Issue 2.1
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A Nanonics
Electrochemical
Application

The Nanonics SECM/AFM 100™ Confocal System SECM with Cantilevered AFM Sensing Nanoelectrodes

Scanning electrochemical microscopy (SECM) has developed into a powerful tool to image or modify surfaces using electrochemistry. SECM has had a large impact on areas such as corrosion, etching of semiconductors, deposition of metal and patterning of surfaces with biomaterials.

In all scanned probe microscopies there must be a signal that monitors the approach of the probe tip to the surface under investigation. In conventional SECM, the Ultramicroelectrode (UME) is brought in close proximity to a surface while generating an

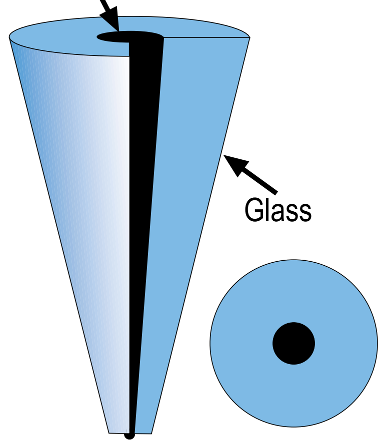

Figure 1: The Tip of an SECM Probe

electroactive species. The latter sense the surface and serve as both a reactant that drives an electrochemical reaction on the surface as well as an UME-surface distance indicator. The feedback current that is measured at the UME depends strongly on the UME-surface distance and the rate of electron transfer on the surface, and it is used to monitor the UME approach.

Conventional UME's are usually produced by fusing a metal wire to the inside of a tapered glass capillary. This design creates a microelectrode with a glass sealing around it, as shown in Figure 1.

Although SECM has significant advantages, in terms of gaining local electrochemical information and in terms of having well-understood imaging and modification mechanisms, it nonetheless suffers from several drawbacks. These include severe limitations on the dimensions of current tips (diameter: 1-50 μm) for electrochemical microscopy and the lack of an independent feedback mechanism that can both place the electrochemical tip within close proximity to the substrate and provide independent topographical information.

These problems have now been resolved by extending the Nanonics award winning cantilevered glass probe technology into the world of SECM.

A crucial component of the integrated SECM/AFM System is Nanonics' patented glass tapering and cantilevering technology for nanoelectrodes.
In this technique, a metal wire is tapered inside a glass capillary to form a glass-sealed, metal nanoelectrode (NE). The probe is then cantilevered so that it can be used in a standard AFM setup.

Figure 2: Nanonics cantilevered SECM/AFM probe

A beam-bounce AFM feedback is used to control the distance between the NE and the surface which is investigated, and the SECM measurements are performed by the central metal electrode.

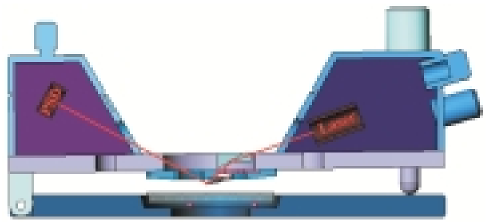

Figure 3: Schematic of the beam-bounce feedback

The substrate and/or nanoelectrode are connected to a standard bipotentiostat with low current ability. The electrochemical cell contains connections for the reference- and counter-electrode.

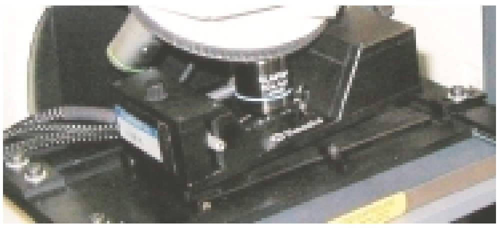

Figure 4: SECM/AFM 100™ mounted on an upright microscope

The use of an AFM feedback mechanism allows

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The Nanonics SECM/AFM 100 Confocal System
SECM with Cantilevered AFM Sensing Nanoelectrodes

