12. Scanning probe techniques (ch. 16)

Scanning tunneling microscopy (STM)
Atomic force microscopy (AFM)
Scanning electrochemical microscopy (SECM)

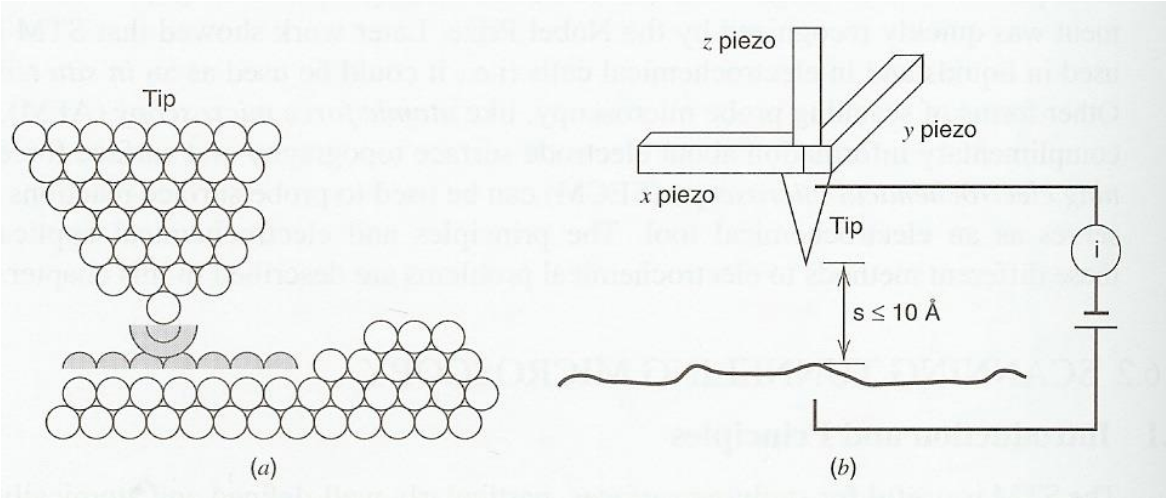
A.J. Bard, L. R. Faulkner, Electrochemical Methods, Wiley, 2001.

Scanning probe techniques

Microscopy: optical → scanning electron or force → STM, AFM

in situ vs. ex situ techniques

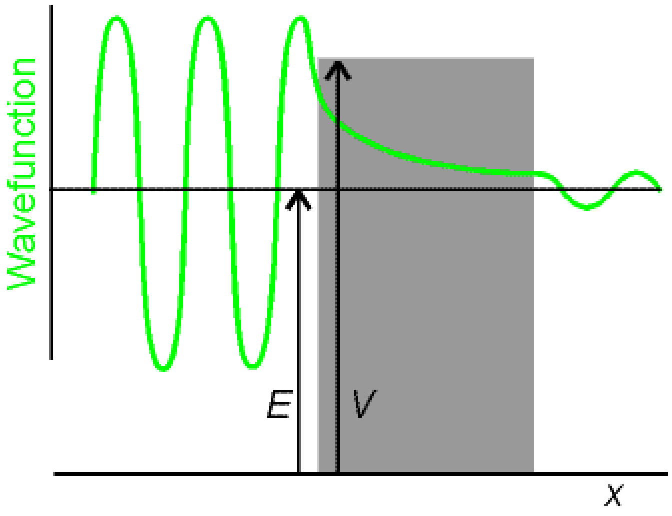
<u>Scanning tunneling microsocpy</u> (STM)

