Epitaxial oxide bilayer on Pt (001) nanofacets

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We observed an epitaxial, air-stable, partially registered (2 × 1) oxide bilayer on Pt (001) nanofacets [V. Komanicky, A. Menzel, K.-C. Chang, and H. You, J. Phys. Chem. 109, 23543 (2005)]. The bilayer is made of two half Pt layers; the top layer has four oxygen bonds and the second layer two. The positions and oxidation states of the Pt atoms are determined by analyzing crystal truncation rods and resonance scattering data. The positions of oxygen atoms are determined by density functional theory (DFT) calculations. Partial registry on the nanofacets and the absence of such registry on the extended Pt (001) surface prepared similarly are explained in DFT calculations by strain relief that can be accommodated only by nanoscale facets. © 2012 American Institute of Physics. [doi:10.1063/1.3678858]

I. INTRODUCTION

Platinum is the most important element for electrocatalysis. Despite being active for forming and breaking chemical bonds, the platinum surface is not easy to oxidize. Yet, according to recent theoretical studies platinumpreferentially oxidize below 1000 K, which implies a need for a protective surface layer. Neither submonolayer oxygen adsorption nor loosely formed oxide layers reported in studies at high oxygen pressure seem sufficient to form proper protective kinetic barriers against oxidation, especially for high-index surfaces. In this paper, we report the observation of an epitaxial oxide bilayer on Pt nanofacets formed by annealing a high-index surface of platinum in air, providing a link between nanoscale surface structure and macroscopic properties of platinum.

Madey et al. have shown that high-index surfaces of some metals form nanofacets by oxygen annealing or heterogeneous deposition. Platinum is one of them, and a high-index platinum surface self-organizes into long and narrow nanofacets when annealed in air. The nanofacets are composed of alternating (001) and (111) facets with a typical size of ~10 nm width and ~1 μm length. Despite the nanoscale dimensions of the facets, we successfully applied synchrotron surface x-ray techniques used before only for extended surfaces. Because the facets are significantly tilted (27°) from the average surface and the x-ray signal-to-background ratios for the nanofacets are weaker than for the extended surfaces, we had to take sufficient time in data acquisition and care in diffraction geometries. We used crystal truncation rods (CTR; Refs. 9 and 10) to determine the positions of Pt atoms on the surfaces of the nanofacets and resonance surface x-ray scattering (RSXS; Ref. 11) to measure the layer-by-layer oxidation states. Since x-ray measurements are relatively insensitive to oxygen atoms, oxygen bonds are inferred from the Pt oxidation states, and oxygen positions are theoretically determined by using density functional theory (DFT). Both (001) and (111) nanofacets were studied, but we will focus on the (001) nanofacets.

II. EXPERIMENTAL

Sample preparation has been described previously and will only be summarized here. A Pt single crystal is cut and polished such that the surface normal is along the midpoint between the [001] and [111] crystal directions, which is about 2° from the [113] direction. The surface is annealed at 1350 K in the dry air to form (001) and (111) facets. The (001) facets are ~10 nm wide in the (110) direction, and are extended along the (110) direction. The nanofacets are stable in air but protected in high-purity argon to maintain cleanliness during experiments. X-ray experiments were performed at beamlines 11-ID-D of the advanced photon source with a six-circle and 12-BM-B with a four-circle diffractometer. For the CTR data, rocking scans were fit to a pseudo-Voigt function to extract the integrated intensity at every L point. For the RSXS data, energy scans were made at the peak position of the rocking scan, and then repeated at the foot of the peak to measure the background. The real part of resonance scattering factors, f′, were obtained from f′′ of EXAFS data for Pt foil and for PtO₂ using the Kramers-Kronig transformation. The x-ray data were reproduced several times using various incident x-ray brightnesses to preclude the possibility of beam-induced surface oxidation.

