Keysight Technologies
Combining Atomic Force Microscopy with Scanning Electrochemical Microscopy

Application Note

Introduction

Scanning probe microscopy (SPM) techniques have found a broad range of applications in characterizing the physical and chemical properties of the surface of interested materials. One technique that is particularly useful for studying localized electrochemical activities at the solid/liquid and liquid/liquid interface is Scanning Electrochemical Microscopy (SECM), which was introduced by Bard and coworkers in 1986[1]. Laterally resolved, *in situ* electrochemical information of surface properties can be obtained by scanning an ultramicroelectrode (UME) at a defined distance across the sample surface. Even though it looks similar to other SPM techniques in the sense that it involves the control of scanning a physical probe across a sample surface, the operation principle for a conventional SECM is quite different. SECM characterizes the localized properties of the electrified solid/liquid and liquid/liquid interfaces by monitoring the electrochemical current. When the electrode is swept across a sample surface, changes in current allow imaging of insulating and conducting surfaces for topology and reactivity information. A detailed introduction of SECM and its applications are found in a separate note.

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The Bifunctional AFM-SECM Probe

SECM imaging is commonly operated in constant-height mode, where the tip is held at a fixed position above the sample surface. The spatial resolution of SECM depends significantly on the size and geometry of the UME and the substrate-to-tip distance. One major drawback of constant height operation in SECM is the lack of sufficient spatial resolution due to current dependent positioning of the microelectrode and the convolution of topographical and electrochemical information. The EC SmartCart probe offered by Keysight Technologies, Inc. provides an innovative solution to this problem, which directly integrates a micro- or nanoelectrode into an AFM probe.

This integrated probe (the AFM-SECM probe) maintains the functionality of both AFM and SECM technique, by integrating a sub-microelectrode recessed from the end of the AFM tip [2]. Consequently, the electrode is located at a pre-defined distance to the sample surface, determined by the height of the actual AFM tip (Fig. 1). Thus, *in-situ* (electro)chemical information on a wide range of homogeneous or heterogeneous electron-transfer processes occurring at surfaces and interfaces can be simultaneously obtained during AFM imaging.

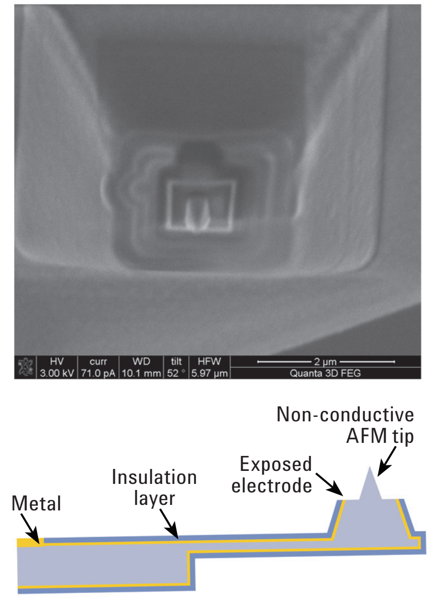

Figure 1. Microfabricated bifunctional AFM-SECM probe. The probe has a frame-shaped electrode recessed from the AFM tip that governs the distance between the electrode and the imaged surface.

AFM-SECM Instrumentation

The combined AFM-SECM system includes a standard Keysight AFM (5500/7500) platform with a built-in bipotentiostat that controls the potential of both the sample (for generation/collection mode) and the tip against the same reference electrode. The bifunctional AFM-SECM tip is mounted to a special SECM nosecone that plugs into a standard AFM scanner (Fig. 2). The tip current, i.e., the current flowing through the tip is measured by a pre-amplifier built into the SECM nosecone, which is located close to the tip itself to minimize

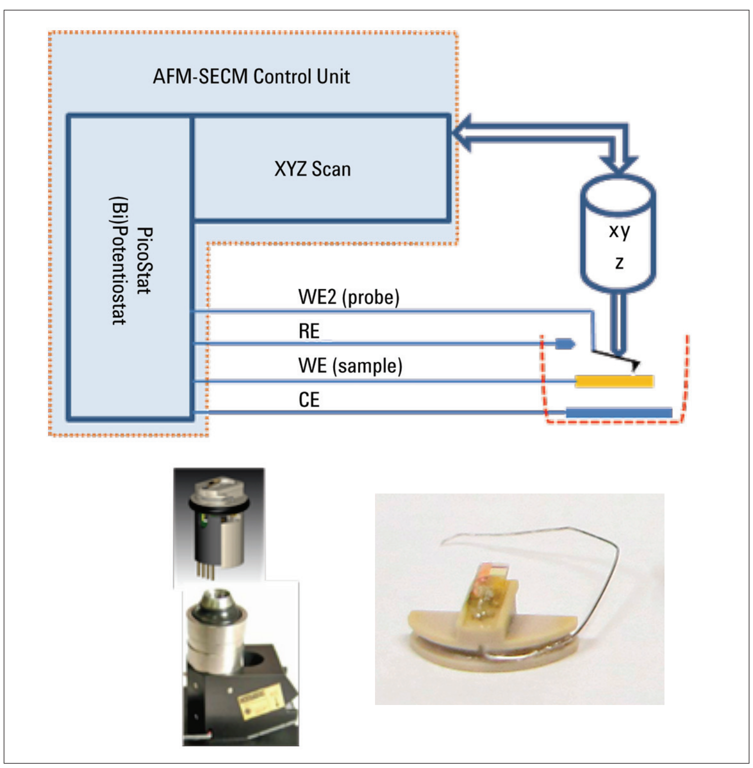

Figure 2. Combined AFM-SECM system includes an AFM control unit and a SECM unit. The EC SmartCart is pre-mounted on a special nosecone that inserts into a standard AFM scanner from Keysight.

