Structure of Au(111) and Au(100) Single-Crystal Electrode Surfaces at Various Potentials in Sulfuric Acid Solution Determined by In Situ Surface X-ray Scattering

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Potential-dependent surface structures of Au(111) and Au(100) single-crystal electrodes in a 50 mM H₂SO₄ solution were investigated at an atomic level using in situ surface X-ray scattering (SXS) techniques. It was confirmed that both the Au(111) and Au(100) surfaces were reconstructed with an attached submonolayer of an oxygen species, most probably water, at 0 V (vs Ag/AgCl). Results at +0.95 V supported a previously suggested model for both the Au(111) and the Au(100) electrodes that, based on infrared and scanning tunneling microscopy measurements, the surfaces were a (1 × 1) structure with the adsorbed sulfate anion and hydronium cation (H₂O⁺). At +1.05 V, where a small amount of an anodic current flowed, adsorption of a monolayer of oxygen species was observed on both surfaces. When the single-crystal gold electrodes were electrochemically oxidized at +1.40 V, the expansion of the gold surface by about one monolayer of Au atoms was observed, suggesting the penetration of oxygen into the surface gold layers (i.e., the formation of two layers of surface oxide). When the surface oxide was reduced at +0.65 V, the surface structure returned back to the structure observed at +0.95 V before the oxide formation (i.e., a (1 × 1) structure with coadsorbed sulfate anion and H₂O⁺). When the potential was reduced to 0 V, the surfaces were reconstructed again but with slightly more random structures than those before the potential cycle.

1. Introduction

Gold is one of the most important materials for various applications, and the structure and properties of low index surfaces of single-crystal gold have been extensively studied not only in ultrahigh vacuum (UHV) but also in electrochemical environments. The surface structures of the single-crystal gold electrodes in electrolyte solutions have been investigated using various techniques, including conventional electrochemical methods, scanning tunneling microscopy (STM), and several optical techniques, and were found to be strongly dependent on the potentials. It is well-known that the potential-induced reversible lifting and restoration of the electrode surface take place around +0.35 V vs Ag/AgCl. At +0.95 V, where a small amount of an anodic current flowed, adsorption of a monolayer of an oxygen species was observed on both surfaces. When the single-crystal gold electrodes were electrochemically oxidized at +1.40 V, the expansion of the gold surface by about one monolayer of Au atoms was observed, suggesting the penetration of oxygen into the surface gold layers (i.e., the formation of two layers of surface oxide). When the surface oxide was reduced at +0.65 V, the surface structure returned back to the structure observed at +0.95 V before the oxide formation (i.e., a (1 × 1) structure with coadsorbed sulfate anion and H₂O⁺). When the potential was reduced to 0 V, the surfaces were reconstructed again but with slightly more random structures than those before the potential cycle.

Potential-dependent surface structures of Au(111) and Au(100) single-crystal electrodes in a 50 mM H₂SO₄ solution were investigated at an atomic level using in situ surface X-ray scattering (SXS) techniques. It was confirmed that both the Au(111) and Au(100) surfaces were reconstructed with an attached submonolayer of an oxygen species, most probably water, at 0 V (vs Ag/AgCl). Results at +0.95 V supported a previously suggested model for both the Au(111) and the Au(100) electrodes that, based on infrared and scanning tunneling microscopy measurements, the surfaces were a (1 × 1) structure with the adsorbed sulfate anion and hydronium cation (H₂O⁺). At +1.05 V, where a small amount of an anodic current flowed, adsorption of a monolayer of oxygen species was observed on both surfaces. When the single-crystal gold electrodes were electrochemically oxidized at +1.40 V, the expansion of the gold surface by about one monolayer of Au atoms was observed, suggesting the penetration of oxygen into the surface gold layers (i.e., the formation of two layers of surface oxide). When the surface oxide was reduced at +0.65 V, the surface structure returned back to the structure observed at +0.95 V before the oxide formation (i.e., a (1 × 1) structure with coadsorbed sulfate anion and H₂O⁺). When the potential was reduced to 0 V, the surfaces were reconstructed again but with slightly more random structures than those before the potential cycle.

