Atomic Imaging of Oxide-Supported Metallic Nanocrystals

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Dramatically enhanced catalytic activities have been observed for a variety of noble metals in the form of nanoparticles supported on oxide surfaces. The formation of metal nanoparticles is governed by the surface free energy, which is, in turn, determined by the atomic bonding across the interface between a particle and a supporting surface. Detailed structural information on multiple length scales, including the atomic scale, is required to gain insight into formation mechanisms and their links to catalytic activity.

A prime example is Pt on SrTiO₃ as a photocatalyst for water splitting. The structure and resulting electronic properties of the Pt/SrTiO₃ interface are also of importance to thin-film technologies such as those used for dynamic random access memory devices. Therefore, predictions of the metal/oxide interface structure, in general, would impact our understanding of numerous chemical and physical processes. Several theoretical investigations have predicted a complex interface structure at the atomic level for ultrathin film coverages from the submonolayer level to several monolayers. Experimentally, direct imaging provides a way to look into the details of the interface structure of supported nanoparticles.

SrTiO₃ (STO) has a room-temperature (RT) lattice constant (a = 3.905 Å, perovskite cubic-P crystal structure) close to that of Pt (a = 3.924 Å, cubic-F). Cross-sectional transmission electron microscopy (TEM) and X-ray diffraction (XRD) studies of various growth methods for Pt on SrTiO₃(001) have shown that close lattice match leads to Pt thin films with strain-relaxed cube-on-cube epitaxy to the substrate lattice, namely, [001]₉ [001]₁ and [010]₉ [010]₁. There are also recent studies of Pt nanoparticles grown on single-crystal STO nanocubes, which are important for catalysis applications due to the enormous gain in surface area.

In addition to electron microscopy, X-ray imaging techniques with 10–100 nm resolution have been initiated for in situ and/or real-time investigations of nanoparticles. Examples are X-ray coherent imaging of strain in supported nanocrystals, nanoparticle imaging using ultrashort X-ray laser pulses, and nanoscale structural imaging by resonant X-ray diffraction microscopy. To complete the picture down to the level of interfacial bonding configurations requires element-specific, atomic-scale imaging of the supported nanoparticles. Herein, we show how this requirement can be met by X-ray standing wave (XSW) 3D atomic imaging, which has previously been applied to bulk impurities and surface adsorbate atoms. We use this non-destructive method to produce atomic-lattice images of supported nanoparticles.

KEYWORDS: nanoparticles · epitaxy · atomic imaging · interface structure · X-ray standing waves · platinum · strontium titanate

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9755
for the first time. Our case study is for the early (low coverage) stages of the nucleation and growth of Pt nanoparticles on the TiO2-terminated surface of SrTiO3(001).

Single-crystal XSW experiments\textsuperscript{21–24} use a selected \( H = hkl \) strong Bragg reflection to generate an \( E \)-field intensity pattern with the periodicity of the diffraction planes \( (d_{hkl}) \). Advancing in Bragg angle through this arc-second-width reflection causes the antinodal planes of the XSW to shift inward by one-half of a \( d \)-spacing, which induces modulations in the characteristic X-ray fluorescence (XRF) signals from atoms above and below the substrate single-crystal surface. In simple terms the phase of this measured modulation is sensitive to the \( \Delta d / d \) positions of the XRF-selected atoms relative to the diffraction planes, and the modulation amplitude senses the fraction of atoms at (or distribution about) this position. More rigorously the modulation measures the model-independent Fourier phase \( \rho_{hkl} \) and amplitude \( f_{hkl} \) for the distribution of XRF-selected atoms. By Fourier summation we produce 3D maps for the surface-deposited Pt and bulk Ti atomic distributions that are used to register (correlate) the Pt lattice relative to the SrTiO3 lattice. This includes a determination of the interfacial offset between the Pt and SrTiO3 unit cells along the \( c \)-axis and an estimation of the Pt occupation fractions for different lattice sites.

