

Keysight Technologies
Oxygen-Free High-Resolution
Electrochemical SPM

Application Note



Introduction

For two decades, scanning probe microscopy (SPM) has provided scientists a unique tool to study *in situ* electrochemical processes with atomic/molecular resolution. During this time, remarkable progress has been made at the interface of electrochemistry (EC) and SPM. New discoveries continue to be reported as the research boundary expands wider and deeper. While the field steadily advances, the requirements for electrochemical scanning probe microscopes also become greater. In addition to clean liquid imaging and atomic resolution, an oxygen-free environment is now considered critical for many EC SPM studies.

In this application note, the oxygen-elimination capability of the standard environmental chamber of the Keysight Technologies, Inc. 5500 AFM is thoroughly characterized. As an example of oxygen-free applications, reductive desorption potentials of alkanethiol self-assembled monolayers (SAMs) on Au (111) surface were measured. *In situ* high-resolution capability was demonstrated with the well-known transition between Au (1 x 1) atomic lattice and Cu ($\sqrt{3} \times \sqrt{3}$) under potential deposition (UPD) structure on Au (111) surface at different electrochemical potentials.

Experiment

For oxygen measurements, a 5500 AFM base with an atomic STM scanner was set up in an environmental chamber the same way as for imaging. The chamber was purged with high-purity nitrogen gas through one of the eight built-in ports. The oxygen concentration inside the chamber was measured with a TPI 708 oxygen analyzer, which can detect the oxygen level down to 0.1%. Lower levels of oxygen were monitored directly from cyclic voltammetry.

An electrochemical cell using 0.1 M H₂SO₄ electrolyte was controlled by an internal potentialstat for the 5500 AFM. The working electrode was hydrogen flame-annealed Au (111) surface, the quasi-reference electrode was Ag wire, and the counter electrode was Pt wire. All potentials were measured against the quasi-reference electrode. The ramp range of cyclic voltammetry was from the beginning of hydrogen evolution to the Au oxidation peak at a rate of 20 mV/sec. The liquid cell was about 6 mm in diameter, providing ~28 mm² working electrode area. The cell and electrodes were thoroughly cleaned in detergent and acid and rinsed with 18 MΩ·cm⁻¹ water before the electrolyte was applied.

For the experiment of reductive desorption of alkanethiol SAMs, hexanethiol (C6), octanethiol (C8), decanethiol (C10), and octadecanethiol (C18) were purchased from Sigma-Aldrich. Cyclic voltammetry was measured in 0.5 M KOH solution, also using Ag for the quasi-reference electrode and Pt for the counter electrode. The ramp was approximately from -0.1 V to -1.2 V with a rate of 10 mV/sec.

For Cu UPD, the electrolyte was 0.1 mM H₂SO₄ containing 5 mM Cu²⁺. Sample potentials were measured against a Cu quasireference electrode. Images were acquired with a small AFM scanner in contact mode.

Results and discussion

I. Oxygen characterization of the environmental chamber

Figure 1 shows a set of cyclic voltammograms for 0.1 M H₂SO₄ on Au (111) at different oxygen concentrations. Green plots represent ramp-down potential and blue plots represent ramp-up. In ambient, where the oxygen is 20.9%, the electrochemical current measured from the counter electrode started to increase as the potential was decreased to 0.1 V, as shown in Figure 1(a). Its amplitude reached a maximum at about -0.02 V

