Introduction to ic-SECM

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Objectives

Provide a better understanding of

1. **What the ic-SECM technique is**
2. **Which information can be obtained**
3. **What the advantage of ic-SECM over dc-SECM is**

Outline

1. **Prerequisite : dc-SECM**
2. **ic-SECM : measurement method**
3. **ic-SECM : data**

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2. **ic-SECM : measurement method**
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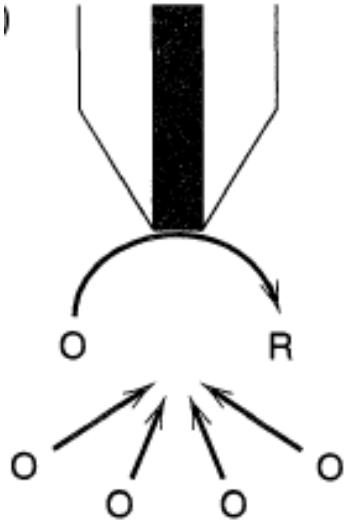
UME in bulk solution

UME : Ultra MicroElectrode

Definition : « At present,
there is no broadly accepted definition of a UME, although there is a general
agreement on the essential concept, which is that the electrode is smaller than the scale of the diffusion layer developed in readily achievable experiments.[1]”

Steady-state response of a disk UME to a Large-Amplitude Potential Step



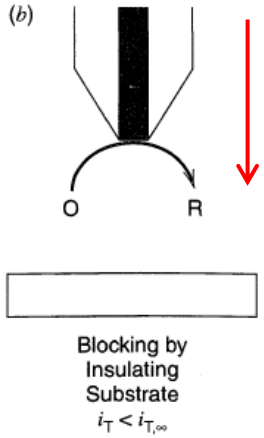
Hemispherical Diffusion (Radial and normal)

$$i_{T,\infty} = 4nFD_O C_O^* a$$

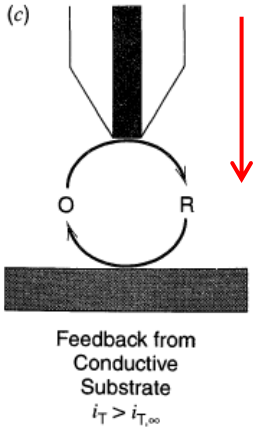
1. A.J. Bard, L. R. Faulkner, Electrochemical Methods, 2nd edition, Wiley & Sons, NYC

Feedback mode : approach curves

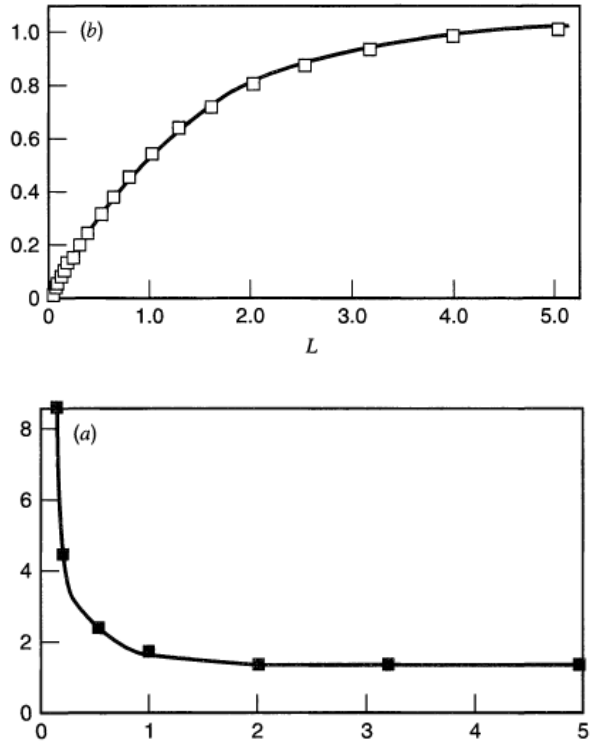
Negative feedback



Positive feedback



Normalized tip current $i_T/i_{T,\infty}$



Normalized electrode – sample distance (d/a)