RESULTS AND DISCUSSION

Following well-established surface preparation procedures,\textsuperscript{25,26} two separate SrTiO3(001) single-crystal substrates were cleaned, etched, and then \( \mathrm{O}_2 \) annealed to obtain atomically flat, TiO2-terminated surfaces. The substrates were then loaded into an ultra-high-vacuum (UHV) chamber located at the Advanced Photon Source 12ID-D station.\textsuperscript{27} The chamber (Figure S1 in the Supporting Information) was equipped with molecular-beam epitaxy (MBE), low-energy electron diffraction (LEED), Auger electron spectroscopy, and XSW facilities. After annealing to 950 °C for 30 min, the SrTiO3(001) surfaces revealed a two-domain \( 2 \times 1 \) LEED pattern, as shown in Figure 1a. Surface XRD- and TEM-based models for the \( 2 \times 1 \) reconstructed surface propose an extra TiO2 layer atop the TiO2-terminated SrTiO3(001) surface.\textsuperscript{28–30} Pt was then deposited from an e-beam evaporator onto the SrTiO3(001) surface with the substrate at 400 °C. On the basis of X-ray fluorescence (with Rutherford backscattering calibration), the substrate with a 10 min Pt deposition time had a Pt coverage of \( \Theta = 0.60 \) monolayers (ML), and for the substrate with 2 min deposition time, \( \Theta = 0.17 \) ML. (1.00 ML = 6.58 atoms/nm\(^2\).) These as-deposited surfaces retained the sharp \( 1 \times 1 \) LEED spots, but weaker half-order spots, as shown in Figure 1b. After a series of annealing steps at increasing temperatures that ended at 910 °C, the \( 2 \times 1 \) sharp LEED pattern was recovered, as shown in Figure 1c. Previously published atomic-force microscopy (AFM) studies of similarly grown ML coverage Pt on SrTiO3\textsuperscript{25} (001) show a surface morphology with nanoparticle formation.\textsuperscript{29}

Using an incident X-ray energy of 12.50 keV, UHV RT XSW measurements were made for the as-deposited surface and after each annealing step for the 0.60 and 0.17 ML Pt/SrTiO3(001) samples. These \textit{in situ} XSW measurements were restricted to observing the modulation in the Pt L\( _\alpha \) and Ti K XRF yields while scanning the incident angle through the SrTiO3(002) Bragg peak. \textit{Ex situ}, open-air, XSW measurements (Figure 2) were then made on each sample with a four-circle diffractometer, positioned just upstream of the UHV chamber. This goniometer allowed the single-crystal substrate to be rotated to several different selected \( hkl \) SrTiO3 Bragg peaks as required for a complete 3D triangulation (or imaging) of the Pt atomic distribution relative to the substrate lattice. The surfaces were then examined by AFM, which showed nanoparticles supported on a surface with flat terraces separated by atomic steps (see Supporting Information). This morphology is consistent with similarly prepared Pt/SrTiO3(001) surfaces.\textsuperscript{26}
For the 0.60 ML Pt/SrTiO$_3$(001) sample the ex situ XSW measured values for the (002) Fourier amplitude, $f_{002} = 0.39$, and phase, $P_{002} = -0.18$, agree with the in situ UHV measured values (see Supporting Information). This strongly indicates the stability of this surface against oxidation and the reliability for attributing the atomic-scale structural results for the ex situ surface to the in situ surface. Figure 2 shows the XSW data and fit for the SrTiO$_3$(002) Bragg peak. The surface Pt L$_x$ and bulk Ti K$_x$ XRF yields are both analyzed. Due to diffuse (incoherent) scattering, the tails of the experimental reflectivity (rocking) curve are higher than the theory for a perfect single crystal. Table 1 and Table 2 list the entire ex situ measured set of $f_{ij}$ and $P_{ij}$ values of Pt and Ti for the 0.60 ML sample, respectively. The summation of these two sets of XSW-measured Fourier components (and their symmetry equivalents) produce model-independent 3D maps of the Pt and Ti atomic distributions,

$$\rho(r) = 1 + \sum_{H \neq 0, \neq \phi} f_i \cos(2\pi P i - H \cdot r)$$

Figure 3a and c show, respectively, the Pt and Ti 3D atomic maps for the 0.60 ML sample as referenced to the SrTiO$_3$ substrate unit cell with Sr at the corners (origin). (b) Projection of the 3D density along the $c$-axis to produce a 1D Pt atomic density as a function of the fractional $c$-axis coordinate, $z$, for the SrTiO$_3$ unit cell. (c) XSW-measured 3D Ti atomic density map. The contour plots in (a) and (c) are at 80%. (d) Proposed interface atomic model of fcc Pt on a double-layer TiO$_2$-terminated SrTiO$_3$-(001) surface, where A, B, and C refer to the three symmetry-equivalent Pt sites. The striped light blue spheres in the extra TiO$_2$ layer represent Ti sites that are on average 50% occupied due to the two-domain $2 \times 2$ reconstruction of the surface.