electromagnetic noises from the line. The major advantage of this setup is the tip is pre-mounted onto a cartridge (bottom right picture of Fig.2), insulted and tested in factory before it is delivered to the customer. The user only needs to plug in the cartridge into the nosecone and is ready to start the experiment. This allows the customer to be released from the challenging and time consuming work that normally required in preparing for an SECM experiment, which includes mounting the tip, making electric contact, insulating the tip, etc., thus allowing the customer to focus on the research instead of on the setup.

AFM-SECM Probe Characterization and Application Example

After a probe is mounted on the cartridge, the electrochemical performance of the probe will be tested in electrolyte solution (0.1 M KCl) containing a standard redox mediator such as 10mM $[Ru(NH_3)_6]^{3+}$. A typical CV of the probe (inset) recorded in the AFM set-up is presented in Figure 3. The steady state current varies with the actual size of the ring electrode. The noise of the measured current is evaluated by measuring the redox current as a function of time at a constant potential. Typical noise level of the measured current is about 10 pA (Fig. 3), allowing customers to perform low current experiments.

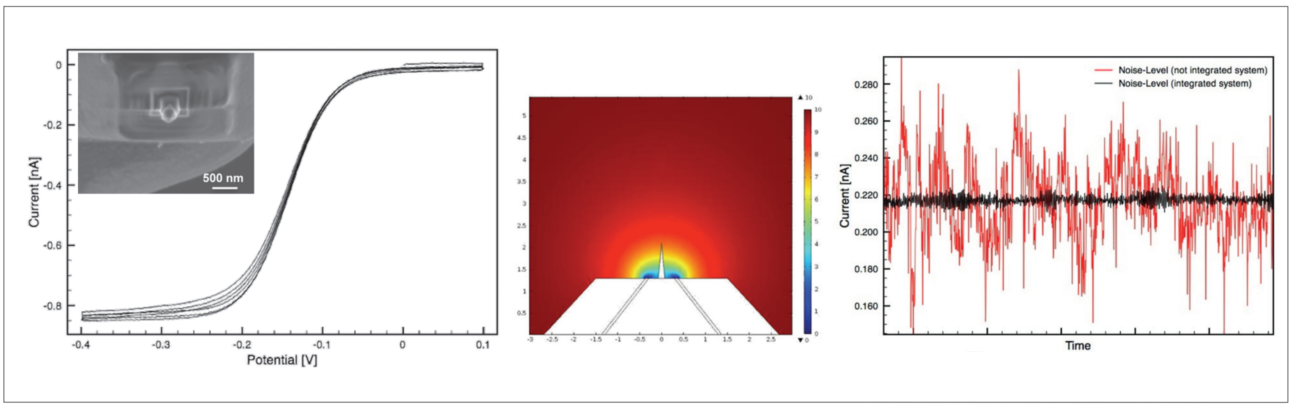

Figure 3. Combined AFM-SECM measurements based on AFM tip-integrated electrodes. Bottom: Simultaneously recorded images showing the topography (left) of the Agilent logo deposited from platinum/carbon composite by an ion beam-induced deposition (SEM image, middle) and the electrochemical image recorded in feedback mode SECM (right).

Results from a simultaneously recorded contact mode AFM and feedback mode SECM experiment on a model sample are presented in Fig. 4 to demonstrate the functionality of the combined AFM-SECM system. The model sample contains