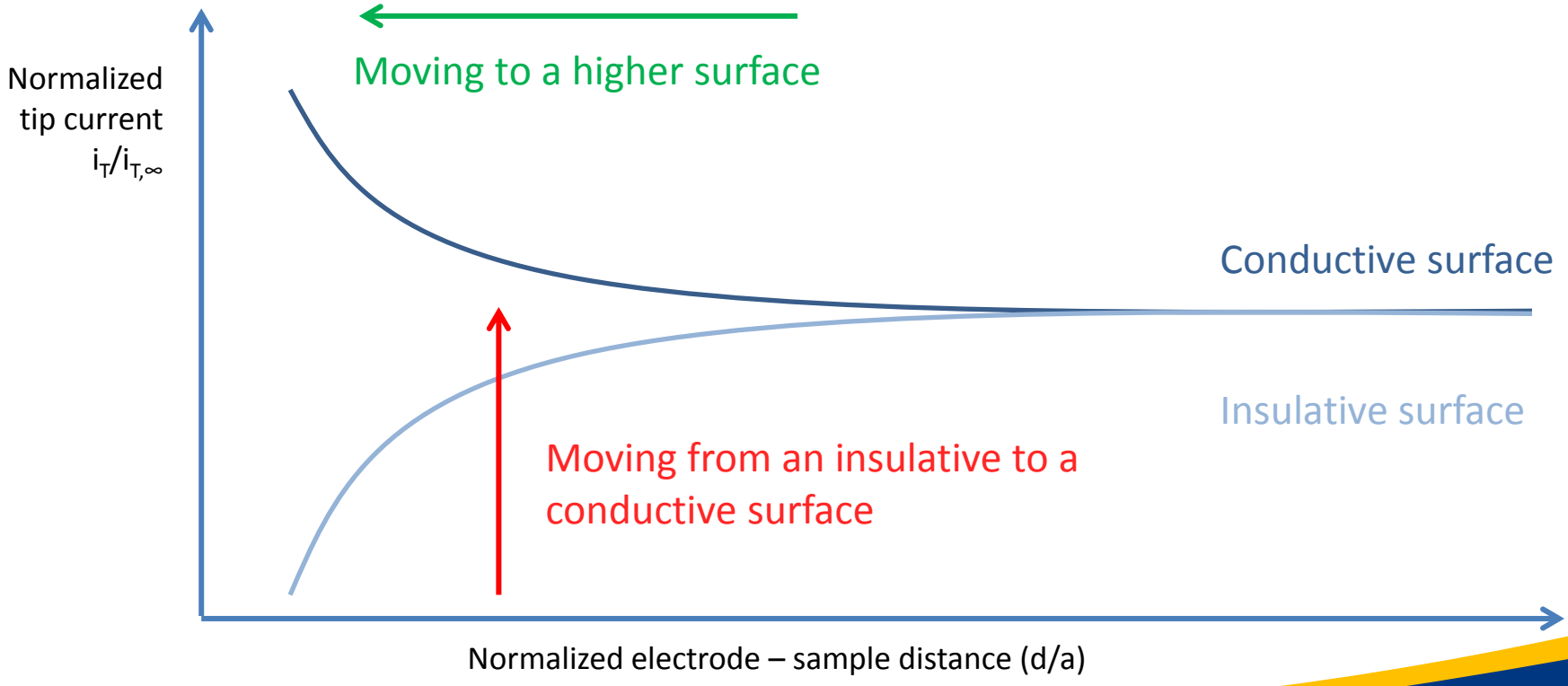
1. A.J. Bard, L. R. Faulkner, Electrochemical Methods, 2nd edition, Wiley & Sons, NYC

Feedback mode : approach curves

As the probe is sufficiently close to the surface, the current changes if :

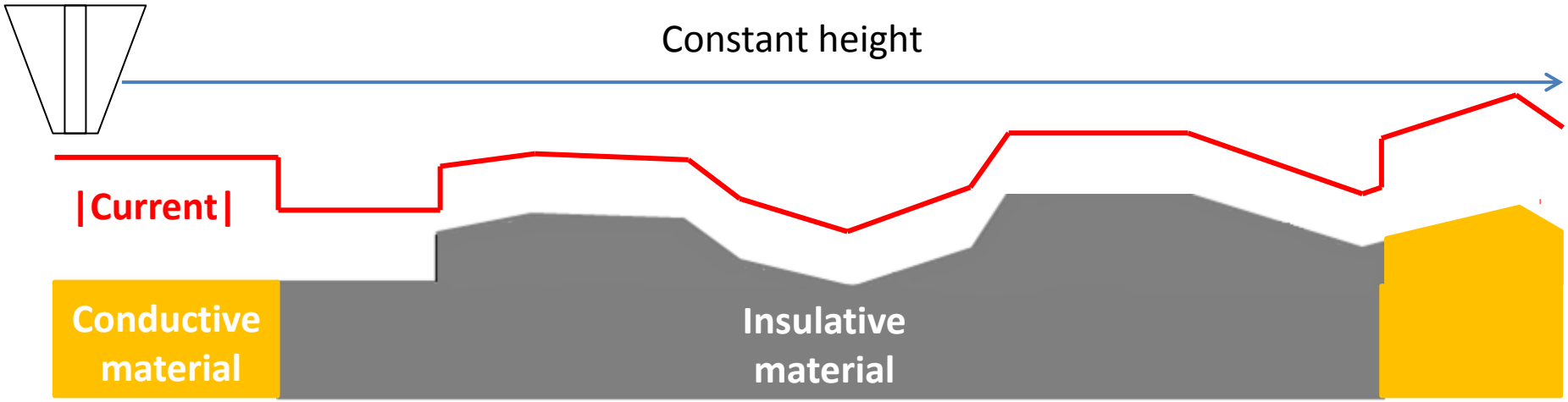
. The conductivity of the surface changes