Although the formation of Au=OH, Au=O, and Au₂O₃ species on the surface has been discussed based on the data of charge and capacitance obtained by conventional electrochemical techniques, the electrochemical techniques cannot provide the structural information. The electrochemical quartz crystal microbalance (EQCM) technique was used to study the anion adsorption on the electrode surface, but this only gives information of mass change on the electrode surface and cannot be applied for single-crystal electrodes. STM measurement provides structural information at atomic resolution but of the outermost layer only. Therefore, the surface structure of the electrode cannot be determined by STM when the surface is covered with adsorbates such as anions. Information obtained by optical techniques contains contributions not only from the electrode surface but also from the bulk. Thus, the surface structures of the single-crystal gold electrodes at atomic resolution for wide potential regions, particularly in the oxide formation potential region, have not been clarified yet.

The surface X-ray scattering (SXS) technique is one of the best methods to investigate the three-dimensional (3D) interfacial structure at an atomic level. Many in situ structural studies at electrode/electrolyte interfaces using the SXS technique have been carried out in the last 15 years.

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example, we determined the structure of the underpotentially deposited (UPD) Ag layers on a Au(111)-(1 × 1) surface.49 As far as the structure of gold electrodes is concerned, Ocko et al. investigated the structures of the reconstructed Au(111) and Au(100) surfaces in electrolyte solutions containing various halogen anions using in situ SXS.39–42 There were, however, no structural analyses of gold single-crystal electrode/electrolyte interfaces in other potential regions using the in situ SXS technique.

In this paper, the potential-dependent structures of single-crystal Au(111) and Au(100) electrodes in sulfuric acid solution in wide potential regions (0 to +1.4 V) were investigated by X-ray reflectivity measurement, one of the SXS methods. Experimentally obtained reflectivity profiles of both Au(111) and Au(100) electrodes at all potentials were well fitted to the profiles, which were calculated using the following interfacial structural models.

2. Experimental

2.1. Materials. Au(111) and Au(100) single-crystal disks (diameter: 10 mm, thickness: 5 mm) were purchased from Surface Preparation Laboratory (The Netherlands). The disks were electrochemically etched in a solution containing 0.1 M HClO4 and 5 mM NaCl5 and then annealed at 850 °C for 10 h under an Ar atmosphere in an electric furnace (Denken, KDF S-70). Ultrapure reagent-grade H2SO4 and HClO4 and reagent-grade NaCl were purchased from Wako Pure Chemicals and were used without further purification. Water was purified using a Milli-Q system (Yamato, WQ-500). Ultrapure N2 (99.9995%) and Ar (99.999%) were purchased from Air–Water. A 6.0 µm thick Mylar film (Chemplex, D) was used as the window of a spectroelectrochemical cell, which was specially designed for the in situ SXS measurements and was made of Kel-F.48

2.2. Electrochemical and In Situ SXS Measurements. Both the cyclic voltammetry and the in situ SXS measurements were carried out using the spectroelectrochemical cell.46 The electrode potential was controlled by a potentiostat/galvanostat (Hokuto Denko, HA-151), and an external potential was provided by a function generator (Hokuto Denko, HB-111). Cyclic voltammograms (CVs) were recorded on an X-151 and 1.20 V for Au(100) were observed. The peaks around L = 3 and 6 for Au(111) correspond to the cubic (1, 1, 1) and (2, 2, 2), respectively, and those around L = 2, and 4 for Au(100) correspond to the cubic (1, 0, 0) and (2, 0, 0), respectively. Between these peaks, the reflectivity was low and depended on the detailed structure of the interface. Structures along the normal direction to the electrode surface were quantitatively determined from the least-square fitting to the reflectivity data with a kinematical calculation based on a specific interfacial model.39,46,53,54 All the fittings were carried out using models of three layers on top of the Au substrate. The amounts of various atoms in each layer were estimated by considering that one monolayer (ML) corresponds to 1.39 Å2. The fitting, a three-layer structure model, where the electron density of the oxygen atom is neglected, was taken as a best-fitted result.

For the gold oxide layers, the contribution of oxygen was neglected, because the electron density of the oxygen atom is only 10% of that of the gold atom.