Table 1. For the 0.60 ML Pt/SrTiO$_3$(001) Case: XSW-Measured $H = hkl$ Fourier Amplitudes, $f_{ij}$, and Phases, $P_{ij}$, for Pt

<table>
<thead>
<tr>
<th>$hkl$</th>
<th>$f_0$</th>
<th>$P_0$</th>
<th>$f_1$</th>
<th>$P_1$</th>
</tr>
</thead>
<tbody>
<tr>
<td>001</td>
<td>0.07(3)</td>
<td>0.07</td>
<td>0.07</td>
<td>0.67</td>
</tr>
<tr>
<td>002</td>
<td>0.39(3)</td>
<td>0.18</td>
<td>0.32</td>
<td>-0.15</td>
</tr>
<tr>
<td>011</td>
<td>0.07(3)</td>
<td>0.06</td>
<td>0.06</td>
<td>0.67</td>
</tr>
<tr>
<td>022</td>
<td>0.22(3)</td>
<td>0.16</td>
<td>0.23</td>
<td>-0.15</td>
</tr>
<tr>
<td>111</td>
<td>0.35(3)</td>
<td>0.13</td>
<td>0.37</td>
<td>-0.07</td>
</tr>
<tr>
<td>222</td>
<td>0.15(3)</td>
<td>-0.08</td>
<td>0.16</td>
<td>-0.15</td>
</tr>
</tbody>
</table>

Table 2. XSW-Measured Fourier Amplitudes, $f_{ij}$, and Phases, $P_{ij}$, for the Bulk Ti Sublattice of SrTiO$_3$(001)

<table>
<thead>
<tr>
<th>$hkl$</th>
<th>$f_0$</th>
<th>$f_1$</th>
<th>$P_0$</th>
<th>$P_1$</th>
</tr>
</thead>
<tbody>
<tr>
<td>001</td>
<td>0.68(3)</td>
<td>0.60(3)</td>
<td>0.59(3)</td>
<td>0.49(3)</td>
</tr>
<tr>
<td>011</td>
<td>0.50(1)</td>
<td>0.00(1)</td>
<td>0.00(1)</td>
<td>0.00(1)</td>
</tr>
<tr>
<td>111</td>
<td>0.98</td>
<td>0.92</td>
<td>0.96</td>
<td>0.85</td>
</tr>
</tbody>
</table>

The takeoff angle ($\alpha$) of the detected Ti K$_x$ XRF emission relative to the surface is also listed. The $P$ values are referenced to the Sr atom at the origin. $\exp(-M) = \exp(-2\pi \chi/\alpha)$ is the Debye–Waller factor, where $\alpha = 0.12$ Å is the thermal vibrational amplitude of the Ti atom at RT.
symmetry-inequivalent adsorption sites on the SrTiO$_3$-(001) surface: the corner site (A site), base-center site (B site), and the two symmetry-equivalent side-center sites (C site). To better quantify the Pt occupation fractions ($c_i$) and heights ($h_i = a_{STO} \cdot z_i$) above the bulk-like SrO plane for the three sites, we used a least-squares global fit of the proposed model to the set of measured Fourier components,

$$F_h = f_h e^{2\pi i \alpha} = e^{-2\pi i (\alpha h_0 + a \cdot r_i)}$$

(2)

where vectors $r_A = (0,0,z_A)$, $r_B = (1/2,1/2,z_B)$, $r_C = (1/2,0,1/2+z_C)$, and $r_{C1} = (0,1/2,1/2+z_C)$ locate the four Pt sites relative to the substrate unit cell origin and $\alpha$ is the width of the Pt distribution (assumed to be isotropic) about these sites. The best-fit determined results are $c_A = 0.16$, $c_B = 0.11$, $c_C = 0.11$, $h_A = 7.69$ Å, $h_B = 7.44$ Å, $h_C = 5.49$ Å, and $\alpha = 0.26$ Å, which agree very well with the numerical analysis of the model-independent 3D map (Figure S10 in the Supporting Information). The occupation ratio between the three sites ($c_A c_B c_C \approx 3:2:2$) is reasonably close to the ratio of an ideal fcc arrangement (1:1:1), where there is an equal number of Pt atoms in each layer.

