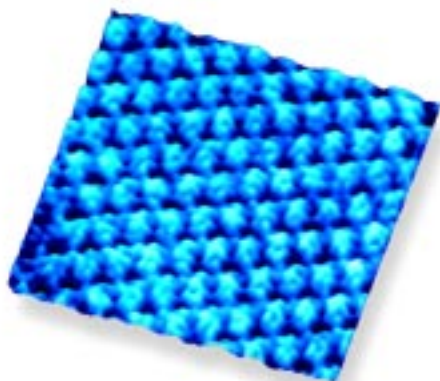# Electrochemical Applications of *Scanning Probe Microscopy*

By M. Ge and J. T. Thornton

Electrochemistry is a technique which is used to control and examine the electron transfer, chemical properties, and surface structure of conducting materials immersed in electrolytes. Electrochemical methods are used commercially for electroplating, batteries, corrosion prevention, electroanalytical sensors and etching of semiconductor materials. In electrochemistry, the properties of the electrode-electrolyte interface are of central interest.


The NanoScope® EC SPMs (from left to right): MultiMode™ EC AFM, EC STM, MultiMode EC STM, and Contact EC AFM, each with their respective electrochemical fluid cells.

In situ STM image of self-assembled monolayer of silicotungstate anions $((SiW_{12}O_{40})^{4-})$ on Ag(111) surface from 20mM HF + 1mM $H_4SiW_{12}O_{40}$. Individual molecules are clearly resolved. 11nm image courtesy M. Ge and A.A. Gewirth, University of Illinois at Urbana-Champaign, USA.

Electrode-electrolyte interfaces are complex systems and experimentally difficult to study. Due to spatial resolution limitations, traditional electrochemical methods alone often are not sufficient to provide an understanding of electrode surface behavior. Therefore, it has become common practice to supplement these methods with other spectroscopic and microscopic techniques. Since molecular and atomic detail of the interface is often the focus, high spatial resolution microscopy has become a necessity.

Scanning Probe Microscopy (SPM) has become an essential tool in the study of electrochemical interfaces in surface electrochemistry. Electrochemical Scanning Probe Microscopy (ECSPM) combines SPM with electrochemical control to study electrode surface structures, properties, and reactivities down to the atomic scale. ECSPM was first introduced into electrochemistry in 1986. By 1990 it had already assumed an indispensable role. The two SPM techniques used for EC applications are scanning tunneling
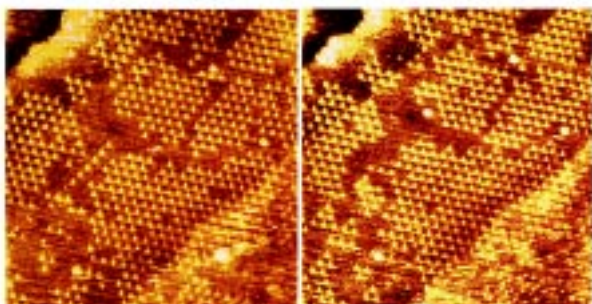
Time-dependent STM images of the Pt(111) electrode in 0.1mM KCN + 0.1M KClO$_4$ taken at 0.6V vs. RHE. The image in a) was taken 20 seconds before the image in b). A small portion of the K$^+$ cations disappeared in a), while the remainder appeared at the low left-hand corner of b), forming new $(2\sqrt{3}x2\sqrt{3})$-R30˚ domains. 30nm images courtesy K. Itaya, Tohoku University, Japan.
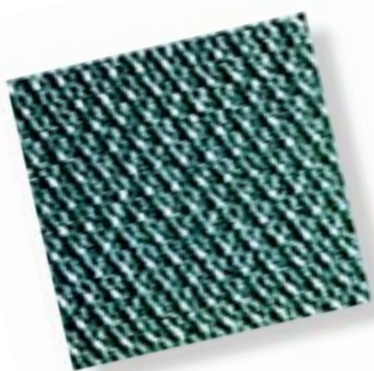
In situ AFM image of (3x3) adlayer structure formed by underpotential deposition (UPD) of a monolayer of Ag on Au(111) in 0.1M H$_2$SO$_4$ + 0.77mM Ag$_2$SO$_4$. Image obtained at 550mV vs. Ag$^{+/0}$. 10nm image courtesy A.A. Gewirth, University of Illinois at Urbana-Champaign, USA.

microscopy (STM) and atomic force microscopy (AFM). Although STM has traditionally had the greatest utility, AFM has become increasingly important in the field.