III. EXPERIMENTAL RESULTS AND DISCUSSIONS

The Pt (001) nanofacets restructure significantly by air annealing. Such restructuring does not occur on the similarly prepared extended Pt (001) surfaces. We find that the
extended surfaces, both (001) and (111),\textsuperscript{12} support only surface adsorption of oxygen in agreement with other studies.\textsuperscript{3,14} Therefore, the oxide layer reported here is unique to nanofacets. The specular rod and two off-specular rods collected from the (001) nanofacets are shown in Figs. 1(a) and 1(b), respectively. The large undulation of the (00L) data between \( L = 1 \) and 1.5 indicates that the facet is significantly restructured. It does not fit to a model allowing only the top layer occupancy to vary, no matter how many layers are allowed to relax and roughen. A model with the top two or more layer occupancies varying, however, results in excellent fits. The best fit was obtained with Pt occupancies of 0.5 monolayers in both the topmost and second layers. The best fit occupancies and surface Debye Waller factors (SDWF) of the topmost layer and the second layer are 59(7) and 51(6)%; 5(3) and 4(3) Å\(^2\), respectively. The top layer contracted by 0.38(3) Å and the second layer expanded by 0.06(3) Å. This contraction and expansion is equivalent to more than 20% change in the lattice spacing from the bulk value. The large SDWF terms with large uncertainties indicate a buckling of potentially several percent of layer spacing in both the topmost and second layers. Note that the excess density beyond 0.5 monolayers in the topmost layer, we believe, comes from the contributions of oxygen atoms. On the other hand, the extended surface Pt (001) prepared similarly shows a smooth specular rod without any undulation\textsuperscript{12} and can be fit to a model varying only top layer occupancy and relaxation, indicating no bilayer formation.

Several off-specular CTRs were collected from the (001) nanofaceted surface. Representative (11) and (11L) scans are shown in Fig. 1(b). Because the oxide structure may be distorted from its bulk equilibrium spacing and may not be fully laterally registered to the underlying bulk lattice, the fits included independent registry parameters for the first and second layers in the [110] and [110] directions. The second layer registries invariably fit to 100%, indicating essentially complete lateral registry. The top layer registries, however, fit to 0.3(3) in the [110] direction, and 0.7(7) in the [110] direction. The partial registries indicate that the oxide layer relieves strain due to lattice mismatch, although large error bars indicate the top layer registries are not well determined statistically. Nevertheless, the elongated facet geometry could account for anisotropic top layer registries; it is easier to relieve strain near facet edges.

Additional information supporting this model comes from (2 × 1) superlattice peaks,\textsuperscript{12} although they were difficult to follow in various \( L \) values due to weak intensity over high backgrounds. Using this information and our fits to the rods, we were able to determine the Pt atom positions at the surface as shown in Fig. 1(c). Every other row of Pt atoms is pulled up by oxide formation, and the unit cell is doubled in the (110) direction.

We measured the oxidation states of surface Pt atoms with RSXS measurements.\textsuperscript{13} When a Pt atom loses outer shell electrons, the core electrons tend to bind more tightly. The corresponding energy shift is generally significant and observable in resonance scans. Near the anti-Bragg \( (L \approx 1) \), the scattering amplitudes of the top layer, second layer, and the rest of the bulk are comparable and the phase differences between them are large. The energy scan through an absorption edge, normally exhibiting a single sharp minimum, shifts and distorts with the oxidation states of the first and second layers. Resonant scattering data were collected at the Pt L\(_3\) edge for the nanofaceted surface, shown in Fig. 2(a), and compared to the similarly prepared extended (001) surface in Fig. 2(b). Figure 2(c) shows the RSXS signal measured from a clean single crystal Pt (111) surface, from Ref. 15.

The double-dip pattern of the data Fig. 2(a) is unique to the bilayer oxide, and stems from shifted resonance signals of different layers interfering with each other. Three independently measured sets of data (circles, squares, and triangles) are overlaid to show the reproducibility. Using the layer relaxations and occupancies obtained from our CTR fits, we fit the edge shifts using the simple formula, \( I(L, E) = |\sum \rho_j f_0^j + f_1^j(E) + if_2^j(E)e^{-i\pi L}|^2 \) where \( \rho_j \) is the occupancy of layer \( j \), \( f_0^j \) is the non-resonance term, and \( f_1^j(E) \) is the real part of the resonance scattering factor obtained from \( f_2^j(E) \) using the Kramers-Kronig transformation. We fit with
two scenarios: varying ratios of two discrete resonance energy shifts of 0 and 11 eV (Pt\textsuperscript{0} and Pt\textsuperscript{4+}) coexisting in a layer, or a single resonance energy shift varying between 0 and 11 eV (Pt\textsuperscript{4+}). In our fit, the former did not produce any reasonable fit, while the latter yielded a good agreement to the data. The final fit values of the shifts were 1.2(2) eV and 2.2(5) eV for the top and second layers, respectively. These fit values indicate that the top layer is fully oxidized to Pt\textsuperscript{4+} (4 oxygen bonds) and the second layer is only partially oxidized, most likely to Pt\textsuperscript{3+} (2 oxygen bonds). This suggests two O atoms per Pt atom in the top layer and one O atom per Pt atom in the second layer.