Results also show that $c_A + c_B + 2c_C = 0.49$. Normally for a perfectly single-crystal substrate, such as Si or Ge, this would mean that only 49% of the Pt atoms are correlated with the substrate lattice. However, this is not a perfect single-crystal substrate, as the diffuse tails of the measured reflectivity (Figure 2) indicate. Using XSW analysis of the Ti sublattice within bulk SrTiO$_3$(001) as a reference, we determine that 0.78 is a better estimation of Pt correlation fraction. (See Figure S11 and discussion in the Supporting Information.) The Ti Kα XRF yield was collected simultaneously with the Pt signal (Figure S2 in the Supporting Information). The analysis results are listed in Table 2. The XRF takeoff angle, $\alpha$, relative to the sample surface is used to calculate the effective thickness of the Ti Kα fluorescence signal, which includes the extinction effect. As an example, the effective thickness sampled by the Ti K XRF yield for the 002 XSW measurement varies from 2.9 μm at the off-Bragg wings of the reflection to 0.5 μm at the center of the Bragg reflection. By inserting the measured coherent fractions and positions (i.e., Fourier amplitudes and phases) of bulk Ti into eq 1, a Ti atomic density map is generated, as shown in Figure 4 and Figure 3c. As it should be, the Ti density maximum is located in the center of the SrTiO$_3$ cubic unit cell. This further validates our XSW analysis procedure. The much weaker subsidiary maxima in the 3D map of Figure 4 are due to the truncation of the Fourier summation.

For the 0.17 ML case, the XSW-measured 3D Pt density map, Figure 5a, also shows an fcc-like structure, but with a vertical shift of ~$(1/2)a_{STO}$. This is quite different from the 0.60 ML case shown in Figure 3a. Therefore, a different interface model is proposed in Figure 5c that shows the first layer of Pt directly above the O atoms in the DL TiO$_2$-terminated SrTiO$_3$. Model-independent and model-dependent analyses (see Supporting Information) both show that the Pt occupation fraction ratio of the three sites is $c_A c_B c_C = 2:2:1$. Unlike the 0.60 ML case, this indicates that at 0.17 ML there are twice as many Pt atoms in the layer containing the A and B sites as in the neighboring layer containing the C site. The 2D projection of this Pt atomic density along the c-axis (Figure Sb) also shows a significant deviation in layer spacing from the ideal fcc arrangement; that is, the two layers have a vertical spacing of 0.4$a_{STO}$, rather than $(1/2)a_{STO}$ (see Supporting Information).

The Pt/SrTiO$_3$(001) interface structures observed by XSW can be attributed to the SrTiO$_3$(001) surface termination, Pt-support interactions, and Pt–Pt interactions. Earlier experiments and theoretical models attribute the Pt intercalation to the formation of a Pt-Sr-O bond, which leads to the observed Pt occupation fraction ratio of 2:2:1.

Figure 4. 2D plane-cuts through 3D titanium atomic density map along the (a) outer surfaces of the SrTiO$_3$ unit cell and (b) interior surfaces of the unit cell. The map is generated by the summation of XSW-measured (hkl) Fourier components listed in Table 2 plus their symmetry equivalents.
studies of the bare 2 × 1 SrTiO₃(001) surface support the formation of a double-layer (DL) TiO₂-terminated surface. We found no reported theory predictions for Pt on the DL TiO₂-terminated surface. However, density functional theory (DFT) calculations for very low Pt coverages on TiO₂-terminated SrTiO₃(001) predict that the Pt–support interaction is stronger than the Pt–Pt interaction, and Pt atoms strongly prefer to adsorb on top of the O atoms. Furthermore, DFT calculations by Asthagiri and Sholl show that as the Pt coverage increases from 0.5 to 1 ML on the TiO₂-terminated SrTiO₃(001) surface, the Pt–substrate bond is weakened due to additional Pt–Pt bonds on the surface. For 1 ML this same DFT study proposes that interface Pt atoms prefer to bind above Ti sites on the TiO₂-terminated surface to continue the fcc-like packing. This leads to the interface structure model proposed in Figure 3d for the 0.60 ML case. The equal occupation of the three symmetry-in-equivalent sites further indicates that the Pt nanoclusters seen in the AFM are primarily built from multiple layers of Pt. The AFM analysis shows that the average Pt nanocluster height is ≈1.5 nm for the 0.60 ML case, which is reasonably consistent with our atomic model and the equal-occupied multiple layer structures. For the 0.17 ML case this AFM measured average height is ≈1 nm. From our measurements of the 0.17 ML Pt/SrTiO₃(001) interface, we propose that a significant fraction of first-layer Pt atoms are not capped off with additional Pt layers. This could lead to a stronger Pt–O interaction as proposed with the interface model shown in Figure 5c.