The practice of ECSPM falls into two categories: *in situ* and *ex situ.* In EC, *in situ* refers to imaging electrode surfaces in a solution environment either with or without potential control. *Ex situ* refers to imaging electrode surfaces after the electrode has been removed from solution. *In situ* imaging reveals the interfacial structures during electrochemical processes which gives direct structural information at electrode surfaces and provides information concerning the progression of an electrochemical process and/or the reversibility of that process. *Ex situ* techniques determine structures of electrode surfaces after electrochemical processes and therefore have certain drawbacks. In some cases, electrochemical procedures are used with the end goal of creating a specifically modified surface. For these applications, *ex situ* SPM is an easy to use method of probing surface topography and the effects of varying electrochemical treatment conditions.

Single-Crystal Metal Electrodes

Great advances have been made in single crystal electrochemistry in the past decade, owing primarily to advancements in the prepara-tion of well-characterized metal single crystal electrode surfaces, i.e., Au, Pt, Ag, Rh, and Cu. Such well-defined surfaces can be obtained by "flame-annealing" techniques, by vacuum

evaporation on suitable substrates, and from polished single crystals. Both *in situ* ECSTM and ECAFM are capable of resolving atomic structures of well-prepared single crystal surfaces in aqueous solutions. This allows the electrode-electrolyte interfacial structures to be determined during an electrochemical process with atomic-scale resolution. The successful practice of ECSPM has largely displaced the use of *ex situ* ultra-high vacuum spectroscopic techniques, which were used during the previous decade.

One of the primary interests of electrochemists is the study of structure-property relationships of electrochemical interfaces — specifically, how structure affects the chemical and electron transfer properties of the electrode-solution interface. ECSPM has proven invaluable in this research by providing a very detailed view of surface structure and its evolution as a function of solution composition and applied potential.

On single-crystal metal electrodes, the focus has been on three phenomena:

• Structure of chemisorbate adlayers

• Electrodeposition of metals

• Reconstruction of the electrode surface as a function of electrode potential

In the study of chemisorption, both inorganic and organic species have been investigated, although more emphasis has been given to chemisorbed atoms and small inorganic molecules. Research has been conducted on the adsorption of anions on low-index faces of Au, Pt, and Ag electrode surfaces.
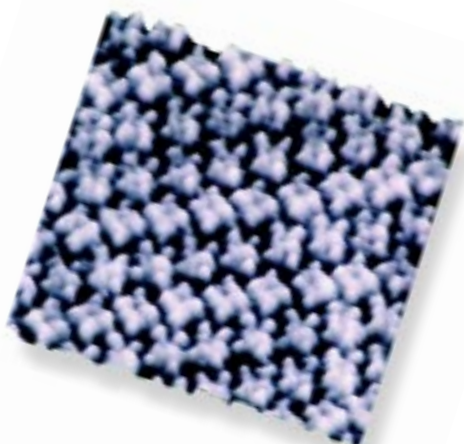
STM image of the 5,10,15,20-tetrakis-(N-methylpyridinium-4-yl)-21H,23H-porphine tetrakis-(p-toluenesulfonate) (TMPyP) array on iodine-modified Au(111) in 0.1M HClO₄ + 5x10⁻⁷M TMPyP obtained at 0.82V vs. RHE. 14nm image courtesy K. Itaya, Tohuku University, Japan.
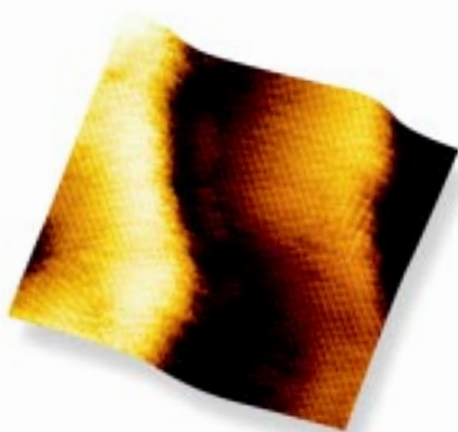
In situ STM image of self-assembled monolayer of silicotungstate anions on Ag(111) surface in 20mM HF + 1mM $H_4SiW_{12}O_{40}$. A square adlattice is formed on the stepped substrate surface. 45nm image courtesy M. Ge and A.A. Gewirth, University of Illinois at Urbana-Champaign, USA.

