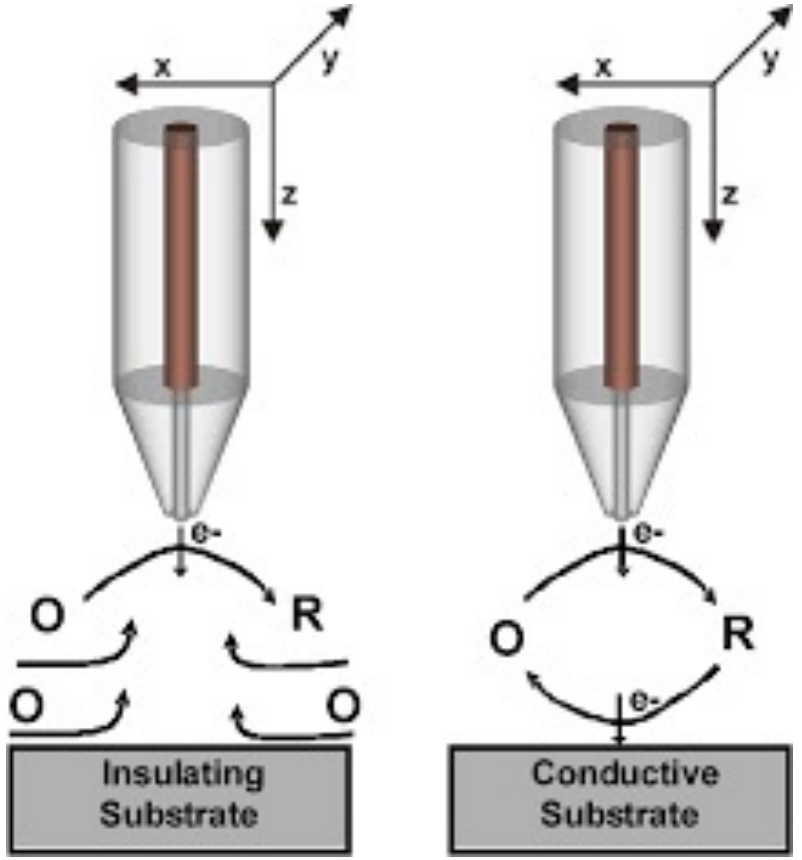
AFM Controlled Scanning Electrochemical Microscopy (AFM/SECM) With Seminal Nanonics Advances

Nanonics Imaging Ltd
www.nanonics.co.il

Straight Glass Pipette Probes with a Platinum Core Are Generally Accepted As The Best Probe for Scanning Electrochemical Microscopy (SECM)

In spite of the Excellence of Glass Probes for SECM Several Issues Have Retarded Advances in SECM.
Principally these issues are:

- The general straight geometry of the glass probes lack atomic force feedback capability
- Thus, the measured electrochemical current has to be used as a feedback mechanism
- As a result the measured current is compromised in its functional relevance due to alterations in current due to feedback
- Also the electrochemical current is not a sensitive feedback as is the case for atomic force microscopy
- Therefore, probe diameters in the 1-3 micron range are standard
- Thus the excellence of glass probes is today seriously compromised in terms of SECM and the resolutions it can achieve

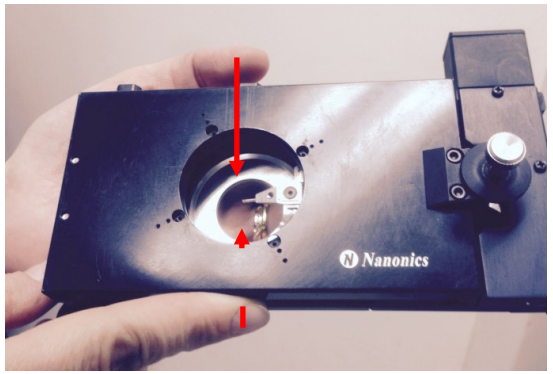


Nanonics' Has Transformed SECM By Resolving The Main Issue Impeding SECM Progress While Maintaining the Proven Excellence of Glass SECM Probes