3. Results and Discussions

3.1. Au(111) Electrode. Figure 1 shows a CV of a Au(111) single-crystal electrode in a 50 mM H2SO4 electrolyte solution obtained under the thick electrolyte configuration. Sharp anodic and cathodic peaks were observed at +1.30 V and +0.91 V, respectively. The former peak can be assigned to the oxide formation and the latter to the reduction of oxide. Inset of Figure 1 shows a CV in the narrower potential range (0 through +1.00 V) with a magnified current scale. A pronounced anodic peak at +0.31 V due to (3/2 × 3 → (1 × 1)) structural transition and a couple of spikes due to an order (at +0.86 V)/disorder (at +0.84 V) transition of adsorbed sulfate anions were observed. Almost no current flowed at potentials more positive than the potential of the order transition peak up to 1.05 V, and

2.3. Procedures. Prior to each measurement, the Au(111) and Au(100) disks were flame annealed using a Bunsen burner or a hydrogen flame and were slowly cooled in air. It was then transferred to the spectroelectrochemical cell with a drop of pure water on the surface to avoid any surface contamination. Measurements were carried out in a 50 mM H2SO4 electrolyte solution, which was deaerated by passing the ultrapure N2 gas through the solution for more than 30 min before it was injected to the cell. The electrode made contact with the electrolyte solution while keeping the potential at 0 V (vs Ag/AgCl), where the electrode surfaces were reconstructed. Only the (111) or (100) face was in contact with the electrolyte solution during the electrochemical measurements. Electrode potential was scanned for the positive direction from 0 V and was stopped at a certain potential, where the SXS measurement was going to be carried out, while keeping the thickness of the solution layer between the electrode and Mylar window at ca. 5 mm (thick electrolyte configuration). After that, the electrode surface was pushed to the Mylar window (thin electrolyte configuration) so that the X-ray scattering by the solution was kept at a minimum and no further electrochemical reaction proceeded. The thickness of the electrolyte layer between the electrode and the window in this configuration was estimated to be ca. 30 µm. The cell was turned over and then the in situ SXS measurement was carried out.48

2.4. Data Analysis. In the reflectivity curves, several peaks of the scattering intensity near L = 0, 3, and 6 (H = K = 0) for Au(111) and near L = 0, 2, and 4 for Au(100) were observed. The peaks around L = 3 and 6 for Au(111) correspond to the cubic (1, 1, 1) and (2, 2, 2), respectively, and those around L = 2, and 4 for Au(100) correspond to the cubic (1, 0, 0) and (2, 0, 0), respectively. Between these peaks, the reflectivity was low and depended on the detailed structure of the interface. Structures along the normal direction to the electrode surface were quantitatively determined from the least-square fitting to the reflectivity data with a kinematical calculation based on a specific interfacial model.39,46,53,54 All the fittings were carried out using models of three layers on top of the Au substrate. The amounts of various atoms in each layer were estimated by considering that one monolayer (ML) corresponds to 1.39 Å2. The fitting, a three-layer structure model, where the electron density of the oxygen atom is neglected, was taken as a best-fitted result.

For the gold oxide layers, the contribution of oxygen was neglected, because the electron density of the oxygen atom is only 10% of that of the gold atom.
only a very small anodic current was observed at potentials more positive than +1.05 V before the oxide formation. These features were exactly the same as those of high-quality Au(111) electrodes, indicating that the quality of the Au(111) surface used in the present study was very high.

SXS measurements were carried out at potentials indicated by arrows A–F in Figure 1, and the reflectivity profiles measured at these potentials are shown in Figure 2. Values of standard errors of the scattered X-ray intensity were shown as error bars in the figure. The structure parameters obtained from the least-square fitting with a kinematical calculation at various potentials are listed in Table 1. On the basis of these values obtained from a fitting, the structures along the direction normal to the surface at the Au(111) electrode/H₂SO₄ electrolyte solution interface were determined as described below.