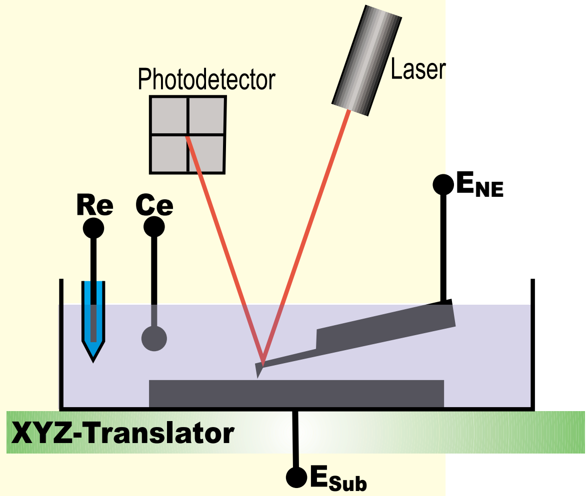


Figure 5: Schematic of SECM/AFM setup with standard AFM feedback

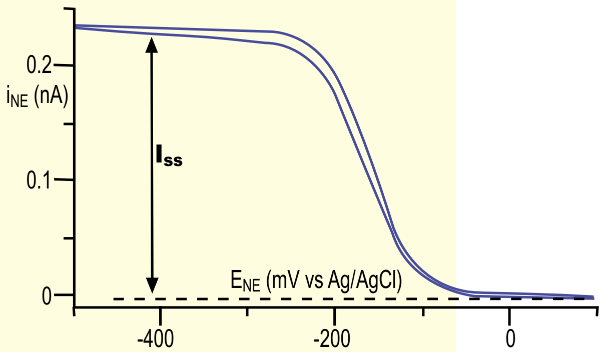


Figure 6: Pt-nanoelectrode, Scan rate: 25 mV/sElectrolyte: 1M KCl + 10 mM [Ru(NH3)6]Cl3

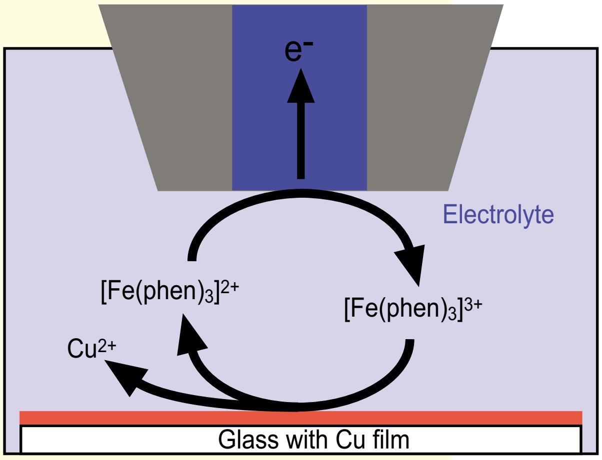


Figure 7: Schematic of electrochemical Cu-etching

simultaneous surface topography and SECM images to be produced. Because the AFM feedback is more sensitive than the standard current feedback, Nanonics is able to design electrochemical tips with diameters as small as 50 nm. Such probes allow one to investigate localized electrochemical properties with a higher resolution than conventional SECM methods.
The Nanonics SECM/AFM 100™ system is based on the NSOM/SPM 100™, the only SPM today that allows for transparent integration with any conventional optical microscope, upright or inverted. The unique design of these Nanonics systems leaves the optical axis completely free, thus allowing a lens to be brought from either the top or bottom.

The free optical axis offers many other advantages. For example, it allows one to combine SECM/AFM with a Raman microscope. An in line Raman would provide additional chemical information by allowing one to monitor a particular critical vibrational frequency.
Nanonics and Renishaw provide for a transparent integration of the Nanonics SECM/AFM with the Renishaw MR1000 MicroRaman. The software and hardware of the two systems are completely integrated, so that a Raman spectrum can be obtained correlated with the position of the cantilevered electrochemical probe. The cantilevered nature of the electrochemical probe not only provides for AFM feedback, but also allows for a free optical axis with an upright microscope. This allows for even opaque substrates to be investigated electrochemically and optically

Finally, the entire SECM/AFM100™ system can also be placed in an environmental chamber, in order to perform measurements under controlled conditions.

Figure 8: The Environmental Chamber for SECM/AFM 100™

Electrochemical Test of the Nanonics Cantilevered Nanoelectrode

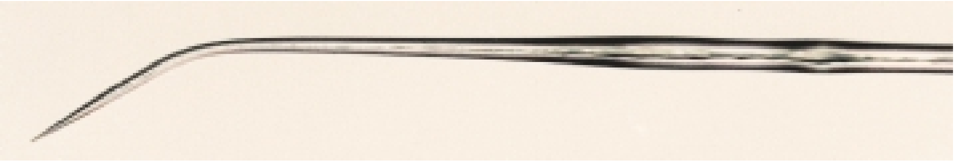
To test the nanoelectrodes, cyclic voltametry is used.

From the measured steady state current (I_{ss}) (see Figure 6), the diameter of the electrode can be calculated according to the following formula:

$I_{ss} = -wFC_{Ox}D4r_0$,

where I_{ss}: Steady state current, w: number of e^- in electrode reaction, F: Faraday constant, C_{Ox}: bulk concentration of Ox, D: diffusion coefficient, r_0: radius of the UME.

In this example, the diameter of the electrode is 180 nm, calculated from I_{ss} = 0.225 nA



SECM/AFM measurements

Cu-etching with an electrochemically generated etchant was chosen as a test system for the combination of AFM with a nanoelectrode. The schematic in Figure 7 shows the electrochemical processes involved in the etching.

During the process, Fe-Phenantrolin is oxidized at the nanoelectrode, and rereduced on the copper surface, where it oxidizes the copper, leaving an etchpit.

