 650 and 900 eV, respectively. Use of these rather high energies reduces diffraction effects and therefore results in more accurate relative coverages, at the cost of reduced resolution. The HRCL spectra were recorded at liquid nitrogen temperature at normal emission. The SXRD measurements were performed at the BM32 beam line of the ESRF with a photon energy of 18 keV.

The calculations were performed with the Vienna *Ab initio* Simulation Package (VASP) [16], using the recently implemented projector augmented-wave (PAW) method, in which the exact valence-wave functions instead of pseudowave functions, as in conventional pseudopotential calculations, are used [17]. The PAW potentials applied in the present study were already described and tested in Ref. [6]. All calculations presented here were performed with the generalized gradient approximations of Perdew and Wang (PW91) [18].

Figure 1a shows an STM image of the surface oxide. The white square in Fig. 1a can be identified as the primitive unit cell (see Ref. [13] and below). By utilizing the presence of the Pd(111)-(1×1) surface in the lower left corner of the image as a ruler, we can determine that one diagonal of the square is equal to the $[2\bar{1}\bar{1}]$ substrate vector and, hence, commensurate, while the other diagonal is incommensurate, in agreement with Ref. [13]. Because of the side lengths of $\sqrt{6}$, for simplicity we will dub it the $(\sqrt{6} \times \sqrt{6})$ structure, in spite of the fact that it is a square structure on a substrate lattice with threefold symmetry. If the surface is annealed at 350 °C, some oxygen desorbs from the surface, and the surface oxide disappears completely, as observed in LEED, HRCLS, and in the STM image shown in Fig. 1b. At this stage, the surface is covered by a (2×2) oxygen overlayer. Additionally, hexagonal 1 ML deep holes are visible in the Pd(111) surface [19]. It is very likely that the defective Pd layer has formed by the Pd atoms of the decomposed surface oxide, which allows us to estimate the number of Pd atoms in the $(\sqrt{6} \times \sqrt{6})$ surface oxide cell by determining the region of the 1 ML deep holes. The $(\sqrt{6} \times \sqrt{6})$ cell covers an area of 6.92 Pd(111) unit cells. Since we find that 31% of the surface in Fig. 1b exhibits holes (corresponding to a Pd coverage of 0.69 ML), we estimate that the number of Pd atoms in the $(\sqrt{6} \times \sqrt{6})$ surface oxide cell is 0.69×6.92 or approximately 5. This approach does, however, not give any information on the oxygen coverage. Instead, we may access the O coverage by HRCLS. Using the known oxygen coverage of 0.25 ML in the $p(2 \times 2)$ structure, we find an oxygen coverage of 0.67 ML, or close to five O atoms per adsorbate unit cell. However, despite the knowledge that we should place approximately five Pd and five O atoms within the $(\sqrt{6} \times \sqrt{6})$ adsorbate unit cell, their exact location can not be deduced experimentally in any straightforward way.