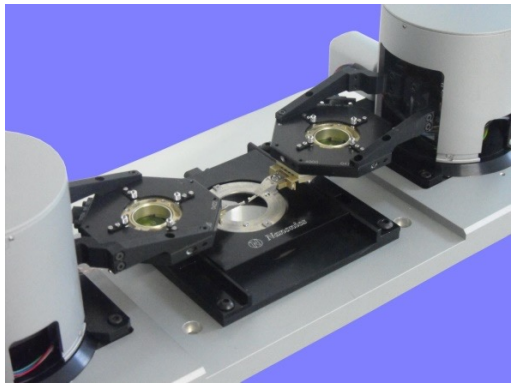
New Horizons in SECM With Nanonics:

- Nanonics has 25 years of expertise in supplying SPM systems with exclusive glass ultrasensitive SPM probe technology
- Using this expertise Nanonics has transformed the excellence of glass SECM straight probes with Nanonics Systems into ultrasensitive AFM with SECM

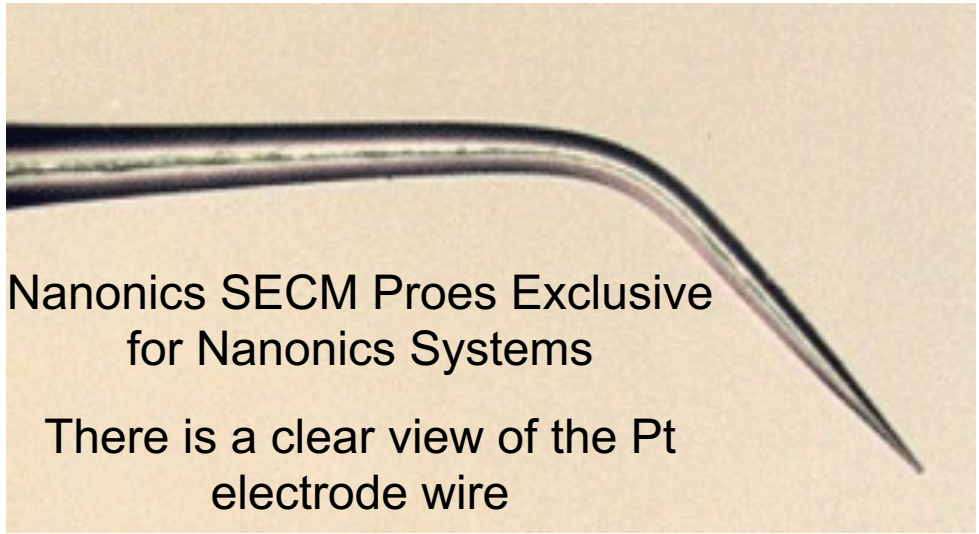
Free optical axis from above and below



Single Probe Series



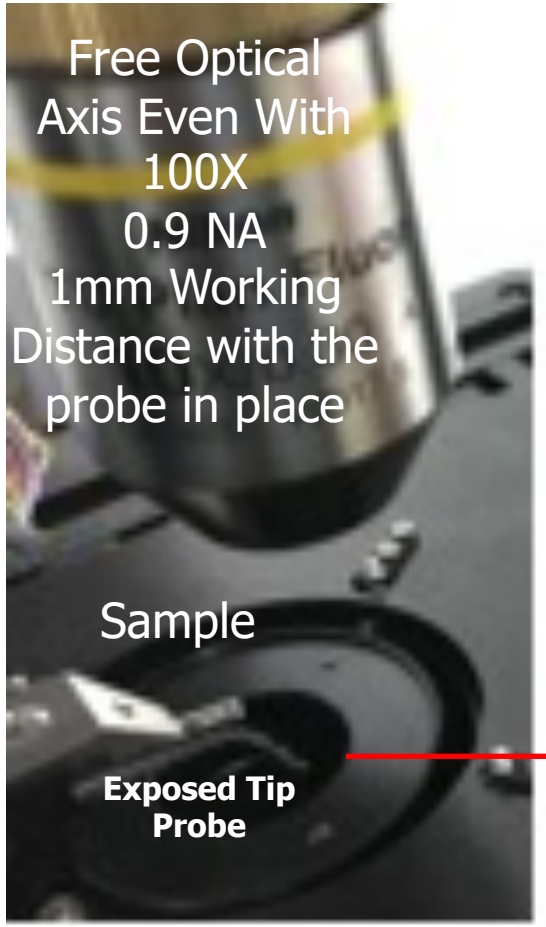
Hydra Multiprobe Series for Investigating Electron Transport with 2 SECM Probes