. The topology of the surface changes



Feedback mode : limit

No Discrimination between topography and surface effects



If both the conductivity and the topography of the substrate change, there is no way to discriminate their contribution to the current. The solution is to keep the electrode to sample distance constant. This can be done using Height Relief but it is using two techniques, two scans and a positional reference is needed.

ic-SECM allows to perform constant tip-to-sample distance measurement with the same technique.

Outline

1. Prerequisite : SECM
2. ic-SECM : principles
3. ic-SECM : measurement
4. ic-SECM : data

ic-SECM

1. The SECM probe is sinusoidally oscillating at a low frequency (tens of Hz) and an amplitude of a fraction (1-4 %) of the SECM electrode radius using a piezoelectric positioner. This amplitude is named Δz_{bulk}.

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5. As a scan is made over the surface, if the probe meets a hill, the measured amplitude $\Delta z_{measured}$ will be lower than Δz_{ic}. The piezo takes the probe up such that $\Delta z_{measured} = \Delta z_{ic}$.

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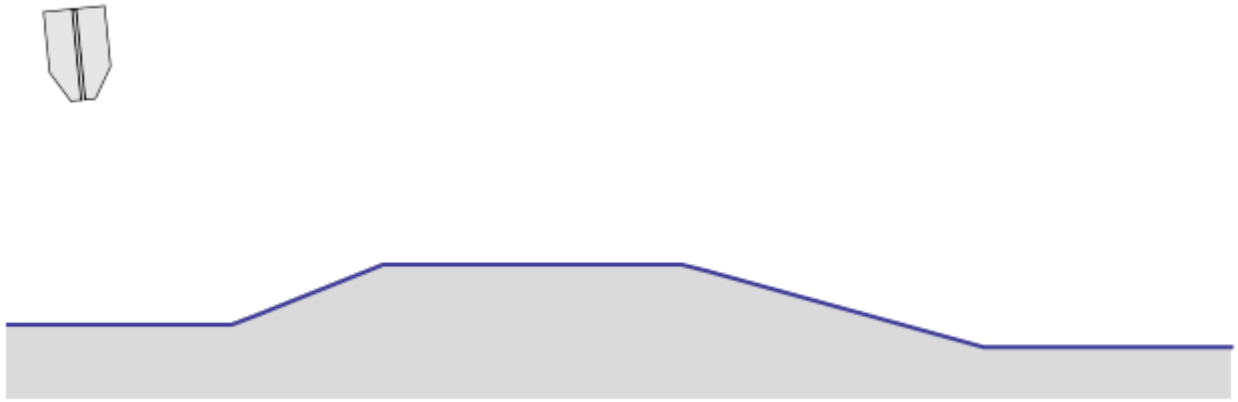
If the probe meets a valley $\Delta z_{measured} > \Delta z_{ic}$. The piezo takes the probe down.

ic-SECM

Click on the figure to see the animation.