A typical example of this is the reversible SO_4^{2-} adsorption/desorption on Au(111) and Rh(111) electrodes under electrochemical potential control[1]. *In situ* ECSTM reveals a ($\sqrt{3} \times \sqrt{7}$) overlayer structure formed by sulfate/bisulfate ions on these two different electrode surfaces. Adsorption of halogen atoms on Au, Ag, Pt, and Pd single crystal electrode surfaces has also been extensively studied, primarily by STM[2] although AFM has also been used in some cases[3]. Various ordered adlattices have been observed, and correlations between adlayer structures and electrochemical potential have been investigated.

Molecularly-defined electrode surfaces are another area of active research. The adsorption of a variety of different small organic molecules on Au and Ag electrode surfaces under potential control has been demonstrated with ECSPM. It was found that porphyrin forms highly ordered adlayers on an iodine-modified Au(111) electrode[4]. Uracil adlayers have been investigated on three low index Au single crystal surfaces in aqueous solutions[5]. ECSTM revealed two types of incommensurate adlayer structures of AuCN formed at different potentials[6]. Self-assembled monolayers of organic molecules on metal surfaces have also been studied extensively by SPM. A typical example is self-assembly of alkanethiolate on Au[7]. An inorganic self-assembled monolayer system — heteropolyanions on well-defined metal surfaces (i.e., Ag(111)) — has also been investigated by *in situ* STM[8].

Underpotential deposition (UPD) is another focus of single crystal electrochemistry. Electrochemical deposition of a metal adlayer on a foreign metal substrate is one of the most structure-sensitive reactions that occur at electrode-electrolyte interfaces. In UPD, monolayers and submonolayers of foreign metal adatoms are deposited on a metal substrate with a potential that is positive relative to its Nernst reversible potential. Both STM and AFM have been applied extensively to determine UPD adlayer structures on single crystal electrodes, e.g., Cu, Bi, Pb, Ag, Hg on Au[9], Pb, Cd, on Ag[10], Cu, Ag on Pt[11] and Cd on Cu[12]. In such studies, UPD adlattices are often found to be different from their corresponding crystalline forms, e.g., open as opposed to close-packed. Such differences may be due to the effect of coabsorbed anions or retained charge in the UPD adlayer. Further investigation is needed to achieve a better understanding of this complex phenomenon. In addition to the study of UPD structures, the correlation between changes in chemical properties and modifications of atomic structures of electrode surfaces has also been explored. It has been shown that an open Bi(2 x 2) UPD monolayer on Au(111) undergoes H_2O_2 electroreduction while a close-packed full monolayer and bare Au(111) are inactive[13].

Reconstruction of metal and semiconductor surfaces is a well-known phenomenon in an UHV environment. To date, most of the studies have focused on the three low index Au and Pt surfaces. For example, a flame-annealed Au(100) single crystal electrode surface exhibits a potential-dependent hexagonal ("hex") reconstruction and under-
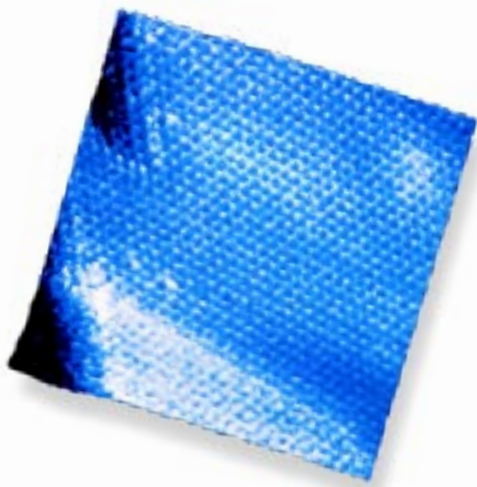
Ex situ STM image showing the atomic structure of a large terrace at the surface of the passive film formed on Ni(111) at 650mV vs. SHE in 0.05M H_2SO_4. 10nm image courtesy P. Marcus, University Pierre et Marie Curie, France.

goes a reversible hex↔(1 x 1) transition in both alkaline and acidic electrolytes[14] and an Au(110) surface transforms from (1 x 1) to (1 x 2) and (1 x 3) in the double-layer region upon decreasing potential[15].