A. At 0 V Before Potential Scan. Best-fit data showed that the interfacial structure at this potential is the Au(111)-(√3 x 23) reconstructed surface covered with 0.74 ML of oxygen species as schematically illustrated in Figure 3A, and the distance between the oxygen species and the topmost Au layer was 2.31 Å (Table 1). The present results are in good agreement with those suggested by Ocko et al. from the X-ray reflectivity data for a Au(111) electrode in a 0.1 M HClO₄ solution containing various halogen anions, where the Au(111) surface was reconstructed in a relatively negative potential region with the Au(111)-(√3 x 23) structure covered with a double layer of water molecules, with the coverage of 0.7 and 0.3 ML for the first and second layers, respectively, and the distance between the first water layer and the topmost Au layer was 2.9 Å.39–41

B. At +0.95 V. Figure 2B shows the reflectivity profiles measured at +0.95 V, which was more positive than the potential of the current spike (Figure 1). Best-fit data showed that at this potential the reconstruction was lifted, and the Au(111)-(1 x 1) substrate was covered, with the first, second, and third layers composed of 0.88 ML of oxygen, 0.22 ML of sulfur, and 0.24 ML of oxygen species, respectively, as schematically illustrated in Figure 3B. The distances between the outermost Au layer and the first, the first and the second, and the second and the third layers were 2.37, 1.08, and 1.86 Å, respectively (Table 1). These numbers are in good agreement with those estimated from a model proposed by Kolb et al., based on STM.20 and by Ataka and Osawa, based on IR.56 They suggested that the sulfate anion (SO₄²⁻ or HSO₄⁻) and hydronium ion (H₃O⁺) were coadsorbed on the Au(111)-(1 x 1) surface with a (√3 x √7)R19.1° structure with a molar ratio of 1:1 through three oxygen atoms and three hydrogen atoms, respectively.

Relatively large root mean square (rms) values of these layers (Table 1) reflect the relatively rough surface of the Au(111)-(1 x 1) as a result of a lifting of the (√3 x 23) reconstructed structure.

C. At +1.05 V. Figure 2C shows the reflectivity profiles measured at +1.05 V, where very small anodic current flowed (Figure 1). Best-fit data showed that the Au(111)-(1 x 1) substrate was covered with the first, the second, and the third layers composed of 1.00 ML of gold, 0.040 ML of gold, and 1.00 ML of oxygen species, respectively, as schematically illustrated in Figure 3C. The distance between the second layer...
slightly different from the value (1.5 Å) obtained by STM 18 calculated from the present data was ca. 2.3 Å. This value was desorbed and oxygen species were adsorbed onto the Au(111)-

Because STM data did not show the real geometric height but closely matched the calculated value (2.14 Å) when the oxygen atom was adsorbed at the atop site of the Au substrate. The schematic illustrations of the Au(111) electrode/H2SO4 solution interface at various potentials. Hydrogen atoms are not shown because their positions cannot be determined by SXS measurements. 55

TABLE 1: Structural Parameters Obtained from the Analyses of the Specular Rod Profiles at Au(111) Electrode/electrolyte Interface at Various Potential Regions as a Three-layers Model on Au(111)*