With the courtesy of J.-P. Diard

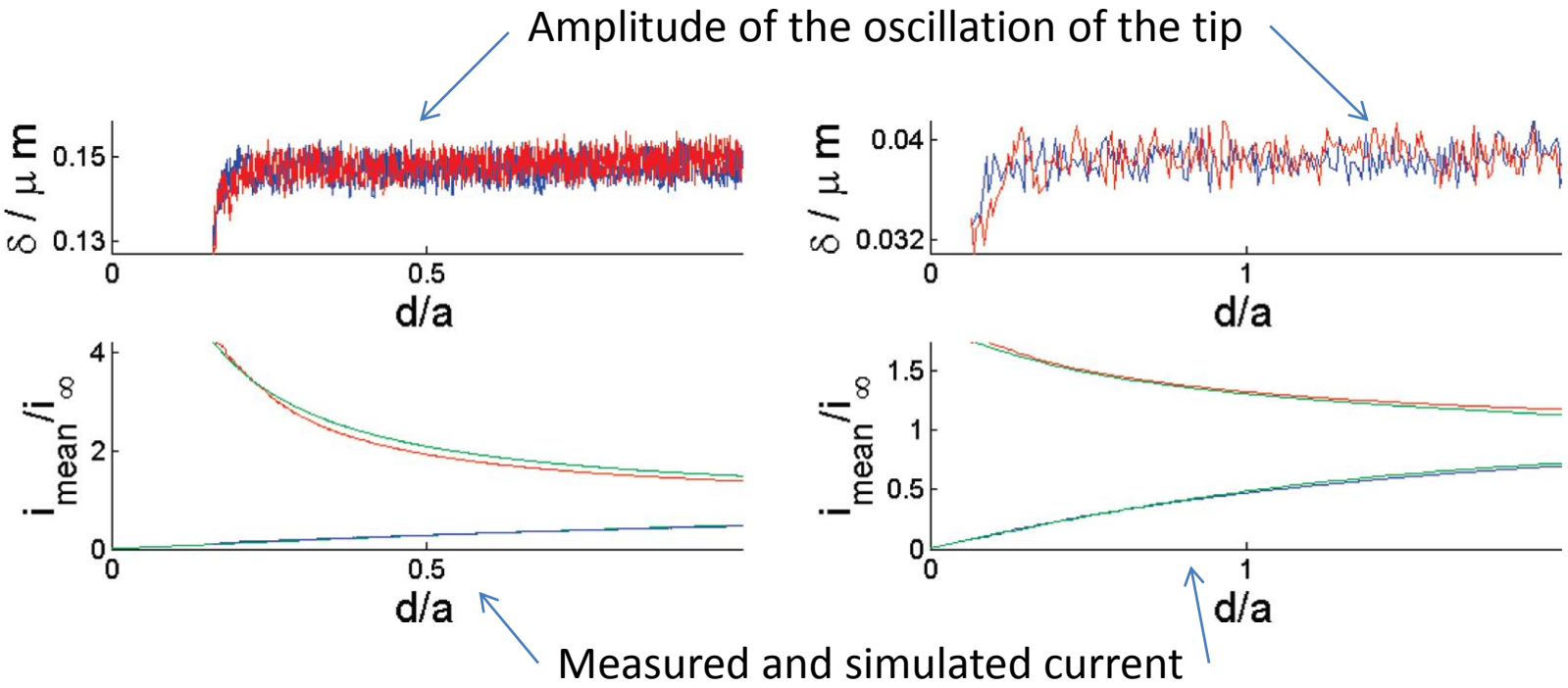
ic-SECM : operating mode

1. The approach curves is performed using the strain gauge sensor. Once the intermittent contact is made the actual measurement scan starts.

2. The topography and the current are measured in a single scan.

3. As the probe is vibrating, it is possible to measure dc and ac current magnitudes as well as the phase of the ac current.

ic-SECM : approach curves



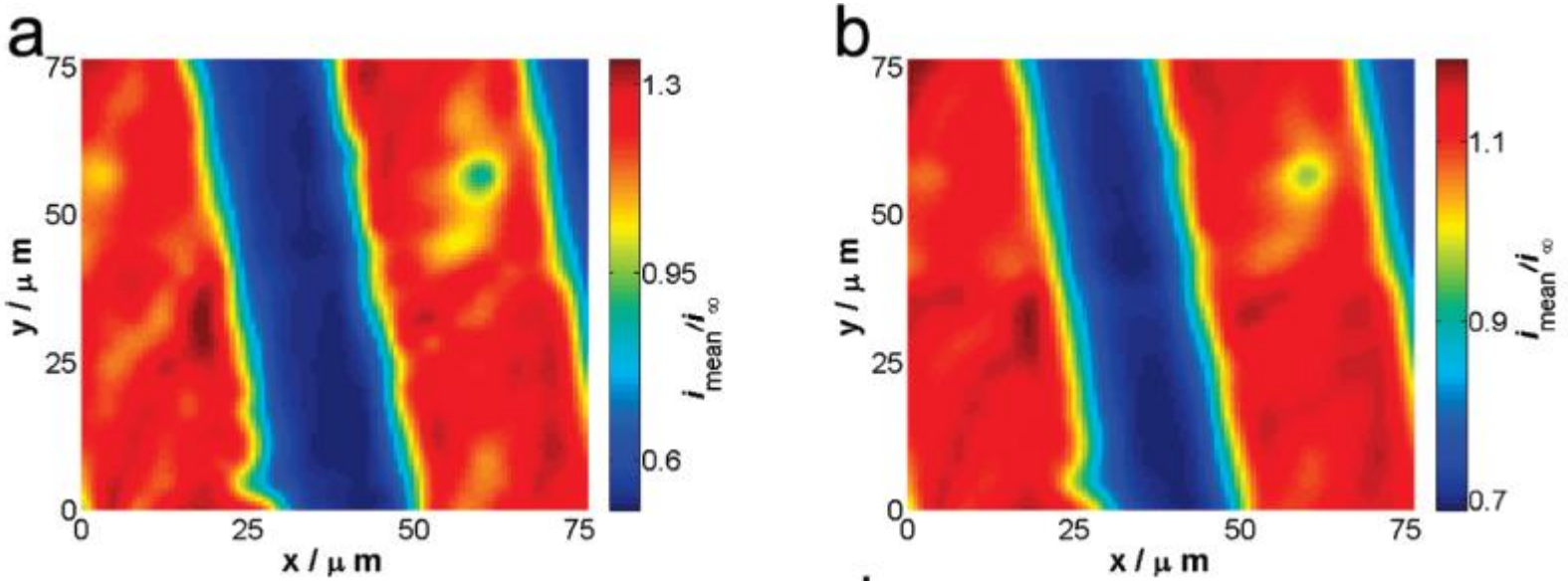
Feedback approach curves to conducting, gold (red), and nonconducting, glass (blue), substrates
Left: 12.5 µm radius Pt disk electrode oscillated at 70 Hz, Δz_{ic} = 145 nm in 0.5 mM FcTMA+.
Right: 1 µm radius Pt disk electrode oscillated at 70 Hz, Δz_{ic} = 39 nm in 2 mM FcTMA+.