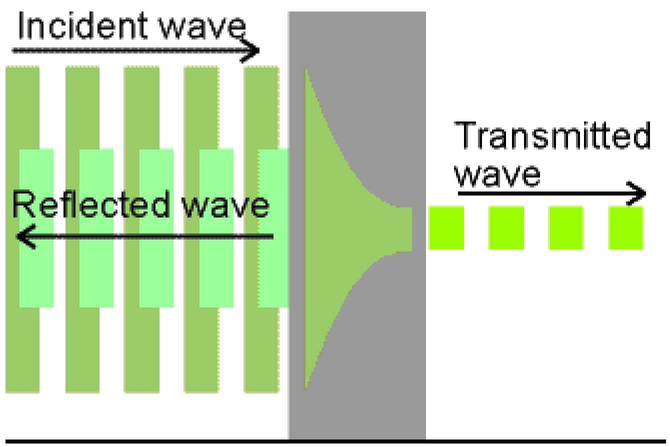


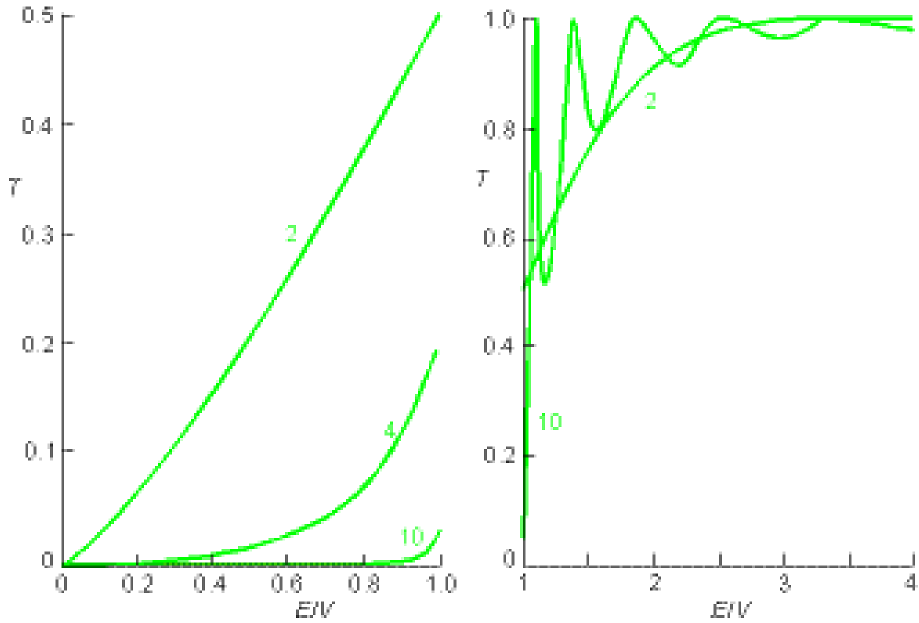
Tunnelling

- if the potential energy of a particle does not rise to infinite in the wall & E < V → Ψ does not decay abruptly to zero
- if the walls are thin → Ψ oscillate inside the box & on the other side of the wall outside the box → particle is found on the outside of a container: leakage by penetration through classically forbidden zones "tunnelling"

cf) C.M.: insufficient energy to escape







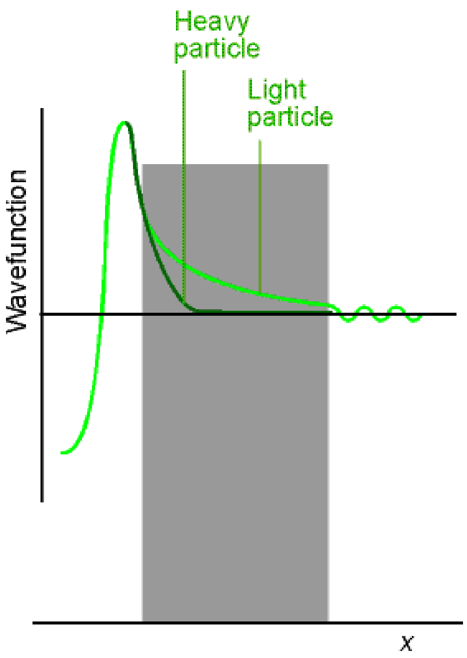
The transition probabilities for passage through a barrier. The horizontal axis is the energy of the incident particle expressed as a multiple of the barrier height. The curves are labelled with the value of $L(2mV)^{1/2}/$. The graph on the left is for $E<V$ and that on the right for $E>V$. Note that $T = 0$ for $E<V$ whereas classically T would be zero. However, $T<1$ for $E>V$, whereas classically T would be 1.