<table>
<thead>
<tr>
<th>Potential Region</th>
<th>f_m1</th>
<th>f_m2</th>
<th>f_m3</th>
<th>f_Au</th>
<th>f_O</th>
<th>f_S</th>
<th>f_Au</th>
<th>f_O</th>
<th>f_S</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 V (before potential cycle)</td>
<td>2.36 ± 0.01</td>
<td>2.37 ± 0.02</td>
<td>2.36 ± 0.02</td>
<td>2.99 ± 0.03</td>
<td>2.36 ± 0.03</td>
<td>2.43 ± 0.03</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.95 V</td>
<td>2.43 ± 0.01</td>
<td>1.08 ± 0.03</td>
<td>2.36 ± 0.01</td>
<td>2.50 ± 0.05</td>
<td>1.07 ± 0.04</td>
<td>2.90 ± 0.02</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.05 V</td>
<td>2.31 ± 0.02</td>
<td>1.86 ± 0.03</td>
<td>−0.08 ± 0.01</td>
<td>1.55 ± 0.04</td>
<td>1.86 ± 0.03</td>
<td>0.43 ± 0.03</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.40 V</td>
<td>1.00 ± 0.01</td>
<td>0.88 ± 0.02</td>
<td>1.00 ± 0.02</td>
<td>0.73 ± 0.02</td>
<td>0.87 ± 0.02</td>
<td>1.00 ± 0.02</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Coverage, ρ_m1/ML</td>
<td>0.09 ± 0.01</td>
<td>0.26 ± 0.02</td>
<td>0.09 ± 0.01</td>
<td>0.63 ± 0.03</td>
<td>0.14 ± 0.02</td>
<td>0.09 ± 0.04</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Coverage, ρ_m2/ML</td>
<td>0.13 ± 0.01</td>
<td>0.50 ± 0.03</td>
<td>0.13 ± 0.03</td>
<td>0.67 ± 0.04</td>
<td>0.13 ± 0.02</td>
<td>0.73 ± 0.03</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Coverage, ρ_m3/ML</td>
<td>0.37 ± 0.02</td>
<td>0.36 ± 0.03</td>
<td>0.99 ± 0.05</td>
<td>1.11 ± 0.03</td>
<td>0.43 ± 0.03</td>
<td>0.39 ± 0.03</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* The atomic form factors, f_m1, f_m2, and f_m3 represent first layer, second layer, and third layer, respectively. The subscripts of m1, m2, and m3 represent first layer, second layer, and third layer, respectively. Distances of z_m12, z_m23, and z_m3 represent atomic distances between the outermost substrate and first layers, between first and second layers, and between second and third layers, respectively.

...and the second layer was less than 1 ML showed that gold atoms coexisted with oxygen atoms, indicating that gold oxide was formed, although we cannot determine the fraction of oxygen atoms in these oxide layers. The schematic illustration of the interfacial structure is shown in Figure 3D. As a result of the penetration of oxygen atoms into the gold surface layers, the distances between the outermost layer of the gold substrate and the first layers and between the first and second layers were 2.90 and 2.50 Å, respectively, and were larger than the value (2.56 Å) of the bulk Au(111).

The above result supports the model proposed by Conway et al. based on the results of conventional electrochemical measurements that the two-atom thick oxide layer was formed as a result of a turnover reaction. 7,8 The total number of gold atoms in these oxide layers was equivalent to 1.04 ML, which was...
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3.2. Au(100) Electrode. Figure 4 shows a CV of a Au(100) single-crystal electrode in a 50 mM H2SO4 electrolyte solution obtained under the thick electrolyte configuration. Sharp anodic and cathodic peaks were observed at +1.11 V and +0.93 V, respectively. The former peak can be assigned to the oxide formation and the latter to the reduction of oxide. Another small anodic current was also observed around +1.05 V. The inset of Figure 4 shows a CV in the narrower potential range (0 through +1.00 V) with a magnified current scale. A pronounced anodic peak due to a hexagonal closed-packing \( (1 \times 1) \) structural transition was observed at +0.39 V. These features were exactly the same as those of high quality Au(100), indicating that the quality of the Au(100) surface used in the present study was very high. SXS measurements were carried out at the potentials indicated by arrows A–F in Figure 4.

Figures 5 shows the reflectivity profiles measured at various potentials shown in Figure 4. Values of standard errors of the scattered X-ray intensity were shown as error bars in the figure. The structure parameters obtained from the least-square fitting with a kinematical calculation at various potentials are listed in Table 2. On the basis of these values obtained from a fitting, the structures along the direction normal to the surface at an Au(100) electrode/H2SO4 electrolyte solution interface were determined as below.

A. At 0 V Before Potential Scan. Best-fit data showed that the reconstructed hexagonal closed-packed Au(100) surface was covered with 1.02 ML of oxygen species, as schematically illustrated in Figure 6A. The distance between the second (gold) and the third (oxygen species) layers (1.98 Å) was shorter, the coverage of the third layer (oxygen species) of 1.02 ML was higher, and the rms value of the second layer (outermost gold layer) of 0.52 was larger than those in the case of Au(111). These values suggest the presence of several Au clusters with oxygen species on the reconstructed surface and indicate that the surface flatness of reconstructed Au(100), even just after annealing and quenching, is slightly less than that of reconstructed Au(111).