Structural changes of the electrode surfaces during oxidation-reduction cycles have also been investigated by ECSPM. An *in situ* STM study has shown the island formation on an atomically-flat Pt(111) surface after potential cycles[16]. Roughening, annealing, and dissolution associated with oxidation and reduction of Au(111) have also been observed[17].

Semiconductor Electrodes

Aqueous solution chemistry, as well as electrochemical-based processing methods, are common steps in semiconductor device manufacture. ECSPM research on semiconductor electrodes is focused on electrochemical etching of semiconductor materials and the preparation of semiconductor thin films by electrodeposition. Various semiconductor surfaces, e.g., Si, Ge, GaAs, n-TiO$_2$, n-ZnO, have been examined by *in situ* SPM in aqueous solutions[18]. Atomic resolution has been obtained on Si(111), Ge(111), and GaAs(111) in electrolytes. Among various semiconductor electrodes, Si has been investigated most extensively due to its importance in VLSI (Very Large Scale Integration) devices. Topographic evolution down to the atomic scale during wet chemical etching of Si in different electrolytes has been investigated by *in situ* STM.

Other Applications

Besides the above described active research areas, ECSPM has also found applications in other areas, such as bulk metal plating, battery research, corrosion, conducting polymers, carbon fiber electrodes, and analytical sensors made by controlled electrode surface modification. In corrosion studies, STM has been used to investigate corrosion and passivation of iron, nickel, chromium and related alloys[19-22]. Among such studies, atomic resolution imaging has been reported for passivated chromium[20], iron-chromium alloy[21], and thin oxide film on nickel[22], revealing the role of defects in passivity breakdown. However, STM is limited to imaging of thin passive layers because the thick passive film prevents electron tunneling. AFM does not have this limitation and can be applied to study thick oxide layers, e.g., aluminum and stainless steel samples. In general, in the cases where the focus is on surface topography in the nanometer to micron length scales, AFM has proven to be simpler and more versatile than STM.

Nanolithography has been conducted in an electrochemical environment using ECSPM. This consists of using the SPM as a probe and surface modification apparatus to control precise surface changes (e.g., deposition or etching) while the surface is immersed in electrolytes. Nanometer-scale electrochemical deposition by STM has been demonstrated by several groups[23]. Reasonable precision has been achieved, usually by a two-step mechanism consisting of defect generation using a bias-pulse, followed by site-selective nucleation and growth at the defects. However, nanometer-scale deposits by this method usually disappear quickly due to dissolution and surface diffusion, and stabilization of the deposited pattern remains a challenge. Enhanced electrodeposition of nanometer-scale Cu features on Cu and Au single crystal surfaces in an electrolyte by AFM has also been reported[24]. A large tip-sample force was applied locally to remove the passive layer on the Cu and Au substrate surfaces forming preferred nucleation sites for further electrodeposition.

Of the AFM techniques, simple contact mode AFM has been used most frequently, but applications for lateral force, TappingMode™, and force modulation imaging modes can be found in ECAFM as well. For example, higher resolution and more stable imaging of electropolished aluminum samples can be performed *ex situ* using TappingMode AFM rather than contact mode AFM.

Discussion

ECSPM has become an indispensable technique in the study of surface electrochemistry and Digital Instruments is proud to be the leader in developing instrumentation for the electrochemical community. We manufacture a full line of EC-capable STM and AFM instrumentation (see below) and are well-versed in your research needs and how to best utilize SPM technology to solve problems of interest to electrochemists. A bibliography of ECSPM publications is available upon request, or may be accessed through our Internet web site at www.di.com.

In situ AFM image of overpotential deposition of Cd on Cu(111) surface obtained in the solution containing 2mM $Cd(ClO_4)_2$ + 0.1M $HClO_4$ at -580mV vs. NHE. Cd hcp crystal structure with sharp edges is clearly shown. The two adjacent lines drawn on the image form an angle of 120˚. 650nm image courtesy M. Ge and A.A. Gewirth, University of Illinois at Urbana-Champaign, USA.