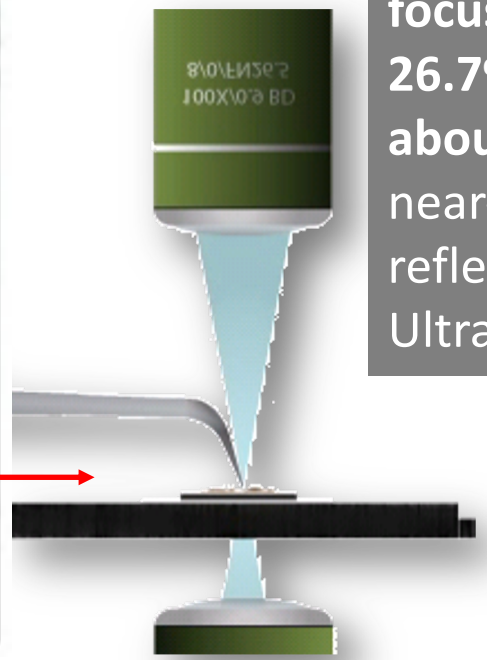


Nanonics SECM Proes Exclusive for Nanonics Systems

There is a clear view of the Pt electrode wire

Such transparent integration with upright microscopes has been a hallmark of Nanonics systems for its establishment 25 years ago



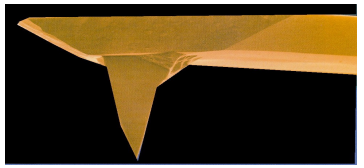


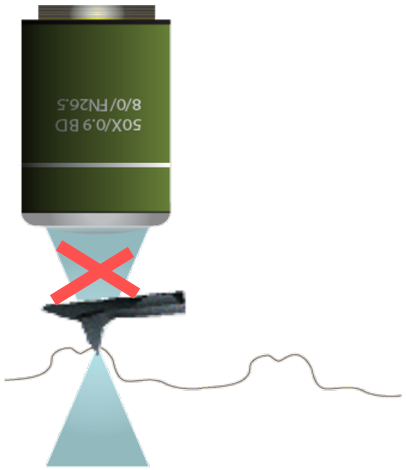
Cantilevered Glass Based AFM Probes
Exclusive for Nanonics' Systems

What customers publish: "…**In our experimental configuration, the tip apex is not shadowed, as the laser beam is a focused beam with a converging angle of 26.7°, while the half angle of the tip is only about 4° . "** [Sun and Shen, Apertureless near-field scanning Raman microscopy using reflection scattering geometry, Ultramicroscopy 94, 237 (2003)]

Compatibility With All Third Party AFM Probes

But Such Probes In General Block The Optical Axis





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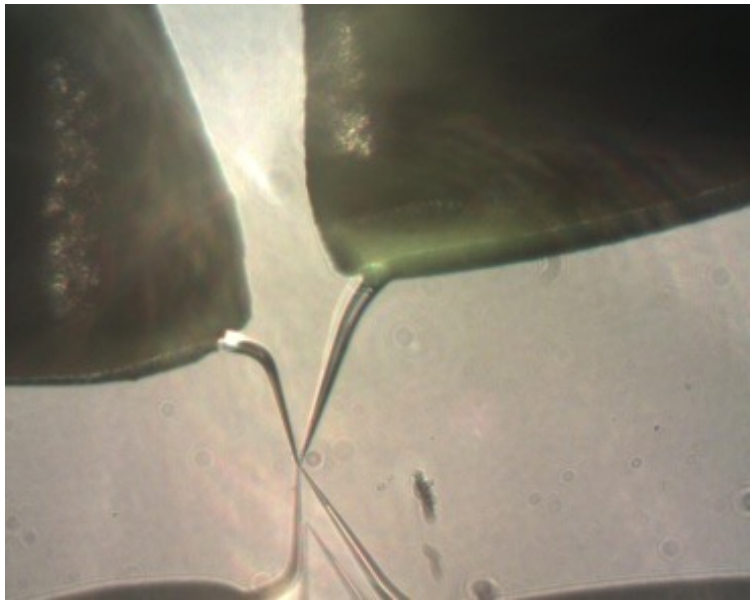
And The Hydra MultiProbe Permits Probes To Be Brought Into Contact & Separated With Nanometric Precision

