In Situ Electrochemical Measurements Using Agilent 7500 AFM

Application Brief

Introduction

EC-SPM essentially combines two valuable, independent techniques: electrochemistry (EC) and scanning probe microscopy (SPM). The electrochemical unit includes a potentiostat and a three-electrode cell that controls the electrochemical state of the working electrode, usually the sample. The scanning probe microscope characterizes the surface of the solid electrode with either a passive or an active probe.

With a passive probe like that utilized in EC-AFM, the potential of the probe is not controlled. Thus, the AFM cantilever acts as an inert probe that monitors the topographic changes of the electrode surface caused by electrochemical processes (using standard AFM imaging modes).

On the other hand, with an active probe like that utilized in EC-STM, a bipotentiostat is used to control both the potential of the sample and the potential of the probe versus the same reference electrode. As with usual STM imaging, the tunneling current between the tip and the sample depends on the potential difference as well as the distance between the two, and is used as the control signal for STM image formation. In EC-STM, the morphological information about the electrode surface under potential control can be imaged in constant-current mode, and the changes in the localized electronic state of the electrode surface with electrochemical potential can be studied using “current vs. voltage” spectroscopy.

EC-SPM can deliver nanometer-scale resolution of the electrode surface in liquid. The true merit of EC-SPM, however, is the capability to control the experimental conditions (e.g., temperature and humidity) and mimic the real-world environment of the sample under test. This is particularly important for energy and corrosion research.

Instrumentation

The Agilent 7500 AFM/SPM microscope is a high-performance instrument that delivers high-resolution imaging with integrated environmental control functions. The standard Agilent 7500 includes contact mode, acoustic AC mode, and phase imaging. It comes with a universal scanner that is capable of operating in both open-loop and closed-loop mode. Switching imaging modes with the 7500 AFM/SPM microscope is quick and simple, a result of the scanner’s interchangeable, easy-to-load nose cones. Every 7500 AFM/SPM microscope utilizes the industry’s lowest-noise closed-loop scanner to provide the ultimate convenience and performance in imaging, without sacrificing resolution or image quality.

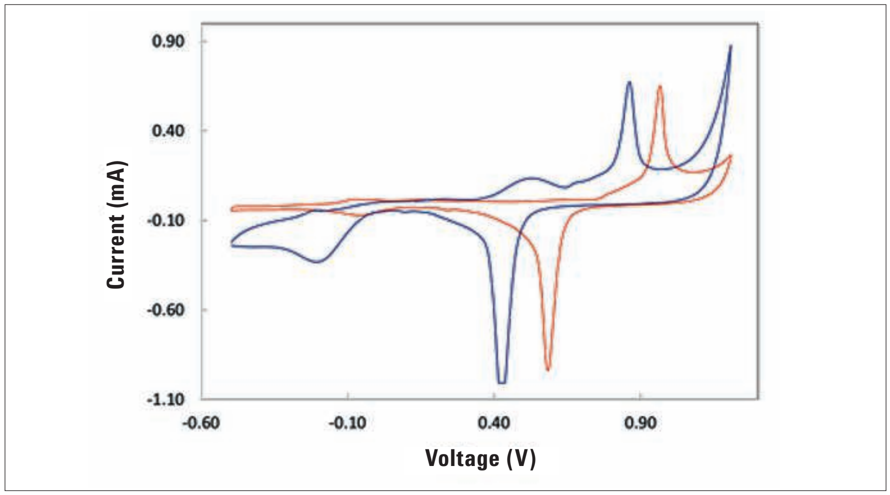
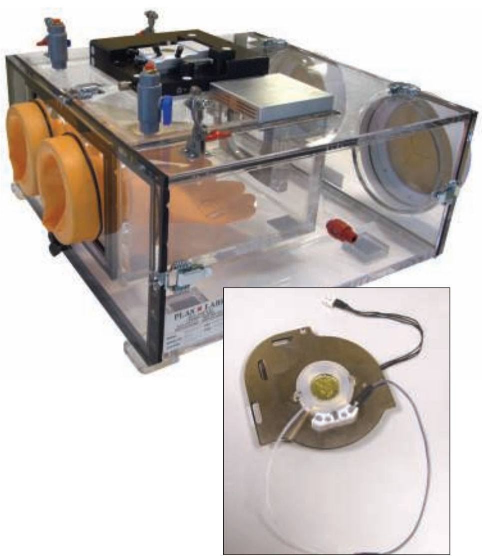


Figure 1. Oxygen level control by glove box. CV of Au in 0.1M H_2SO_4 recorded after 1 hr in N2 (red) and 30 min after exposure to air (blue).



Microscope on glove box. Inset: sample plate with the mini reference electrode (Ag/AgCl).

An optional EC glove box designed specifically for use with the 7500 features a dual-chamber design that allows samples to be prepared under environmental control (e.g., humidity, temperature, oxygen levels, reactive gases) in one area and then moved to an inner chamber directly underneath the microscope's head/scanner. An optional mini reference electrode (Ag/AgCl) provides a true reference and controls sample potential. The 7500 head on the glove box can be placed inside the Agilent Pico IC isolation chamber.

The Agilent 7500 can also be equipped with an optional bipotentiostat that enables stable electrochemistry control in either EC-AFM or EC-STM mode. The bipotentiostat offers a series of different sensitivity settings (10 nA/V, 100 nA/V, 1 µA/V, 100 µA/V, and 1 mA/V) covering four orders of magnitude of currents from 10 pA to 10 mA. Coupled with a specially designed liquid cell that allows the use of a mini-reference (Ag/AgCl) electrode for true potential control, instead of a quasi Ag wire reference as other EC-SPM systems do, the Agilent 7500 provides an outstanding imaging system for electrochemistry research.