CONCLUSIONS

In summarizing this first XSW imaging of atoms in supported nanoparticles, we observed the fcc cube-on-cube epitaxial structure for submonolayer Pt grown on SrTiO₃(001) surfaces by MBE. We experimentally show for the first time that different interface structures of Pt are formed with different initial Pt coverages, which could be further explained by the surface termination of SrTiO₃(001) and the interactions of Pt–Pt and Pt–support. Our proposed atomic-scale interface models, which start with a TiO₂ double-layer SrTiO₃(001) surface, indicate that at a very low coverage (0.17 ML) Pt prefers to bond on top of the O atoms due to the strong Pt–support interaction. However, at a higher coverage (0.60 ML) smaller Pt nanocrystals are formed with stronger Pt–Pt interaction, which causes the interface Pt atoms to bond above Ti atomic sites. Equal occupation in the three symmetry-in-equivalent sites indicates those Pt nanocrystals have two or more complete Pt layers locally, which is in contrast to our finding of unequally occupied layers for the 0.17 ML case. This atomic-level metal/perovskite interface study is important for understanding subsequent physical and chemical properties in electronic and catalytic applications.

METHODS

Preparation of Substrates. Strontium titanate (SrTiO₃) single crystals were oriented, cut (10 × 10 × 1 mm³), and polished parallel to the (001) by OKEN (Japan). SrTiO₃(001) substrates were ultrasonicated for 10 min in deionized water (18 MΩ·cm) and subsequently etched in a hydrofluoric acid buffer solution for approximately 30 s. The substrates were then rinsed in deionized water and dried in Ar gas. To produce atomically flat terraces, the substrates were loaded into a tube furnace with O₂ flow (≈100 sccm) and annealed at 1050 °C for 5 h. After annealing in O₂, the substrates were mounted on a tantalum sample plate using spot-welded tantalum wire and loaded into an X-ray Surface Science ultra-high-vacuum multichamber (Figure S1 in the Supporting Information) located at the 12ID-D undulator BESSRC-CAT station at the Advanced Photon Source (APS), Argonne National Laboratory. The vacuum chamber was maintained at a base pressure of 2 × 10⁻¹₀ Torr and equipped with a reverse-view low-energy electron diffraction (LEED; PHI), Auger electron spectroscopy (AES: PHI), and an electron-beam evaporator source (Omicron).

Platinum Growth. Prior to platinum deposition, the substrates were annealed at 950 °C for 30 min in the UHV chamber using a resistive tungsten filament heater placed behind the sample. Auger analysis showed clean surfaces with negligible carbon contamination. A 1.5 mm diameter Pt rod was placed inside the e-beam evaporator to deposit Pt thin films. Platinum was deposited onto the atomically clean SrTiO₃ (STO) surface, which was held at 400 °C. After cooling to RT the “as deposited” (002) XSW measurement was made. The sample was then annealed to a series of increasing temperatures, cooled to RT, and given a 002 XSW measurement. The series of annealing temperatures were 0.5 h at 500 °C, 1 h at 700 °C, 1 h at 800 °C, and 1 h at 910 °C.

Characterizations. LEED measurements were taken before Pt deposition, after Pt deposition, and after the 910 °C annealing step.
scattering. One monolayer is defined as 6.58 atoms/nm².

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Supporting Information Available: Details of the experimental setup and XSW analysis. This material is available free of charge via the Internet at http://pubs.acs.org.

REFERENCES AND NOTES


32. Because the surface breaks the symmetry along c-axis, the bulk fcc symmetry-equivalent B and C sites become symmetry-inequivalent.