The tip oscillation of 1-4% of the electrode radius does not affect the mass transport of the redox species. The dc current response is still diffusion-limited.

2. K. McKelvey, M.A. Edwards, P.R. Unwin, Anal. Chem. 2010, 82, 6334–6337

ic-SECM : maps

Parallel gold bands (25 µm width, 20 µm pitch) on a glass microscope slide



a) dc current on the forward scan (ic-mode)
b) dc mean current on the backward scan with constant tip-sample distance of 1 µm

The conductive gold bands can be clearly seen.
There is more contrast on the ic picture because the probe is closer to the surface.

2. K. McKelvey, M.A. Edwards, P.R. Unwin, Anal. Chem. **2010,** 82, 6334–6337

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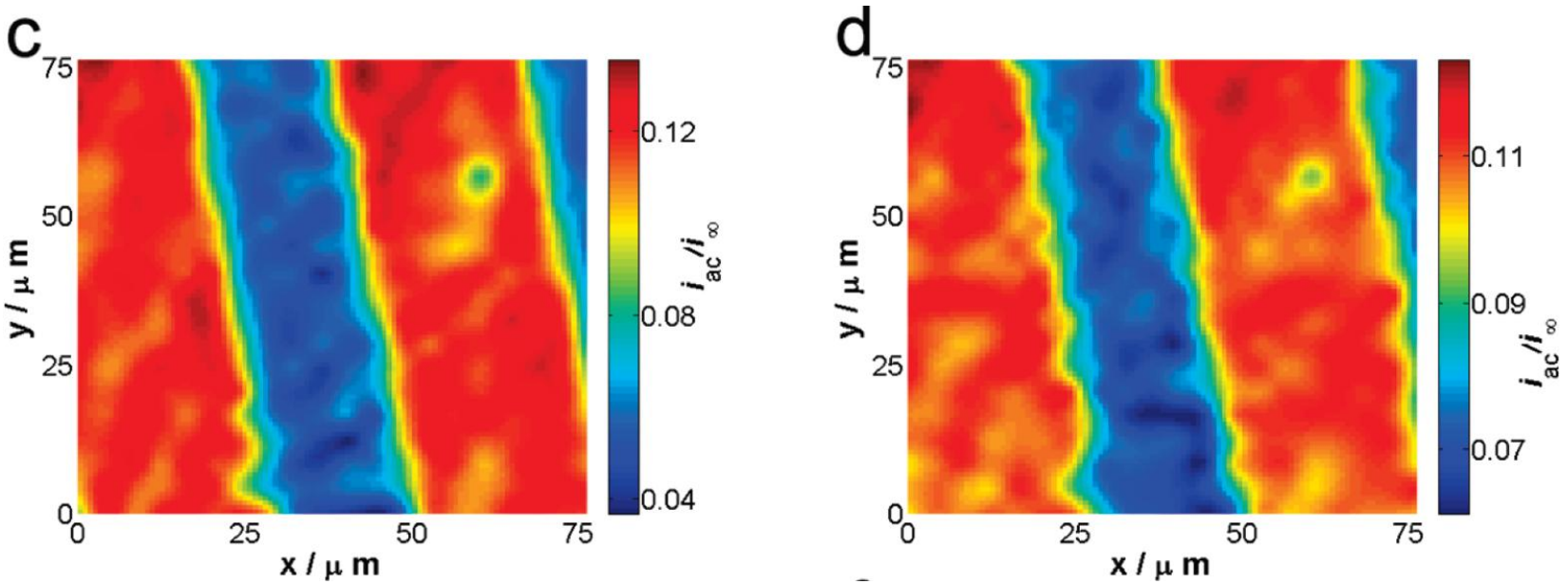