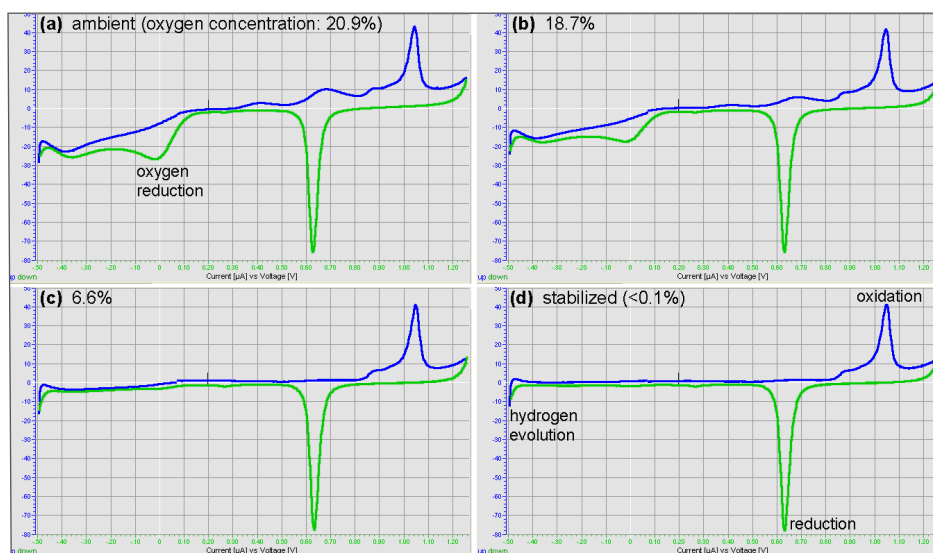
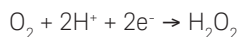


Figure 1. Cyclic voltammograms for 0.1 M H₂SO₄ on Au (111) at different oxygen concentrations.

(versus Ag quasi-reference electrode). This potential corresponds to the reduction of the oxygen in the electrolyte to hydrogen peroxide.



After the oxygen-reduction peak, the strong background current continues. Sensitive electrochemical processes in this range would be very difficult to detect because of the presence of oxygen.

With the decrease of the oxygen concentration inside the chamber, the amplitude of the background current below 0.1 V was decreased noticeably, as shown in Figures 1(b) and 1(c). When the oxygen was not detectable, the voltammogram was stabilized (Figure 1(d)). The stabilized voltammogram remained unchanged for hours with continuous purge of nitrogen.

It took less than 5 minutes of continuous nitrogen purge at a pressure of 10 to 20 psi to reduce the oxygen concentration of the chamber from ambient to 0.1%. In order to reach the level where the oxygen was not detectable, as shown in the stabilized voltammogram, approximately an additional 15-minute purge was needed.

Figure 2 shows six continuous cyclic voltammograms in 21 minutes of nitrogen purge, starting from ~5% oxygen concentration. Slight changes on the background current below 0.1 V were still observable in the first 12 minutes, as shown in Figures 2(a) to 2(c). From Figure 2(d), 15 minutes after purge, the voltammograms became stale, indicating that there was no detectable oxygen inside the chamber.



Figure 2. Continuous cyclic voltammograms in 21 minutes of purge from ~5% oxygen concentration.

The standard environmental chamber for the 5500 AFM is not designed for vacuum. If the nitrogen flow is completely **Move this text to page 5** chamber, driven by the entropy force tam-

mogram after the nitrogen flow was stopped. Oxygen became detectable after 20 to 30 minutes, as seen from the slightly observable background current below 0.1 V in Figures 3(e) and 3(f). With a slightly positive pressure, the chamber can be kept oxygen-free for many hours.

