Step-by-step Investigation of Atomically Flattening Processes of Au(111) Single Crystal Surfaces

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ABSTRACT

Flattening processes of a commercially available Au(111) single crystal surface were step-by-step investigated using atomic force microscopy (AFM), scanning tunneling microscopy (STM), energy dispersive X-ray (EDX) spectroscopy, and X-ray photoelectron spectroscopy (XPS) from a micron scale to an atomic dimension. AFM images in a micron scale showed that there were many scratches with a few nm depth on the as-received Au(111) disk surface. SEM, EDX, and XPS results indicated that there were surface contaminations such as carbon and silicon species. As a first, these contaminations could be removed by dipping the disk in concentrated H2SO4 and then in boiling concentrated HF. The scratches described above were disappeared after annealing by a gas flame, which is a most popular method for Au(111) single crystal preparation. After the electrochemical polishing and annealing in an electric furnace under argon atmosphere, finally, atomically flat Au(111) surfaces with dimensions of more than 500 × 500 nm² were obtained. With increasing of annealing period, larger terraces were obtained.

Keywords : Au(111) Single Crystal, Flattening, Atomic Force Microscopy, Scanning Tunneling Microscopy

1. Introduction

Electrochemical reactions take place not only on atomically flat terraces, but also on steps and kinks. In order to strictly understand electrochemical reaction mechanisms at an atomic level, however, electrochemical reactions should be observed on single crystal electrode surfaces with an ordered atomic arrangement, which means wider terraces, because electrochemical reaction mechanisms on terraces are different from those on steps and kinks.1–3 Since Clavilier et al. investigated single crystal electrodes4 and since in situ scanning probe microscopy (SPM) techniques, including scanning tunneling microscopy (STM) and atomic force microscopy (AFM), were employed in electrochemistry,5,6 the use of single crystal electrodes has dramatically spread in the past three decades. Among them, the Au(111) single crystal electrode is one of the most useful electrodes, because it is relatively easy to prepare and purchase. Moreover, Au(111) was often used as a substrate for alkyl thiol self-assembled monolayers (SAMs), which are chemisorbed on the gold surface with a high molecular density and high degree of orientation.7,8 Facet planes, which can be prepared by the heating of a gold wire with a gas flame, were usually used as Au(111) electrode substrates in the SPM measurements. However, this plane cannot be used for the normal electrochemical measurements, because not only the facet planes but also other planes are exposed to the electrolyte solution. Therefore, the surface should be mechanically polished and used in a meniscus mode for the electrochemical measurements. Single crystals can be commercially available and there are some reports using the commercially available Au(111) single crystal disks as electrodes,6,9,10 or as a substrate for the SAMs during the electrochemical measurements.11,12 However, there are few detailed reports about the fundamental preparation methods of atomically flat Au(111) single crystal surfaces. Actually, as-received Au(111) single crystal disk surfaces and the disk surfaces after mechanical polishing exhibit many scratches and many small particles, that must form during the polishing and/or delivering, which were observed in this work. Thus, the surface must be cleaned and made atomically flat for the precise electrochemical measurements. Therefore, we report here the cleaning and flattening processes of the Au(111) single crystal surface after various treatments using AFM, STM, scanning electron microscopy (SEM), energy dispersive X-ray (EDX) spectroscopy, X-ray photoelectron spectroscopy (XPS), and electrochemical measurements.

2. Experimental

2.1 Materials

The Au(111) single crystal disk was purchased from Surface Preparation Laboratory (The Netherlands). Ultrapure reagent grade chemicals such as H2SO4, HClO4, HF, and NaCl were obtained from VWR International and used as received. Ultrapure N2 and Ar gases (99.999%) were purchased from AIR LIQUID. Platinum wire as a counter electrode was purchased from Nilaco, and Hg/HgSO4 (sat. Na2SO4) as a reference electrode was purchased from AutoLab. The electrode potential values were referenced to the reversible hydrogen electrode (RHE). Ultrapure water was obtained by a Milli-Q purifying system (MILLIPORE).