The data collected from the (001) single-crystal extended surface shows very different characteristics. We fit this data the same way, retaining the fitted relaxations and occupancies from the single-crystal (001) measurements, for which the top-layer has occupancy 28(2)% (Ref. 12) and is composed of nanoscale adislards.\textsuperscript{16} The fits indicate that the nano-islands are fully oxidized to Pt\textsuperscript{4+}, while the exposed surface between nanoscale islands is barely oxidized. This suggests Pt interfacial oxides may be stable only on nanoscale structures. Comparison of fits and the tabulation of fit parameters between (100) nanofacet, (111) nanofacet, (100) extended surface, and (111) extended surface will be presented in Ref. 12.

**IV. COMPUTATIONAL RESULTS AND DISCUSSIONS**

The positions and bonding of oxygen atoms to the platinum atoms are determined by DFT. The calculated surface energies are plotted as a function of the change in oxygen chemical potential $\Delta \mu_O(T, p_{O2})$ in Fig. 3. According to the (1 × 1) calculations without Pt restructuring, which does not fit our x-ray data, as the surface cools, the oxygen coverage will increase to 1/4 at $\sim$1350 K, 1/2 at $\sim$1200 K, and 1 at $\sim$680 K.

In DFT calculations, symmetric supercells for non-reconstructed low oxygen coverage (<1 ML) surfaces and asymmetric supercells ($\sqrt{2} \times \sqrt{2}$) for 1 ML oxygen coverage with 7 layers (28 Pt) were considered in periodic slab calculations for the determination of the lowest energy structure at each oxygen coverage. The theoretical value of the Pt lattice parameter ($a_{Pt}$) optimized at the GGA level was 3.98 Å, and a vacuum region of 4 × $a_{Pt}$ was used throughout. Details of methods for the DFT calculations of surface energy changes due to oxygen coverage are previously published.\textsuperscript{17,20} Here, we neglect the contribution to the surface free energy coming from the change in vibrational entropy of the surface with oxygen coverage, since the surface vibrational entropy itself is typically of the order of few meV/Å.\textsuperscript{18} Following the procedure outlined by Reuter and Scheffler,\textsuperscript{18} the oxygen chemical potential at $T$ and $P_{O2}$ is simply related to the chemical potential at $T$ and atmospheric pressure, with data for enthalpy and entropy of the oxygen gas obtained from the thermochemical tables.\textsuperscript{19}

Motivated by the theoretical results reported by Seriani et al.,\textsuperscript{21} we investigated the effect of strain for PtO-like structures that best describe our x-ray measurements. We adjusted the lattice parameter, starting with 3.98 Å, in increments (0%, 5%, 6%, and 9%) along the [110] long nanofacet direction (0%, −2%, and −4%) along [110] to fit the PtO lattice parameters. The calculation of the surface energy changes and the bulk compensation were done using the same method.\textsuperscript{20} The results clearly show that the PtO-like structures have much lower energies than the O/Pt (001) (1 × 1) 1 ML configuration, and more importantly, that the strain lowers the overall surface energy of O 1 ML on the Pt (001) surface quite significantly. With the inclusion of these new thermodynamically stable structures, the surface of Pt (001) will reconstruct from the bare surface directly to a 1 ML PtO-like top layer structure under increased oxygen coverage and strained conditions. Note that in a small range of chemical potentials near $-1.5$ eV the computations predict $\frac{1}{3}$ ML O (1 × 1) structure to be competitive with either clean or PtO-like structure. The $\frac{1}{4}$ ML O (1 × 1) structure was not observed in our experimental measurements, but partial oxygen coversages were observed on extended (001) Pt surfaces previously. For a 1 ML PtO-like top layer structure, the surface energies corresponding to 6% and 9% strains are practically identical for oxygen chemical potentials $\Delta \mu_O(T, p_{O2})$ higher than $-1$ eV. The oxygen atoms in these new stable PtO-like structures are a little higher than the top Pt atoms. For both unstrained and 6% strained lattices, the in-plane Pt–O bond length in the top layer is 2.01 Å, and the bond length of the second layer Pt to the top layer O is 2.07 Å. The main difference between the 6% strained structure and the unstrained structure is in the O superstructure, which is a quasi-square lattice with O–O spacing 2.82 Å along [110], and 2.85 Å and 2.79 Å along [110] for the unstrained structure and (2 × 1)-like lattice with 2.99 Å along [110] and 2.66 Å and 2.98 Å along [110] for the strained structure. In addition, the Pt-Pt layer spacing is contracted by $\sim$5% in the 6% strained lattice. The stability of the high
FIG. 3. Surface energy as a function of oxygen chemical potential for Pt (001) surface with various oxygen coverages. The arrow indicates the direction energy barrier was calculated.