For Investigation of Nanotransport of Electron Transport, Conductivity, Optical & Thermal Phenomena



What customers publish: ” Collisions between both tips were effectively prevented by a proximity detection mechanism based on mechanical interaction between both tips. The minimum distance between both tips is reached when both tip coatings touch..” Klein et al, NanoLett. 14, 5010 (2014)

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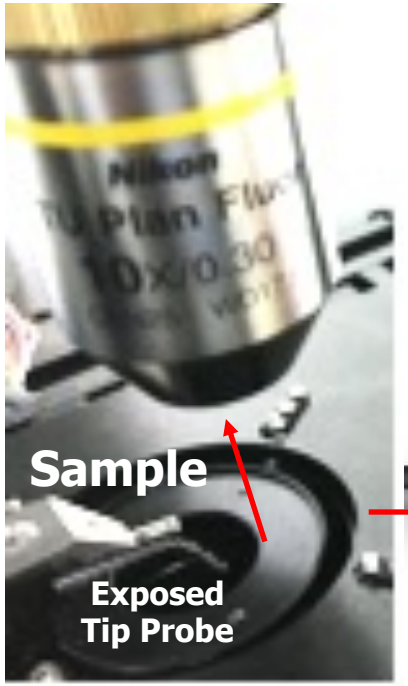
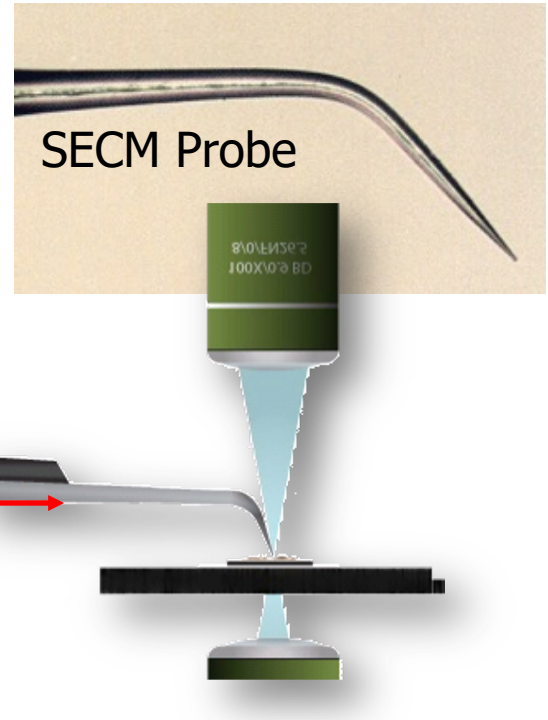
Cantilevered Glass Based AFM Probes Exclusive for Nanonics' Systems





Allowing The Probe To Be In Place With Optical Objectives with 100X 0.9NA 1mm Working Distance and Water Immersion Objectives