2.2 Procedures

The Au(111) surface was cleaned and flattened by several methods such as i) keeping in concentrated H2SO4 for a night, ii)
keeping in boiling concentrated HF for an hour, iii) flame-annealing by a gas burner for a few minutes, iv) electrochemical polishing in 0.1 M HClO₄ containing 5 mM NaCl at a constant current of 0.01 µA for 2 days, and v) annealing in an electric furnace (HTM Reetz GmbH, LOBA 1100-28-200-1) at 900°C for several hours under ultrapure Ar atmosphere.

2.3 Apparatus

The AFM measurements were performed using a MultiMode V (Veeco Instruments, Inc.) in air at room temperature. The cantilevers (Arrow NC-W, Nanoworld) were used for tapping mode and the cantilevers (NP-S, Bruker) used for contact mode. Their force constants were 42 and 0.24 N/m, respectively. Most of AFM images were observed by tapping mode, but only atomic image was observed by contact mode. STM measurements were performed using an Agilent 5500 SPM microscope. STM images were obtained in air at room temperature with a Pt/In wire. The SEM/EDX measurements were carried out using a QUANTA 200 (FEI Company) using TaLIII electron beam. The XPS measurements were carried out using a K-Alpha (Thermo Fisher Scientific) using the AlKα X-ray beam. The electrochemical measurements were carried out using a potentiostat and function generator system (Solartron, 1286) in a conventional three-electrode cell in the meniscus mode. Before the measurements, the electrolyte solution was deaerated by purging with ultrapure N₂ for more than 30 minutes.

3. Results and Discussion

3.1 Storage in conc. H₂SO₄ (step i)

Figure 1(a) shows an AFM image of the as-received Au(111) surface without any treatments. It can be clearly seen in this figure that there were many scars like a skin on the surface. Although depth of them was only a few nanometers, length of them was more than a few hundreds nanometers. These scars seemed to be formed during mechanical polishing of the crystal surface. Moreover, these scars were not clearly seen in this image probably due to organic impurities on the surface. Actually, two oxidation current peaks not only due to surface oxide formation of the Au(111) surface but also due to an oxidation of the surface organic contamination at 1.6 V (vs. RHE) and 1.4 V, respectively, were observed in the cyclic voltammogram (CV), shown in Fig. 1(b). In order to remove such organic contamination, the disk was kept in conc. H₂SO₄. Figure 1(c) shows the AFM image of the Au(111) surface after keeping in conc. H₂SO₄ overnight. The scars on the Au(111) surface were clearly seen, indicating that surface organics were completely removed.

3.2 Storage in boiling HF (step ii)

In order to confirm the removing of organics, SEM and EDX measurements were carried out. Figure 2(a) shows the SEM image of the Au(111) disk surface after storage in conc. H₂SO₄. Some black dots with a size of a few hundreds nanometers can be seen. These dots should be elements except gold. In order to check which elements these dots were, one of these dots was analyzed by the EDX measurement. Figure 2(b) shows EDX spectrum of the dot, which was observed in the SEM image [Fig. 2(a)]. We clearly found that dot consisted of silicon and oxygen, indicating that SiOₓ species existed on the surface, which might be got mixed during mechanical polishing. Thus, in order to remove surface contaminations such as SiOₓ, the Au(111) disk was kept in boiling HF for an hour. Figure 3 shows X-ray photoelectron spectra of the Au(111) disk surface before and after the HF treatment. A peak around 103 eV in the spectrum before the HF treatment [Fig. 3(a)] also indicated that SiOₓ species existed on the surface. As expected, after the HF treatment, the Si 2p peak due to SiOₓ species disappeared [Fig. 3(b)], showing that contaminations were completely removed from the surface.