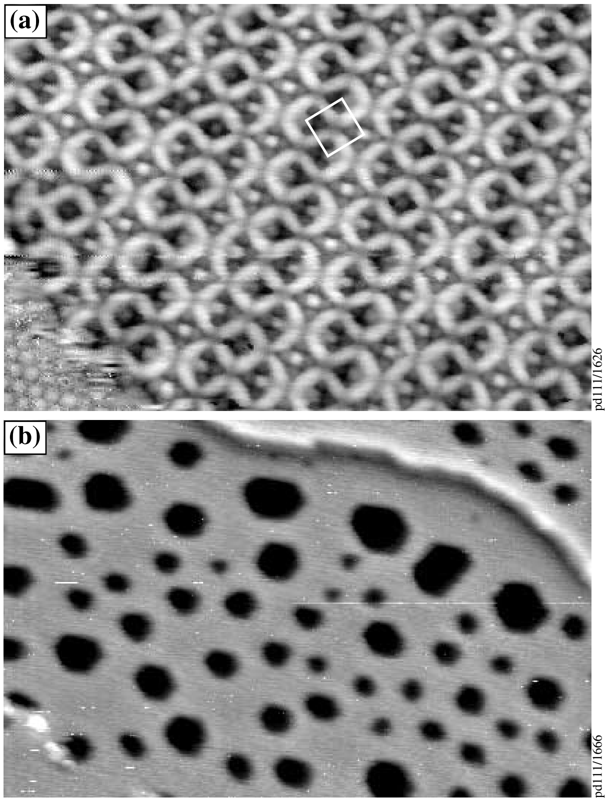

FIG. 1. (a) STM image (10 nm wide, -0.5 mV, 3.5 nA) of the surface oxide. Note the (1×1) periodicity of the Pd(111) surface in the lower left corner. (b) STM image (50 nm wide, -1 V, 0.7 nA) after the surface oxide has been reduced by annealing to 350 °C.

In order to gain information on the precise atomic structure, an extensive search of the configuration space was performed by first-principles simulated annealing molecular dynamics. In a first step, a single $(\sqrt{6} \times \sqrt{6})$ unit cell was simulated on a two layer thick frozen Pd(111) substrate as shown in Fig. 2a. In the direction of one of the cell diagonals (marked as "$2\sqrt{3}$"), the substrate is commensurate, but in the second one the substrate had to be compressed by a factor $8/6.92$ to reach commensurability. On the compressed substrate, the global energy minima of Pd_5O_4, Pd_5O_5, and Pd_5O_6 adsorbate layers were sought by first melting the adsorbate layers at 3000 K, then cooling them in 20 ps (20 000 time steps) to 1000 K, and finally quenching each annealed structure into the nearest local energy minimum. Of the three simulated compositions, only the final Pd_5O_4 structure had a larger oxygen adsorption energy than bulk PdO or a hypothetical $p(2 \times 1)$ oxygen overlayer with 0.5 ML coverage. This is a prerequisite for the formation of the surface oxide, however, since otherwise the $p(2 \times 1)$ oxygen overlayer would form at higher oxygen coverage.

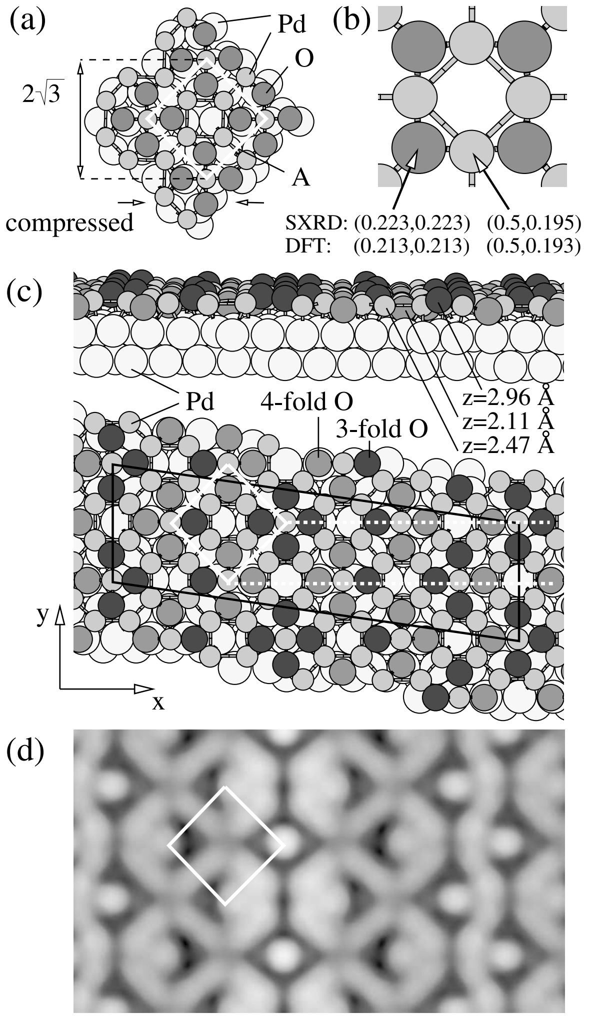

FIG. 2. (a) Final structure of a simulated annealing run for Pd_5O_4 on a compressed Pd(111) substrate. (b) Experimental (SXRD) and average theoretical (DFT) positions of atoms given in multiples of the lattice vectors of the adlayer (unit cell is rotated by 45° compared to the other panels). The experimental error was found to be ±0.08 Å and ±0.01 Å for the O and the Pd atoms, respectively. (c) The atomic arrangement of a 7 times replicated Pd_5O_4 overlayer on the Pd(111) substrate resulting in the lowest energy. The supercell is shown by the black lines, whereas the white square indicates the unit cell of the adsorbate. (d) STM simulation for the structure shown in frame (c), based on the Tersoff-Hamann approximation [20].