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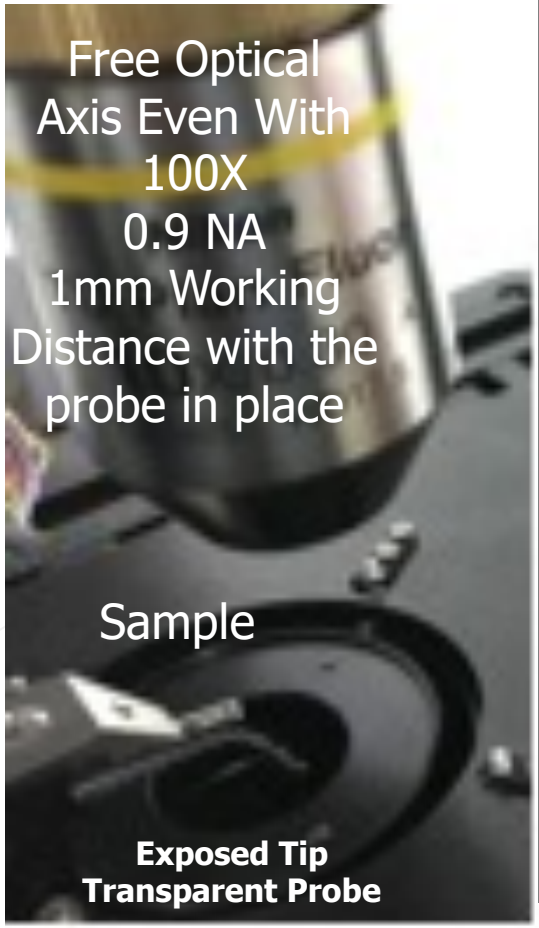
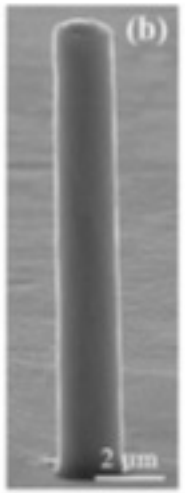


AFM Sensing Cantilevered Glass SECM Probe with Tuning Fork

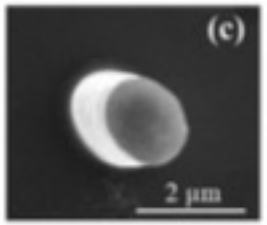
What customers publish:

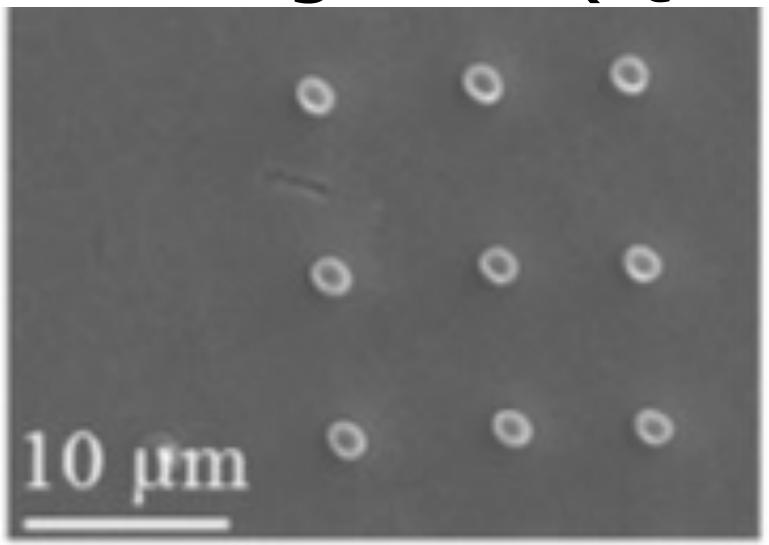
" measurements were carried out in non-contact mode at a constant separation distance of 4–8 nm from the surface using a Nanonics Multiview 2000 AFM equipped with a long AFM probe specially made for electrochemical measurements. The accurate separation distance is deter- mined based on the error caused during tip positioning by a system generated feedback. The AFM probe tip with a frequency of 39.95 kHz and a Q factor (quality factor) of 1500 helps in providing better stability for performing scans in liquids." Nanoscale, **2018**, 10, 6962

3D electrochemical deposition of Copper pillars with no jump to contact high rigidity quartz crystal tuning fork (QTF) nanopipettes



100:1 Aspect Ratio





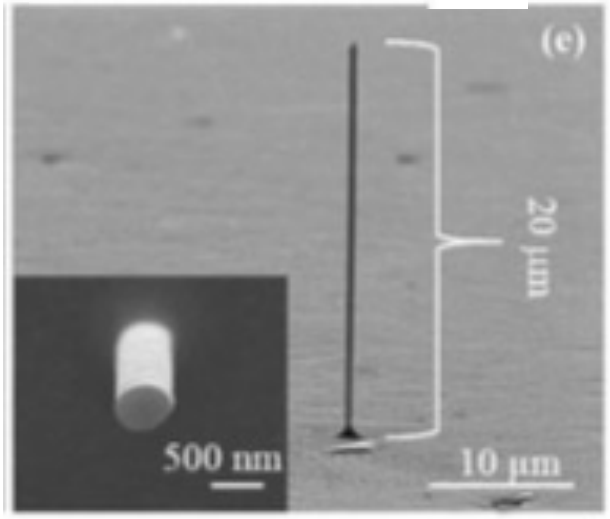


Table 1. The effects of the micropipette inner diameter on the printed Cu pillar diameter, deposition current, deposition current density, and average deposition rate.