Examples of EC-SPM Measurement

Electrochemical SPM has been applied to study a wide range of systems, including surface adsorption, film growth and dissolution, membrane ion transport, battery, fuel cell, photovoltaic, and catalysis. The examples below highlight only the basic EC-SPM capabilities of the Agilent 7500.

Oxygen-Free and Controlled Environments

Environmental control is critical for many EC-SPM experiments. For example, it has long been recognized that electrochemical processes are significantly affected by the amount of oxygen existing in the experimental environment. Therefore, the electrolyte and the cell in regular electrochemical experiments are often deoxygenated by purging inert gases such as N2 and Ar before or during the experiment.

The integrated environmental control system for the 7500 is capable of temperature control, humidity control, liquid exchange, and more (see Figure 1). This control is particularly useful for the sample preparation and transportation

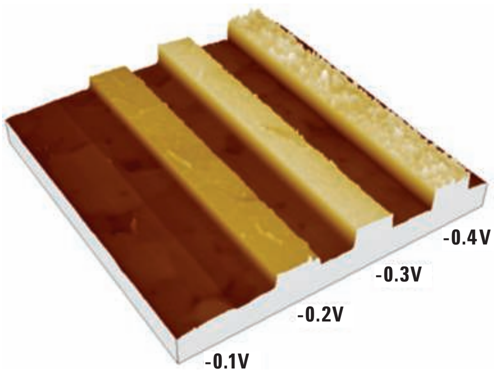
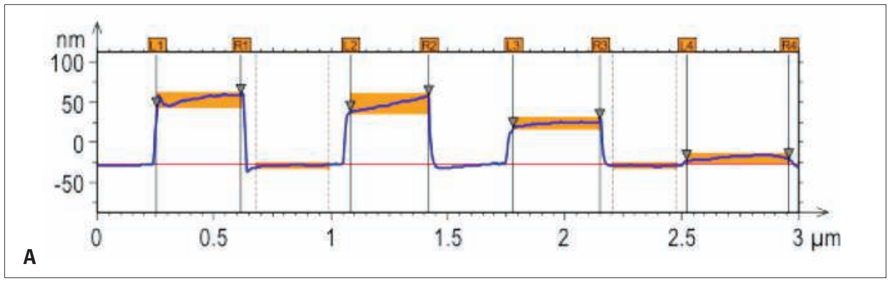


Figure 2. Three-dimensional EC-AFM topography image of Cu films deposited at different overpotentials.



Cu/Au \ Voltage	0.4 V	-0.1 V	-0.2 V	-0.3 V	-0.4 V
Thickness (nm)	0	10.4	53.0	77.2	84.2
Roughness (nm)	2.78	3.29	3.81	5.79	10.3

B

Figure 3. (A) Averaged topography line profile from the AFM image. (B) The estimated thickness and surface roughness of the Cu films deposited at different overpotentials.

often required for battery studies. With the help of the 7500's environmental control system, clean and "oxygen-free" conditions can be achieved to ensure proper electrochemical experiments. The oxygen level can be reduced from ambient (~21%) to less than 1% in about 5 minutes by N2 purging.

Copper Electrodeposition on Au

Electrodeposited copper is used extensively in microelectronics and microelectromechanical systems (MEMS), particularly in chip metallization such as contacts and interconnects and the filling of vias. As these processes and devices are continually driven toward the nanoscale, the need for more research into conditions affecting the electrochemical plating process arises. Electrochemical SPM techniques have been extremely beneficial in understanding the dynamics of nucleation and growth processes, and how additives and adsorption can inhibit or enhance these processes.

The simple experiment presented here examines the effect of overpotential on the kinetics and film properties of Cu deposition on epitaxial Au(111)/mica surface. The electrolyte used was 15 mM $CuSO_4$ in 0.1 M H_2SO_4 and the potential was controlled against a quasi-reference electrode (Cu/Cu^{2+}). The electrode potential was pulsed for 2 sec to -0.1, -0.2, -0.3, and -0.4 V sequentially. After each pulse, the electrodeposited Cu film was kept at 0.0 V for imaging by AFM for about 2 minutes, then stripped off at 0.4 V before the next pulse. Figure 2 shows the films deposited at each of the different overpotential values, and imaged by contact AFM.

Since the rate of Cu deposition is highly dependent on the overpotential applied, which in turn affects surface properties such as the roughness of the film, the kinetics and surface roughness for film growth can be evaluated by EC-SPM. For example, the thickness of the Cu films deposited during the pulse experiment can be measured from the averaged line profile shown in Figure 3(A). The estimated thickness and surface roughness of each film are presented in Figure 3(B).

Summary

EC-SPM has been proven to be an indispensable tool for direct, high-resolution studies of physicochemical processes, providing an atomic and molecular basis for understanding the kinetics and thermodynamics of electrified interfaces. Application of electrochemical SPM will continue to impact and drive research in diverse disciplines, including energy, corrosion, and life sciences.

AFM Instrumentation from Agilent Technologies

Agilent Technologies offers high-precision, modular AFM solutions for research, industry, and education. Exceptional worldwide support is provided by experienced application scientists and technical service personnel. Agilent's leading-edge R&D laboratories are dedicated to the timely introduction and optimization of innovative and easy-to-use AFM technologies.

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Published in USA, September 27, 2013
5991-3298EN

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