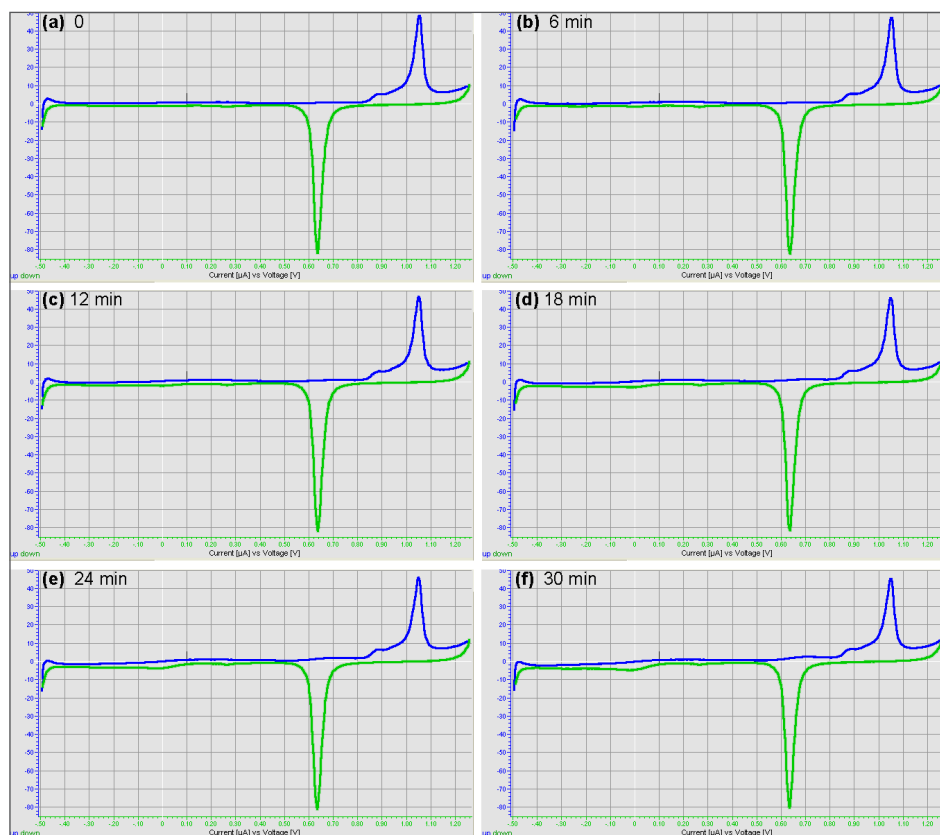


Figure 3. Continuous change in cyclic voltammograms after the nitrogen flow was completely stopped.

II. Reductive desorption of alkanethiol SAMs

As an example, an oxygen-free environment was used to study the reductive desorption of alkanethiol SAMs on Au (111) surface. Depending upon the number of carbon atoms and the type of end group on the alkanethiol molecule, the desorption potentials of alkanethiol SAMs vary from around -0.7 V to -1.0 V (versus Ag quasireference electrode).

Move to Page 5

Each of the C6, C8, C10, and C18 SAMs was prepared by leaving a Au (111) film in ethanol solution containing 2 mM of the corresponding molecules overnight. Figure 4 plots the reductive desorption voltammograms of all four SAMs. The measured desorption potentials of C6, C8, C10, and C18 were -0.69 V, -0.74 V, -0.85 V, and -0.98 V, respectively. These potentials are all below the oxygen-reduction potential. Without an oxygen-free environmental chamber, the peaks will not be visible because of the strong background current in the presence of oxygen, as shown in Figure 1.