Additionally, only this structure results in a theoretical STM image (not shown) which roughly agrees with the experiment. For the Pd_5O_5 overlayer, the additional fifth oxygen atom was located in the fourfold site in the center of the unit cell shown in Fig. 2a. For the Pd_5O_6 overlayer, the sixth additional O atom was located slightly below the overlayer in the position marked A in Fig. 2a. In both cases, the adsorption energies for the additional oxygen atoms were very small (100–300 meV). The three simulated annealing calculations therefore strongly suggest a Pd_5O_4 adsorbate unit cell. In a second step, we simulated seven adsorbate unit cells with this composition on a three layer thick Pd(111) slab, containing 48 atoms per layer, as indicated in Fig. 2c. A single k point with the coordinate $(0, 1/4, 0)$ was used for this calculation. For this supercell, the mismatch between the adsorbate and the substrate is only 1% in the direction of the second diagonal $[(7/2)\sqrt{2}\,\sqrt{6}/12]$, and now the surface oxide cell was compressed by 1% to reach commensurability with the substrate. To determine the exact registry of the oxide layer to the substrate, we tried several starting configurations with differently aligned surface oxide layers and relaxed the geometry. The optimal final positions are shown in Fig. 2c. We find two types of Pd atoms in the surface, one Pd atom per unit cell having four oxygen neighbors, and four Pd atoms with only two neighboring oxygen atoms. The fourfold coordinated Pd atoms are located above the densely packed Pd atom rows (dashed lines in Fig. 2c). The other Pd atoms are positioned above bridge or hollow sites. We also find that half of the oxygen atoms are bonded only to the in-plane Pd atoms (threefold O), whereas the second half—those located above Pd atoms in the subsurface layer—are also coordinated to subsurface Pd atoms (fourfold O). In turn, the oxygen atoms exhibit a considerable buckling of approximately 0.85 Å, leading to the peculiar Persian-carpet-like pattern observed both in the experimental (Fig. 1a) and the simulated [20] STM image (Fig. 2d). The agreement between the theoretical and experimental STM images is almost perfect giving strong support for the structure proposed. This structure has neither the stoichiometry nor structural similarity to any plane of the only comparable bulk oxide, PdO. Concerning the energetics, the surface oxide is found to have an oxygen binding energy of $E_{\mathrm{ads}} = 1.24$ eV, between the $p(2 \times 2)$ O overlayer ($E_{\mathrm{ads}} = 1.36$ eV) and a fictitious $p(2 \times 1)$ oxygen overlayer ($E_{\mathrm{ads}} = 0.95$ eV). The binding energy per oxygen atom is also significantly higher than in bulk PdO ($E_{\mathrm{ads}} = 0.98$ eV). This indicates that the surface oxide is thermodynamically stable at intermediate oxygen pressures and may therefore play an important role in catalysis if conditions are suitable. Finally, we note that the HRCLS measurements suggested a slightly higher oxygen coverage, and believe that this is related to the fact that the preparation of a perfect $p(2 \times 2)$ oxygen structure used as a reference is difficult.