c) amplitude of the current oscillation on the forward scan (ic-mode)
d) amplitude of the current oscillation on the backward scan with constant tip-sample distance of 1 µm

They show the same underlying features, but with a greater dynamic range.
The ic i_{ac} image (panel c) again shows more sensitivity than the constant distance i_{ac} image (panel d) because of the closer tip-substrate separation.

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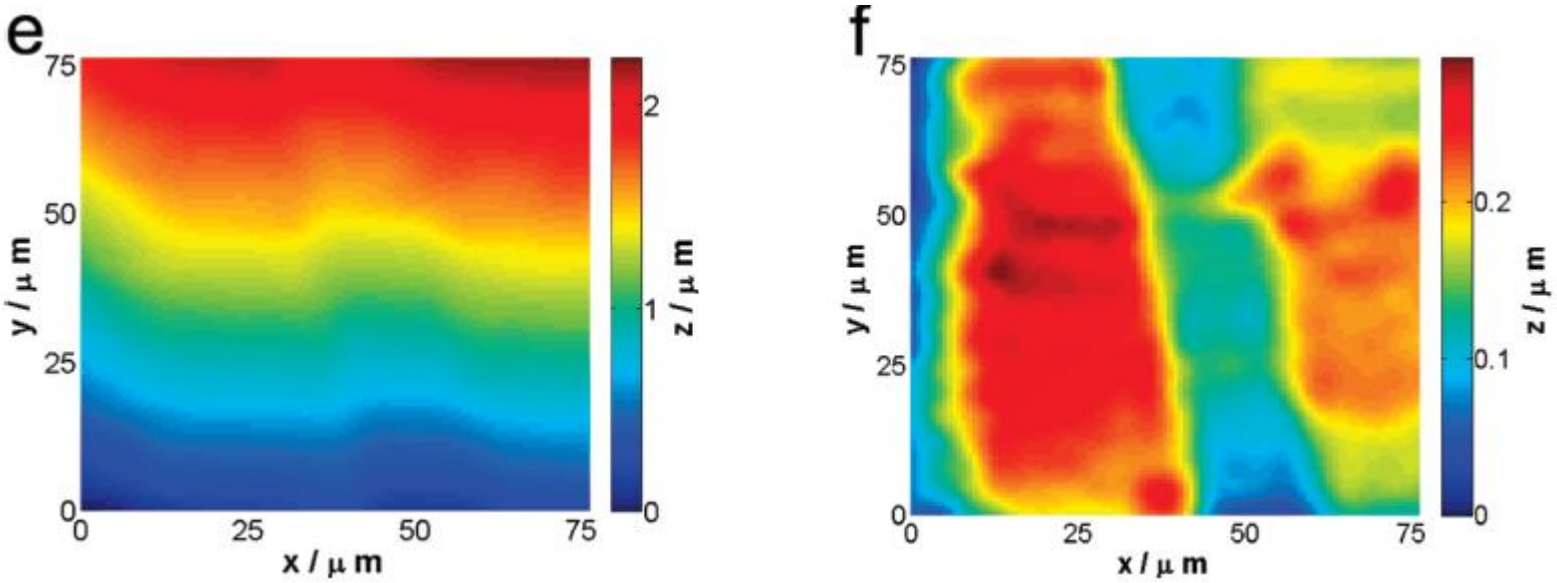


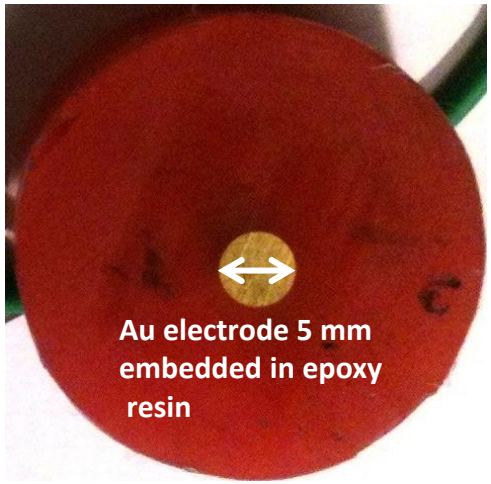
e) Topography image obtained in the forward scan
f) Tilt removed topography

Removing the tilt make the gold bands appear at a height of around 200 nm above the glass slide, which is coherent with lithography.
Note that their location is shifted compared to the electrochemical map due to the fact that the side of the glass sheath is touching the sample.