3.3 Flame-annealing (step iii)

After the HF treatment, in order to remove the scratches which were observed by AFM [Fig. 1(b)], the Au(111) disk surface was flame-annealed for a few minutes, which is a most popular method for Au(111) single crystal preparation. Figure 4(a) shows the STM image after the flame-annealing. By the flame-annealing, scratches were completely disappeared from the surface. Moreover, terraces with a size of ca. 30 nm and steps with a height of ca. 0.3 nm were observed. Relatively sharp oxidation current peak in the CV [Fig. 4(b)] also indicated that the surface became flatter as a (111) face.

3.4 Electrochemical polishing (step iv)

After the above treatments, in order to make the terraces wider,
the Au(111) surface was electrochemically polished in 0.1 M HClO₄ containing 5 mM NaCl with a constant current of 0.01 µA over 2 days. Figure 5 shows the STM image of the Au(111) disk surface after the electrochemical polishing. The disk surface became flatter as compared with that before this treatment [Fig. 4(a)], indicating that the electrochemical polishing is more suited to flatten the Au(111) surface than the flame-annealing, because of a layer-by-layer dissolution of the Au surface. However, the thickness of the top terrace to the bottom terrace in Fig. 5 was ca. 1.5 nm, i.e., the numbers of the terrace was 5–7 in the 1 µm² image, indicating that many terrace layers still existed on the disk surface even after the electrochemical polishing. In addition, some particles, which should be Au, were present at a kink site on the surface. These Au particles seemed to be precipitated and aggregated after once dissolving.

3.5 Electric furnace annealing (step v)
Finally, the Au(111) surface was annealed using the electric furnace at 900°C under Ar atmosphere for an hour, 5 hours, and 24 hours, in order to remove the particles, which were observed at the kink site in Fig. 5 and to make wider the terraces, i.e., to reduce the number of terrace. Figure 6 shows the AFM images of the Au(111) disk surface after the electric furnace annealing for several periods. As can be clearly seen, the Au(111) disk surface became flatter and
the numbers of terrace decreased with increasing annealing period. Actually, very wide Au(111) terraces (more than 500 × 500 nm²) were obtained after 24 hours annealing [Fig. 6(c)]. The numbers and size of particles, which were observed before this treatment (Fig. 5), decreased and increased, respectively, with increasing annealing period. It is considered that the redundant gold atoms, which were appeared during making wider terraces, were assembled at the kink sites. Moreover, triangle edges can be observed in the STM image [Fig. 7(a)] and gold atomic image was observed by AFM in contact mode [Fig. 7(b)]. In addition, the sharp oxidation and reduction peaks, which were as exactly same as one measured at the typical Au(111) electrode, were observed [Fig. 7(c)], indicating that the (111) atomic arrangement on the most of all area of the Au(111) disk surface was obtained.

Figure 6. (Color online) AFM images of the Au(111) disk after annealing in the electric furnace for (a) an hour, (b) 5 hours, and (c) 24 hours.

Figure 7. (Color online) (a) STM image (I_tip = 0.5 nA, V_sample = 0.3 V) and (b) AFM image (contact mode) of the Au(111) disk surface after all treatments. (c) CV of the Au(111) electrode after all treatments, measured in a deaerated 50 mM H₂SO₄ with a scan rate of 20 mV s⁻¹. Inset: CV with an expanded current scale in the potential range between 0.3–1.3 V, measured with a scan rate of 5 mV s⁻¹.

4. Conclusions

Flattening processes of commercially available Au(111) single crystal surface were step-by-step investigated using atomic force microscopy (AFM), scanning tunneling microscopy (STM), scanning electron microscopy (SEM), energy dispersive X-ray (EDX) spectroscopy, and X-ray photoelectron spectroscopy (XPS). We found major factors in preparing atomically flat surface, such as removing contaminations and annealing for longer time after electrochemical polishing. Flame-annealing is generally used to make facet, however, it has been proved that its effect is for only
small area. Longer annealing by electric furnace has most impact to flatten the Au(111) disk surface. Finally, the Au(111) surface with much wider terraces more than 500 × 500 nm² can be prepared.

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