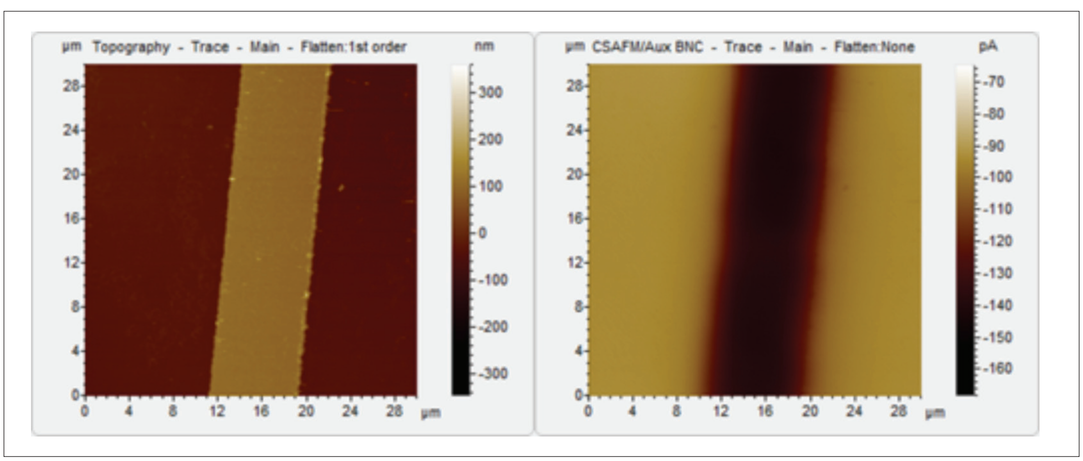

Figure 4. Topography (left) and SECM (right) images of an Au/Si sample recorded in 1 mM FeMethanol solution/0.1 M KCl with a combined AFM-SECM probe biased at 240 mV vs. Ag/AgCl. Topography image shows the deposited Au strip on Si substrate, and the SECM image shows a corresponding larger current on the conductive Au surface.

conductive (gold stripes) and non-conductive (Si wafer) regions coexisting on the surface. This Au/Si sample was imaged in contact mode AFM in a 1 mM FeMethanol solution/0.1 M KCl solution with the AFM tip-integrated electrode biased at 240 mV vs. Ag/AgCl. The simultaneously recorded topography and current images are shown in Figure 4. The SECM image was obtained in the so-called feedback mode, while the sample was not biased during the experiment. Due to the feedback effect, as explained above, the SECM current is smaller on the insulating Si surface, and is larger on the conducting Au surface.

A second example of AFM-SECM imaging is present in Figure 5. The sample is Pt-coated glass slide with FIB-structured patterns, an Agilent logo. Images are recorded in AFM contact and SECM feedback mode in 10 mM $[Ru(NH_3)_6]^{3+}$/0.1 M KCl. The SECM image (left in Fig. 5) revealed some changes in conductivity which are not clearly visible in the corresponding topography image.

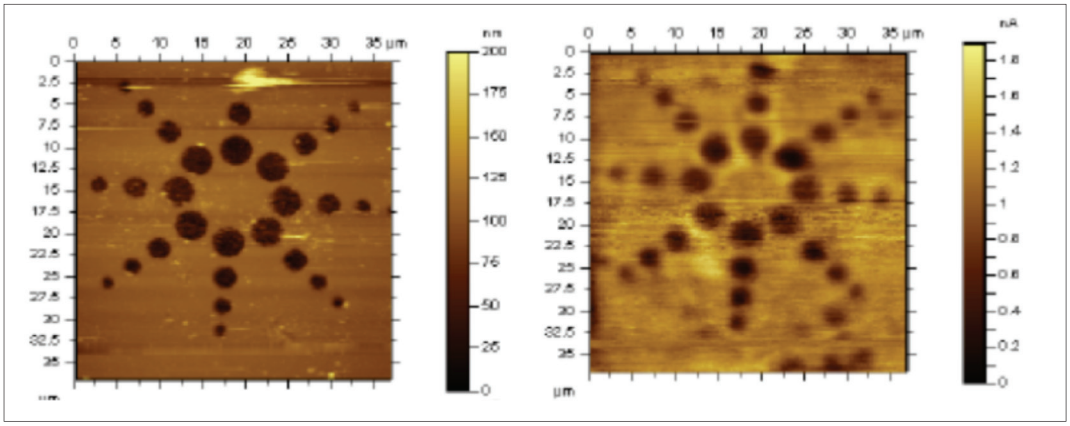

Figure 5. Images recorded in AFM contact and SECM feedback mode in 10 mM $[Ru(NH_3)_6]^{3+}$/0.1 M KCl; sample: Micro-structured Platinum-coated glass slide with non-conductive star patterned.

The imaging power attainable by combining information on the surface morphology with localized (electro)chemical data can be applied to a wide variety of complex engineering and biological problems, ranging from corrosion science to life sciences. For example, modification of the integrated electrode surface with enzymatic biosensing interfaces results in imaging amperometric nanobiosensors [3,4]. In addition, boron-doped diamond can be used as electrode material [5], resulting in a combined probe with exceptional properties in terms of robustness and potential window. The integrated SECM functionality is not limited to amperometric experiments, also imaging potentiometric microsensors (e.g. Ir/IrO_x or Sb electrode for laterally resolved pH measurements), or thin film amalgam microelectrodes (Au/Hg or Pt/Hg) for imaging stripping voltammetry (e.g. for heavy metal detection) are envisaged.

Summary

This combined AFM-SECM approach with bifunctional probe provides topographical and correlated electrochemical information with high spatial and temporal resolution, thereby enabling the transformation of scanning probe microscopic techniques into multifunctional devices useful in industrial and academic environments for fundamental or applied interests. The innovative probe design eliminates certain intrinsic drawbacks in conventional SECM, providing high-resolution topographical information correlated with electro(activity) information of the sample. The unique design of the SECM nose cone with the pre-mounted probes on exchangeable cartridges allows users to perform SECM measurements without having to deal with the time consuming process of experimental setup.

References

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