Pipette size [µm]	Pillar diameter [µm]	Current, *I* [nA]	Current density [mA cm^{-2}]	Average deposition rate [nm s^{-1}]
1	1.5	5	283	90
1	1.5	6	340	105
0.4	0.55	1	421	160
0.4	0.61	1.2	411	130
0.1	0.23	0.3	722	300
0.1	0.27	0.4	699	230

What customers publish:

"The development of a 3D electrochemical deposition system, which combines meniscus-confined electrodeposition (MCED) with atomic force microscope (AFM) closed-loop control and has a submicron resolution, is described. Thanks to the high rigidity of the hollow borosilicate glass (or quartz) tip and quartz crystal tuning fork (QTF), combined with the QTF's high force sensitivity, the use of a solution-filled AFM tip in air is successful." *Adv. Mater. Technol.* **2020**, 1900827

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Full Optical Integration Permits On-line Spectral Characterization Including Raman Chemical Identification With Electrochemical Analysis

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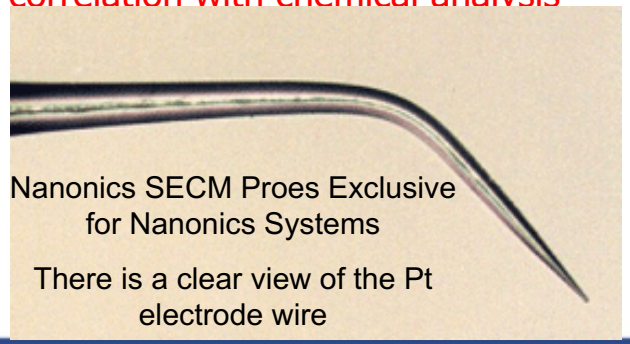
- The tuning fork AFM feedback methodology is used allowing for water immersion objectives and permits ultra high force sensitivity of the AFM with SECM down to pico Newtons
- This allows Nanonics to transparently unify SECM and Raman for electrochemical correlation with chemical analysis



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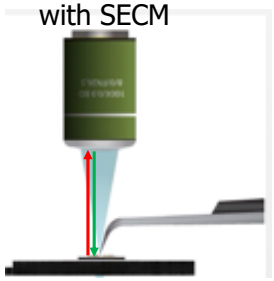
Raman MicroSpectroscopy