B. At +0.95 V. Figure 5B shows the reflectivity profiles measured at +0.95 V. Best-fit data showed that the first, the second, and the third layers on the Au(100)-(1 \( x \times 23 \)) surface with a (1.4 \( x \times 3.6 \)) structure with a molar ratio of 1:1 through two oxygen atoms and three hydrogen atoms, respectively. Relatively large rms values of these layers are due to the relatively rough surface of the Au(100)-(1 \( x \times 1 \)) as a result of a lifting of the reconstructed hexagonal closed-packed structure.

C. At +1.05 V. Figure 5C shows the reflectivity profiles measured at +1.05 V, around which only a very small anodic current flowed (Figure 4). Best-fit data showed that the first, the second, and the third layers on the Au(100)-(1 \( x \times 1 \)) substrate were composed of 1.00 ML of gold, 0.16 ML of gold, and 1.01 ML of oxygen species, respectively. The schematic illustration of the interfacial structure is shown in Figure 6C. The distance between the second (gold) and the third (oxygen species) layers (1.98 Å) was shorter, the coverage of the third layer (oxygen species) of 1.02 ML was higher, and the rms value of the second layer (outermost gold layer) of 0.52 was larger than those in the case of Au(111). These values suggest the presence of several Au clusters with oxygen species on the reconstructed surface and indicate that the surface flatness of reconstructed Au(100), even just after annealing and quenching, is slightly less than that of reconstructed Au(111).
species) layers was 0.26 Å, which was very small, indicating that the gold surface was expanded. This result indicated that the adsorbed sulfate anion at +0.95 V was desorbed, and oxygen species were adsorbed on the Au(100)-(1×1) surface. The height of the layer of oxygen species calculated from the present data was ca. 2.3 Å, showing that the oxygen species were adsorbed at the atop site of the underlying Au(100)-(1×1) surface.

D. At +1.40 V. As observed at the Au(111) electrode, when the potential was kept at +1.40 V, X-ray scattering intensity from the Au(100)/electrolyte solution interface changed with time, even in the thin electrolyte configuration. Thus, the SXS measurement was carried out not at +1.40 V but at +1.10 V. The positive-going potential scan was reversed at +1.40 V and was scanned negatively with a scan rate of 20 mV s⁻¹. As soon as the potential became +1.10 V, the potential scan was stopped, the electrode surface was pushed to the Mylar window, and reflectivity measurement was started. Data obtained at this potential was considered to be the one at +1.40 V as was the case at the Au(111) electrode.

Figure 5D shows the reflectivity profiles measured at +1.10 V. Best-fit data showed that the first, the second, and the third layers on the Au(100)-(1×1) substrate were composed of 0.73 ML of gold, 0.43 ML of gold, and 1.01 ML of oxygen species, respectively. As was case at the Au(111) electrode, the first and the second layers should consist of Au oxide, as a result of a turnover reaction. The schematic illustration of the interfacial structure at this potential is shown in Figure 6D.

The total number of gold atoms in these oxide layers was 1.16 ML, which was exactly the same as that of the coverage of the reconstructed Au(100) surface observed at 0 V. This result indicates that only the gold atoms in the outermost layer are electrochemically oxidized in the potential cycle up to +1.40 V, confirming that we can calculate the real surface area of Au(100) from the charge of the oxide reduction peak as in the case for the Au(111) electrode.

E. At +0.65 V. Figure 5E shows the reflectivity profiles measured at +0.65 V, which is more negative than that of the oxide reduction peak in Figure 4. Best-fit data showed that the first, the second, and the third layers on the Au(100)-(1×1) substrate were composed of 0.61 ML of oxygen species, 0.22 ML of sulfur, and 0.41 ML of oxygen species, respectively. This result closely matched that obtained at +0.95 V in the positive-going scan. Furthermore, the distances between the substrate and the first layer, the first layer and the second layer, and the second layer and the third layer (Table 2) were all in good agreement with those obtained at +0.95 V before the oxide formation. Thus, the interfacial structure at this potential is same as that obtained at +0.95 V in the positive-going scan (Section B), indicating that the sulfate and H₂O²⁻ were coadsorbed with a (1.4×3.6) structure through two oxygen atoms and three hydrogen atoms, respectively, as schematically illustrated in Figure 6E. One must note, however, that lateral order of the adsorbates cannot be confirmed based only on the reflectivity data.