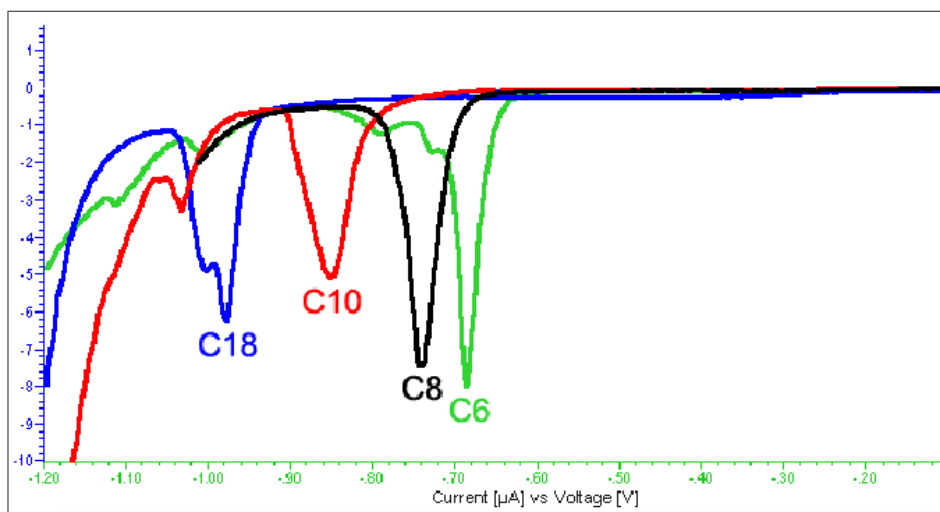


Figure 4. Voltammograms showing reductive desorption of C6, C8, C10, and C18 SAMs on Au (111).

III. High-resolution *in situ* EC SPM

Figure 5 demonstrates a typical experimental result of routinely observed Cu UPD deposition on Au (111). Figure 5(a) shows a continuous change of the topography image while the potential was ramped from 327 mV (top) to 157 mV (bottom). At 327 mV, the Au (1 x 1) atomic lattice was clearly resolved. After passing the UPD peak at ~0.24 V, SO_4^{2-} ions started to form $(\sqrt{3} \times \sqrt{3})$ structure. Near the bottom of the frame, when the potential reached 157 mV, SO_4^{2-} lattice was fully developed and clearly resolved. Figure 5(b) shows the reverse process from $(\sqrt{3} \times \sqrt{3})$ SO_4^{2-} structure to Au (1 x 1) atomic lattice while the potential was ramped from 157 mV (bottom) to 300 mV (top). Both atomic and molecular structures were clearly resolved. This *in situ* transition between the two states was very reproducible and easy to control.

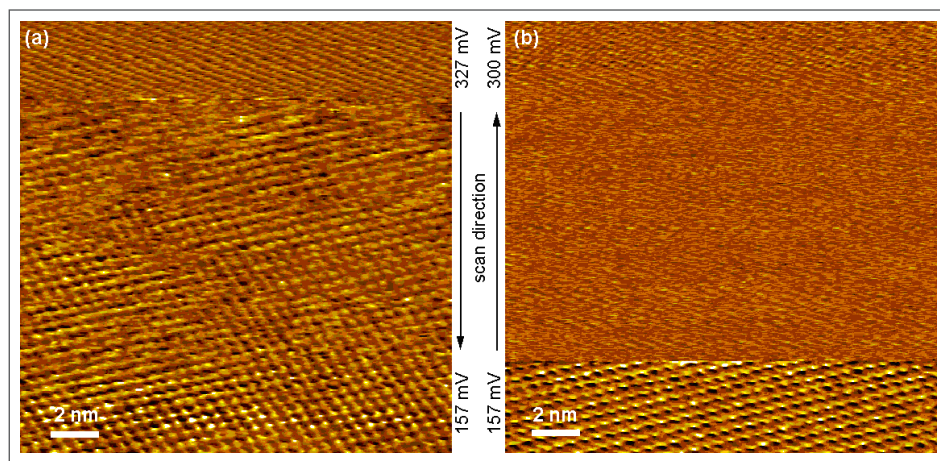


Figure 5. Transition between Au (1 x 1) atomic lattice (top) and SO_4^{2-} ($\sqrt{3} \times \sqrt{3}$) structure (bottom) on Au (111) surface during ramp of the sample potential.

Conclusion

The standard environmental chamber of the Keysight 5500 AFM has been fully characterized on its oxygen-removal ability. Reductive desorption potentials of alkanethiol SAMs were measured as an example to test the oxygen-free environmental chamber. Reproducibly observed atomic and molecular structures in the Cu UPD experiment clearly demonstrated the capability of the 5500 AFM for high-resolution *in situ* electrochemical SPM research.

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