Figures 9/10 show images and linesections of Cu before (inset) and after etching (2x2 μm, inset 1x1 μm, z-scale of 10 nm). An etchpit is clearly visible in the larger image, taken after the etchant was generated for at the tip 30 minutes. The tip was in intermittent-contact with the substrate for the entire time.

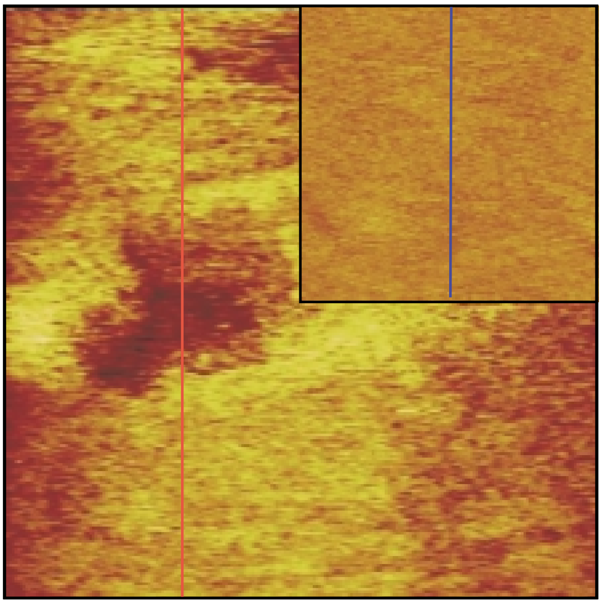


Figure 9: Electrochemical etching with a Nanonics AFM cantilevered Pt nanoelectrode, Substrate: sputtered Cu on glass, Electrolyte: 2 mM [Fe(bipy)$_3$](ClO$_4$)$_2$ in 10 mM Acetate buffer, Reference electrode: Ag pseudo-reference, Counter electrode: Pt wire,
Potentials: Sub=not connected, NE=400 mV (normal)/1050 mV (etching)

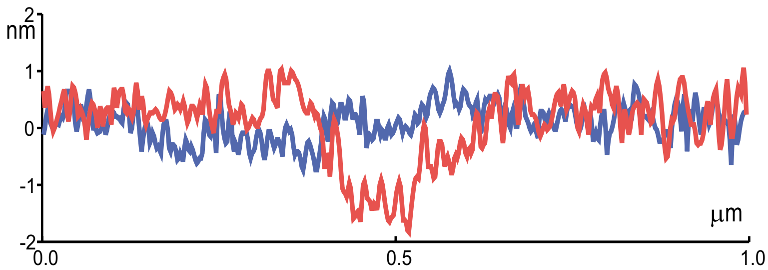


Figure 10: Linesections taken in the locations indicated in Figure 9. The etchpit is clearly vivible.

NSOM/SPM-100™ Technical Specifications

Modes of Operation

Near-field Optical Microscopy	Transmission, reflection, collection, fluorescence.
Atomic Force Microscopy	Contact, non-contact, intermittent contact (shear force optional)
Feedback Mechanism	Optical beam deflection (Shear Force optional)
Confocal Microscopy	Transmission, reflection, fluorescence
SECM	Electrochemical measurements with AFM feedback

Scanning/Sample

Scanner	Piezo electric flat scanner (thickness 7 mm) Scan Range: 70 μm Z-range, 70 μm XY-range (30 and 10 μm on request), Maximum load: 75 g.
Step Size	< 1 nm for 70 μm scanner, < 0.1 nm for 10 μm scanner
Sample Positioning	Inertial piezo motion (6 mm range, accuracy 1μm)
Maximum Sample Size	16 mm diameter, custom mounts for larger samples available

Probes

NSOM Probes	Cantilevered or straight, pulled optical fiber probes, apertured silicon cantilevers
AFM Probes	Cantilevered, pulled glass probes or commercial AFM probes

Electrochemical Probes

Electrode Material	Pt / Au / Ag, custom materials on request
Electrode Diameter	> 50 nm
Wire Diameter	50 μm
Insulator Material	Borosilicate glass
Insulator Thickness	~ 0.5 μm
Force Constant	> 3 N/m
Resonant Frequency	80 - 390 kHz
Cantilever Length	350 - 1000 μm
Cantilever Height	350 - 1000 μm

Optics

Viewing/Detection Optics	Free optical access to the sample from top and bottom for optical observation of the sample (all conventional far field modes of operation are available) and for detection of the NSOM signals with any optical microscope (upright, inverted) or other optics.

Controller/Software

Controller	Nanonics/Topaz (Digital Instruments, RHK, Park Scientific and Topometrix controllers can also be used to control the NSOM/SPM100 microscope)
Software	Quartz software for Nanonics/Topaz controller (Win 95/98 and NT). Real time image display, image acquisition (up to 8 channels) and analysis, 3D rendering
Electrochemical Control	An external Potentiostat/Bipotentiostat with low current ability is used, with external computer control of electrochemical signals.

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