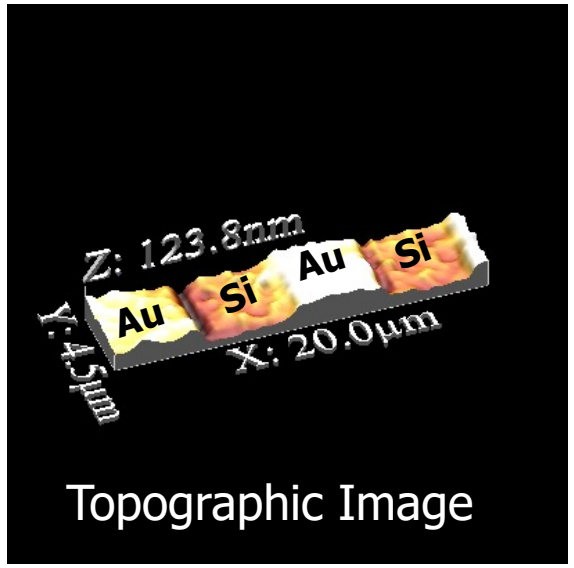
SECM Atomic Force Microscopy

Laser Excitation and Raman Scattering with SECM

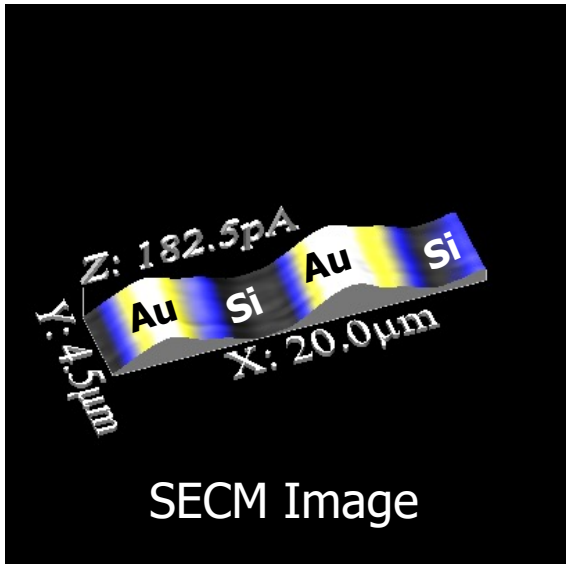


AFM Raman

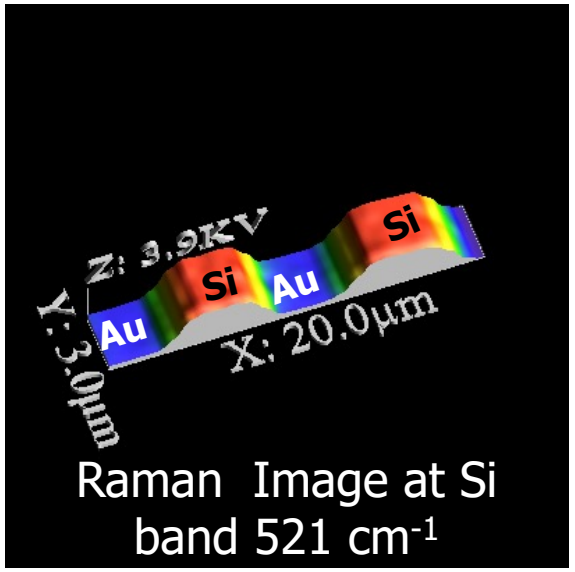
Integrate with Any MicroRaman



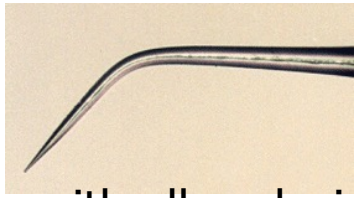
Topographic Image



SECM Image

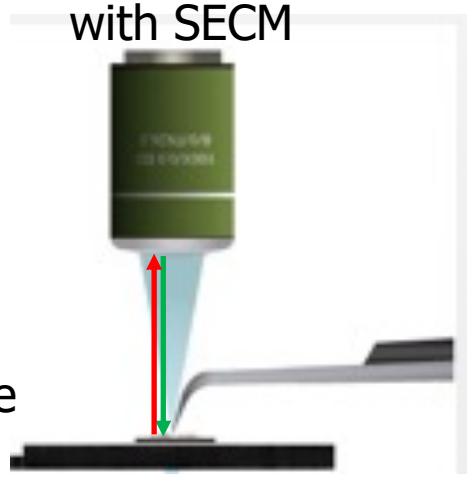


Raman Image at Si band 521 cm^{-1}



As with all exclusive Nanonics probes the geometry of the probes and the instruments permit such unique applications in liquid like TERS and SECM with Raman

Laser Excitation and Raman Scattering with SECM



The above data was obtained with the probe inserted into a water immersion objective which is critical since without such an ability the Raman signal is low to non-existent

Come up to a new world of stand alone SECM by adding AFM

- Get all standard modes of SECM such as SVET (Scanning vibrating electrode technique) and LEIS (localized electrochemical impedance spectroscopy) etc
- *But* with on-line AFM one has the ability to get not only micrometric but also nanometric imaging since AFM provides an independent feedback mode conventional SECM does not provide. This is essential to separate topography from electrochemical current which one needs to know independently.
- Thus, ultrasmall electrodes down to 100nm can be used which were previously impossible to employ
- Also allow important upgrades such as on-line Raman for chemical characterization along with ionic currents unavailable with previous SECM approaches
- Today SECM systems without AFM are missing the full picture without an independent feedback separating topography from electrochemical current and without accurate control of distances from the surface.