The structure of the surface oxide resulting from the *ab initio* calculations was confirmed by SXRD measurements. To avoid the difficulties caused by the incommensurability, we have restricted the fit to the oxide layer, neglecting scattering by the substrate. We find that the unit cell deviates from a perfect square by only ≈1%. Assuming a planar layer with only two free parameters (in-plane coordinates compatible with $p4mm$ symmetry), an analysis based on 14 nonequivalent superstructure reflections with $l = 0.5$ (grazing incidence, 1.5°) results in an excellent fit ($\chi^2 = 0.48$). The resulting in-plane coordinates match the *ab initio* results (average over seven cells in Fig. 2c) within 0.02 Å for Pd and 0.1 Å for O (see Fig. 2b). Because of the high quality of the data, the results

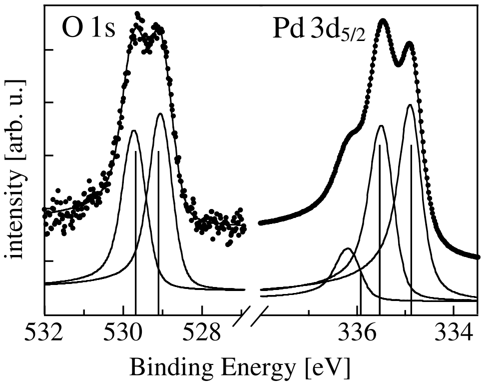

FIG. 3. HRCL spectra from the O $1s$ and the Pd $3d_{5/2}$ levels of the surface oxide [21]. Calculated binding energies (averages over groups of atoms with equivalent sites) are indicated as vertical lines.

are also quite sensitive to the oxygen atoms. Adding an O atom in the center of the cell (as found by the simulated annealing calculations for Pd$_5$O$_5$) results in $\chi^2 = 4.1$, ruling out such a possibility.

Further support for our structure model comes from the HRCL spectra (Fig. 3). The Pd$3d_{5/2}$ level consists of three components, the bulk component at 334.88 eV and two oxygen induced components shifted towards higher binding energy by 0.62 and 1.3 eV, respectively. The peak shift of the Pd atoms with two oxygen neighbors is roughly half that of Pd atoms with four O neighbors, and the measured intensity ratio of these peaks (1:0.22) corresponds well to the number of Pd atoms in the respective sites (4:1 according to our model). The calculated shifts, including both the initial state and the final state effects, agree reasonably well with the experimental data. The core level energies calculated for the Pd layer directly below the surface oxide layer are almost exactly the same as for bulk Pd, explaining why no additional component is observed. Turning to the O $1s$ level, the spectra show two components with a binding energy shift of 0.75 eV and an intensity ratio close to 1:1 [21]. We remind the reader that half of the oxygen atoms bind to only three Pd atoms in the surface layer, whereas the second half also binds to one subsurface Pd atom. Our calculations indeed yield a shift of 0.51 eV between the average O $1s$ energies of the two types of oxygen atoms, in reasonable agreement with experiment. It should be added that the peak splitting observed experimentally cannot be attributed to subsurface oxygen since variation of the emission angle does not lead to any significant changes of the ratio of the peak intensities, except for diffraction effects.

We conclude that the structure of the surface oxide on Pd(111) has been resolved. We found an almost coplanar Pd$_5$O$_4$ overlayer, forming a two-dimensional oxide on the close-packed Pd(111) substrate. An important insight gained by the present study is that two-dimensional oxides showing no resemblance to bulk oxides can form at a metal surface. Concerning both structure and energetics, the two-dimensional oxide is an intermediate phase between an oxygen overlayer and a bulk oxide and should therefore have interesting consequences for heterogeneous catalysis. Our study is also unique because the atomic structure was resolved by an advanced theoretical investigation, i.e., an extensive search of the configuration space by first melting and then crystallizing Pd$_x$O$_y$ overlayers of different composition on a Pd(111) substrate. The only experimental input required for such a procedure is, in principle, the periodicity of the overlayer which can be determined by LEED or STM. In the present case, the number of Pd atoms in the oxide layer was determined by a well chosen experiment reducing the number of required molecular dynamics simulations considerably. SXRD and HRCLS measurements as well as the perfect agreement of the simulated STM image with experiment confirmed the structure.

This work was sponsored by the Austrian *Fonds zur Förderung der wissenschaftlichen Forschung,* The Swedish Natural Science Research Council, and the ESRF providing beam time on BM32. Support by the MAX-lab and BM32 technical staff is gratefully acknowledged.

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