The oxygen coverage of the top layer in our model can be explained for the $(2 \times 1)$ missing-row reconstruction by an upshift of the surface Pt $d$-bands due to outward relaxation of the Pt surface atoms (low coordinated Pt ridge atoms), and hence a stronger Pt–O bond. This relaxation, further enhanced in the strained lattice, also reduces the O–O repulsion and even gives rise to an attractive O–O interaction which lowers the overall surface energy.

Bader charge analysis shows that in the case of 6% strained PtO-like structures there is a charge transfer from Pt to O atoms, with the main transfer coming from the top Pt atoms, losing about 1.1 electron charge each. The second layer Pt atoms lose about 0.5 electrons each. The oxygen atoms gained about 0.8 electrons each. Although it is difficult to compare quantitatively the Bader charges to the $L_3$ energy shift, they are in qualitative agreement assuming the Pt–O bonds are of covalent character. The RSXS results indicated the top layer Pt atoms were in the +4 formal oxidation state, and most of the second layer Pt atoms were +2, which gives a similar ratio as calculated Bader charge.

We calculated the energy barriers for the transformation from 1 ML O/Pt (001) to the PtO-like structure for both strained and unstrained surfaces using the nudged elastic band method, by slightly lifting and shifting every other surface Pt to the same height as the adsorbed oxygen atoms. In both unstrained and 6% strained lattices, the transformation occurs rather smoothly with 1 eV and 1.64 eV energy barriers, respectively. This result shows that the thermodynamically predicted stable PtO-like structures can also be kinetically reached from 1 ML structures at experimental conditions. However, structural optimizations at fixed strain values between 0% and 6% strain indicate that there is no barrier for the transformation from the structure with no strain to the one with 6%, as the surface energy continuously decreases with the increase of strain. Hence, the likely kinetic pathway to PtO-like strained structures proceeds from 1 ML O on $(1 \times 1)$ Pt (001) structure to unstrained PtO-like structure with 1 eV barrier, then consequently relax further to PtO-like strained structures without barrier, as strain is easier to accommodate nanofacets than in extended surfaces.

V. CONCLUSIONS

Our observation suggests the stability of Pt surface oxides depends on the size of the surface. Our data suggest that the oxide layer is stressed, and the presence of facet edges...
can release some of the strain. Extended surfaces, on the other hand, have no such mechanism. It is also reasonable to assume that edges preferentially bind atomic oxygen adatoms, a precursor for oxide clusters at step edges observed on Pt (111) terraces.\textsuperscript{24} The structure is not a kinetically locked metastable structure, since the bilayer oxide can be easily restored by thermal annealing to above 600 K after the oxide is removed by electrochemical CO oxidation reaction.\textsuperscript{12} Our DFT calculation suggests that the observed nanoscale faceting can be driven by nanoscale oxide formation as seen in Ir(210).\textsuperscript{25} In nanoscale surfaces of Pt, we believe, stress-relieving epitaxial oxide, not possible in extended surfaces, can form and is resistant to further oxidation even when the oxide is as thin as a single or bilayer.

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