2. K. McKelvey, M.A. Edwards, P.R. Unwin, Anal. Chem. **2010,** 82, 6334–6337

ic-SECM : M470 maps

Sample :



Conditions :

15 µm Φ Pt SECM probe.

Rg ~10. Distance to surface: in-contact, control by “Intermittent Contact” mode (400 nm vibration at 455 Hz, control point at 80%).

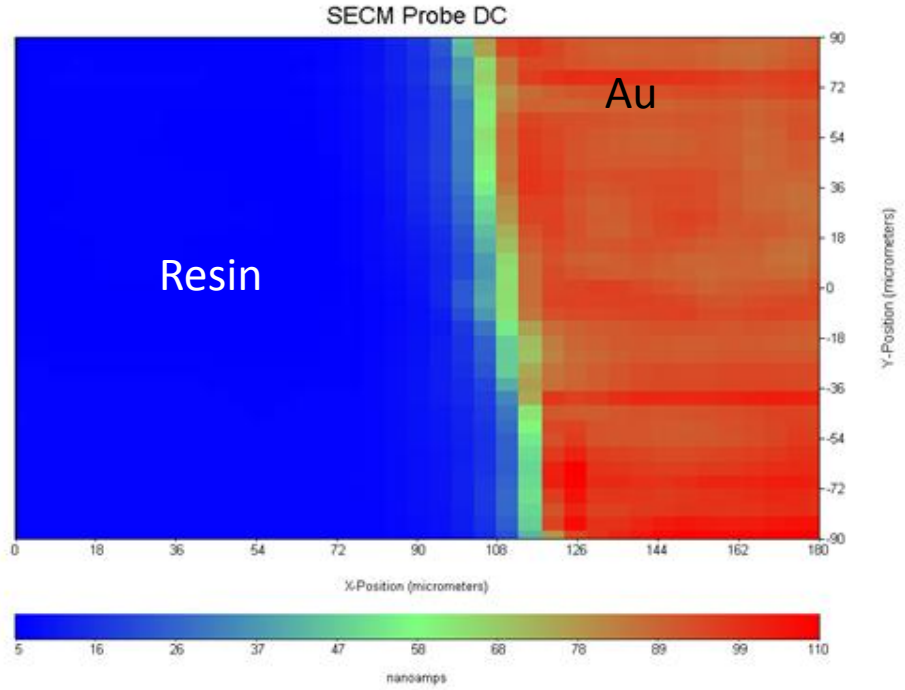
Solution: 10 mM KI solution + 100 mM KCl

Measurement at 455 kHz (vibration amplitude) over edge of 5mm Φ Au sample

DC bias = +0.7 V *vs.* ref. screen printed Ag/AgCl.

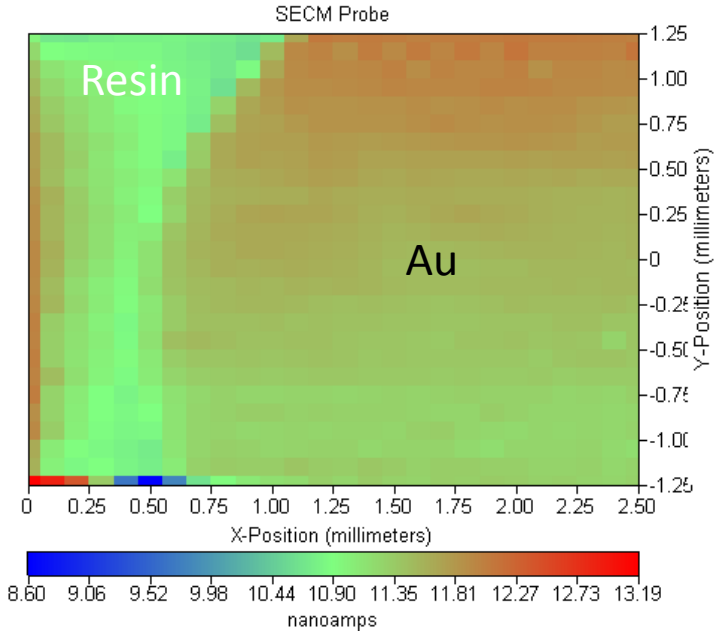
Bulk current : 14nA

ic-SECM : M470 maps



dc measurement in ic-mode (ic-SECM)