F. At 0 V. Figure 5F shows the reflectivity profile measured at 0 V after a potential cycle. Best-fit data showed that the Au(100)-hexagonal closed-packing reconstructed surface was covered with 0.99 ML of oxygen species, as well as that measured at 0 V before the potential cycle; the first, the second, and the third layers on the Au(100)-(1×1) substrate were composed of gold, gold, and oxygen species, respectively. The schematic illustration of the interfacial structure is shown in Figure 6F. The comparison of the structural parameters measured at 0 V before and after the potential cycle showed that the distances between the first and second layers and between the second and third layers, coverage of O and Au atoms in the outermost two layers, and rms values of the all three layers became slightly larger after the potential cycle. These results indicate that small Au clusters existed on the reconstructed hexagonal closed-packed Au(100) surface (i.e., the surface was roughened). This is in good agreement with the well-known fact that once the gold electrode surface is oxidized, oxygen atoms penetrate into the outermost gold layer, and the electrode surface is roughened even after the complete reduction of the surface oxide.22,52 The degree of the roughening on Au(100)


### Conclusion

The potential dependent structures of single-crystalline Au(111) and Au(100) electrodes were investigated in a sulfuric acid solution in wide potential regions (0 through +1.4 V) at an atomic level using an in situ SXS technique. At all potentials, the obtained reflectivity profiles were well-fitted using schematic three-layer models for the interfacial structure along the direction normal to the surface. It was confirmed that both Au(111) and Au(100) surfaces were reconstructed with an attached submonolayer of oxygen species at 0 V, the reconstruction was lifted, and the sulfate anion and H$_3$O$^+$ were coadsorbed at both electrodes at +0.95 V, as previously reported for both electrodes.

At +1.05 V, where a very small anodic current flowed, adsorption of a monolayer of oxygen species at the atop site of both the Au(111)-(1×1) and Au(100)-(1×1) surfaces was suggested. When the single-crystalline gold electrodes were electrochemically oxidized at +1.40 V, the gold surface was expanded by ca. one monolayer of Au atoms. The formation of two layers of surface oxide as a result of a penetration of oxygen into the surface gold layer was suggested. When the surface oxide was reduced at +0.65 V, the surface structure returned back to the (1×1) structure with coadsorbed sulfate anion and H$_2$O$^+$. When the potential was reduced to 0 V, both surfaces were reconstructed again but with slightly more random atomic arrangement than before the potential cycle.

### Acknowledgment

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### References and Notes


### Table 2: Structural Parameters Obtained from the Analyses of the Specular Rod Profiles at Au(100) Electrode/electrolyte Interface at Various Potential Regions as a Three-layers Model on Au(100)$^{x}$

<table>
<thead>
<tr>
<th>Potential (V)</th>
<th>f$_{Au}$</th>
<th>f$_{O}$</th>
<th>f$_{S}$</th>
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**Note:**

The atomic form factors, $f_{Au}$, $f_{O}$, and $f_{S}$ are of Au, O, and S, respectively. The term $f_m$ means the atomic form factor of specie of m. The subscripts of m1, m2, and m3 represent first layer, second layer, and third layer, respectively. Distance of $z_{m1}$, $z_{m2}$, and $z_{m3}$ represent atomic layer distances between the outermost substrate and first layers, between first and second layers, and between second and third layers, respectively.

![Figure 6](image-url)  
**Figure 6.** The schematic illustrations of the Au(100) electrode/H$_2$SO$_4$ solution interface at various potentials. Hydrogen atoms are not shown because their positions cannot be determined by SXS measurements.
(53) X-ray scattering by hydrogen atoms is so weak that we cannot determine the chemical nature of oxygen species, which can be an oxygen atom, OH, OH− ion, water molecule, H2O2, or sulfate anion, although sulfate anion can be distinguished by using the information for sulfur atoms.
(54) Kondo et al.