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NanoScope® Electrochemical Scanning Prbe Microscopes

Digital Instruments' NanoScope Electrochemical Scanning Probe Microscopes (ECSPMs) incorporate the proven and highly successful NanoScope SPMs and control systems with advanced electrochemical microscopy capability. The superior scan control, low noise operation, and ease-of-use of the NanoScope ECSPMs make it easy to acquire images on both the atomic and macroscopic scales. STM and contact mode AFM can both be used for *in situ* investigations. *Ex situ* operation can be performed with these techniques plus a wealth of other oscillating cantilever modes, including our patented TappingMode AFM. Our focus on ease-of use, performance, versatility and innovation have made the NanoScope ECSPMs the most productive electrochemical SPMs available, with more peer-reviewed publications than any other commercial ECSPM.

System Description

The ECSTM is composed of a microscope support which houses a bipotentiostat, an STM scan head, and the electrochemistry fluid cell. A TipView™ ECSTM configuration is also available with the MultiMode™ SPM. The ECAFM package includes an external potentiostat fixture that attaches to the base of the contact mode AFM or MultiMode AFM, and an EC fluid cell. Both microscopes include software that provides computer control of the potentiostat and microscope, as well as simultaneous recording of both electrochemical and topographical data. Either or both microscopes may be purchased as part of a complete system or added to an existing system at any time. The flexibility and modularity provided by the NanoScope's digital feedback control system allows the electrochemical microscope to be added easily, without the need for additional electronics. Further flexibility can be provided with the optional Signal Access Module™ which provides easy access to all input and output signals of the SPM control system.

Other standard features include:

- Complete computer controlled potentiostat/galvanostat
- Potentiostat/galvanostat operation fully integrated with SPM imaging (Bipotentiostat/galvanostat configuration for ECSTM)
- Linear scan and cyclic voltammetry at 0.1mV/s to 1.0V/s
- Programmable complex electrode waveforms including combined ramps and square waves
- Holding STM tip at constant potential with respect to either the working electrode or reference electrode.
- Programmable voltammetry mode
- Voltammogram function modes include Current, Log Current, and Charge
- Digital coulometry
- Display of voltammetry (I vs. E) and temporal (I or E vs. t) plots with selectable graph ranges
- Up to 60,000 data points of electrical data stored with each image
- Automatic image collection during EC run

Specifications

Bipotentiostat/Galvanostat
- Output compliance voltage: ±12V
- Applied voltage range: ±10V
- Potential resolution: 0.3mV
- Reference input impedance: $>10^{11}\Omega$

I/E Converter
- Max. current: 10mA
- I/E ranges: 10µA/V, 100µA/V, and 1mA/V standard
- Output voltage range: ±10V
- Resolution: 0.006% of full scale

STM Cell
- Material: Kel-F, Teflon
- Internal volume: ≈0.2mL
- Reference electrode: Pt, Ag, Cu, or user defined
- Auxiliary electrode: Pt, Au
- Dimensions of cell assembly: 12mm x 19mm x 6mm

AFM Cell
- Cell body material: Glass
- Internal volume: ≈50µL
- O-ring material: Silicon or ethylene/propylene
- Reference electrode: Cu, Pt, Ag, or user defined
- Auxiliary electrode: Pt, Au
- Dimensions of cell assembly: 30mm x 30mm x 7mm

Microscopes and Products
- Electrochemical Scanning Tunneling Microscope
- Fluid Cell for Electrochemical STM
- Electrochemistry AFM Converter for the Contact AFM and LFM
- Fluid Cell for Contact Electrochemical AFM
- Electrochemistry AFM Converter for the MultiMode AFM
- Fluid Cell for the MultiMode Electrochemical AFM
- Electrochemistry STM Converter for the MultiMode AFM
- Electrochemistry STM Fluid Cell for the MultiMode AFM

For product descriptions on other features of the NanoScope Electrochemical SPM system, see the following related data sheets: NanoScope MultiMode Scanning Probe Microscope, NanoScope IIIa Scanning Probe Microscope Controller, NanoScope Signal Access Module for Custom Applications, and The NanoScope *E* Scanning Probe Microscope System. Note that an additional base is required for electrochemistry AFM/STM operation of MultiMode SPMs equipped with the Extender™ Electronics Module. Call our sales or customer support groups for details.