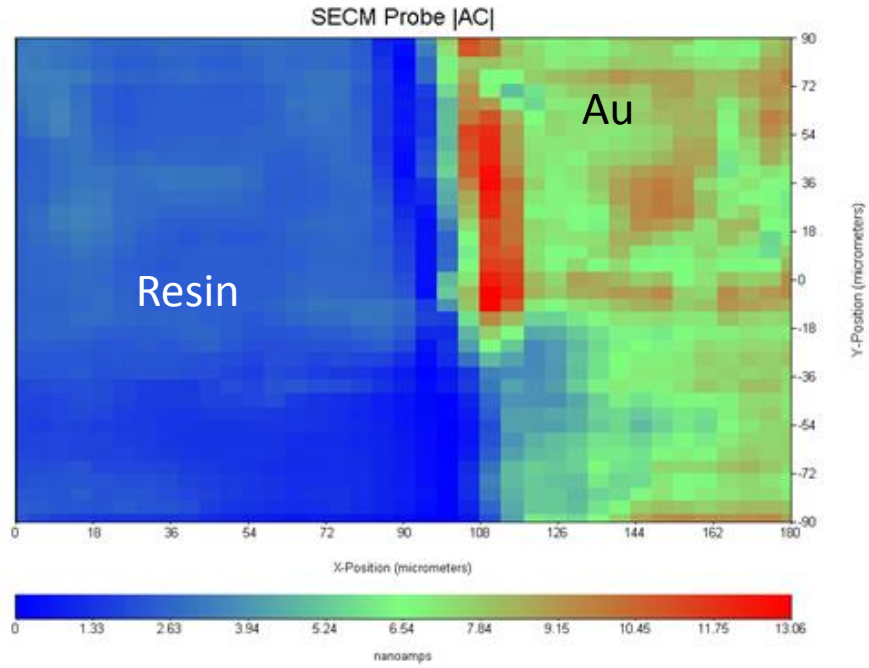
ΔI_{max} : 105 nA

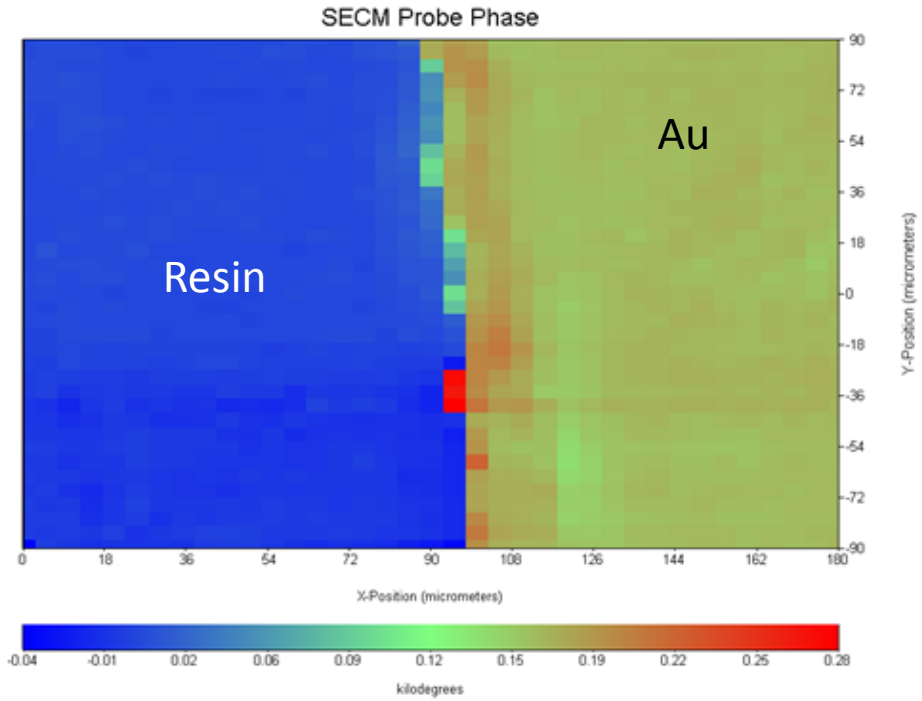


dc measurement in constant height mode (dc-SECM)

ΔI_{max} : 4.59 nA

ic-SECM : M470 maps





The Au gold electrode can clearly be visualized.
Different features can be seen on the Au electrode with the ac current modulus.

Topography can also be measured with a resolution of 20 nm.

Additional remarks

ic-SECM is a technique that can only be used so far with hard materials or hard samples.

It cannot be used with soft materials such as biological tissues, gels…

Conclusions

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. ac current modulus and current phase can provide different information from the sample.

Thank you for your attention !