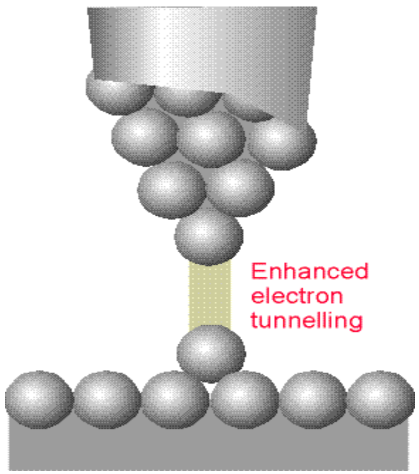
enhanced reflection (antitunnelling)

- high, wide barrier $\kappa L >> 1$

$\Rightarrow$ T decrease exponentially with thickness of the barrier, with $m^{1/2}$

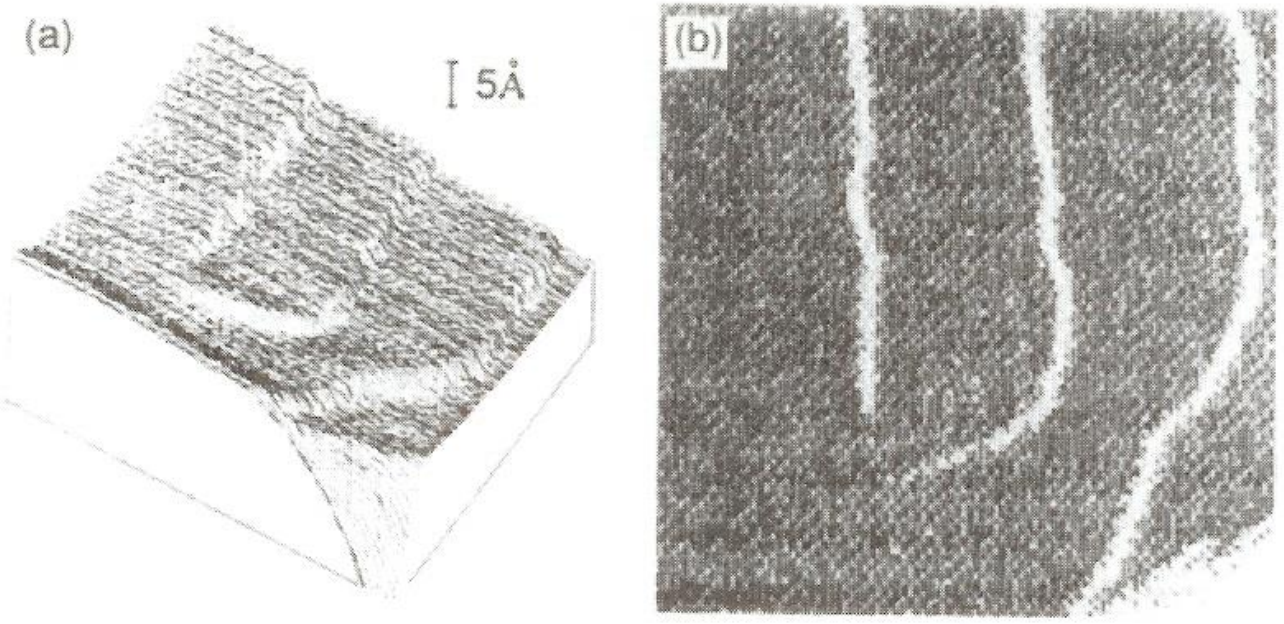
$\Rightarrow$ low mass particle $\rightarrow$ high tunnelling *tunnelling is important for electron



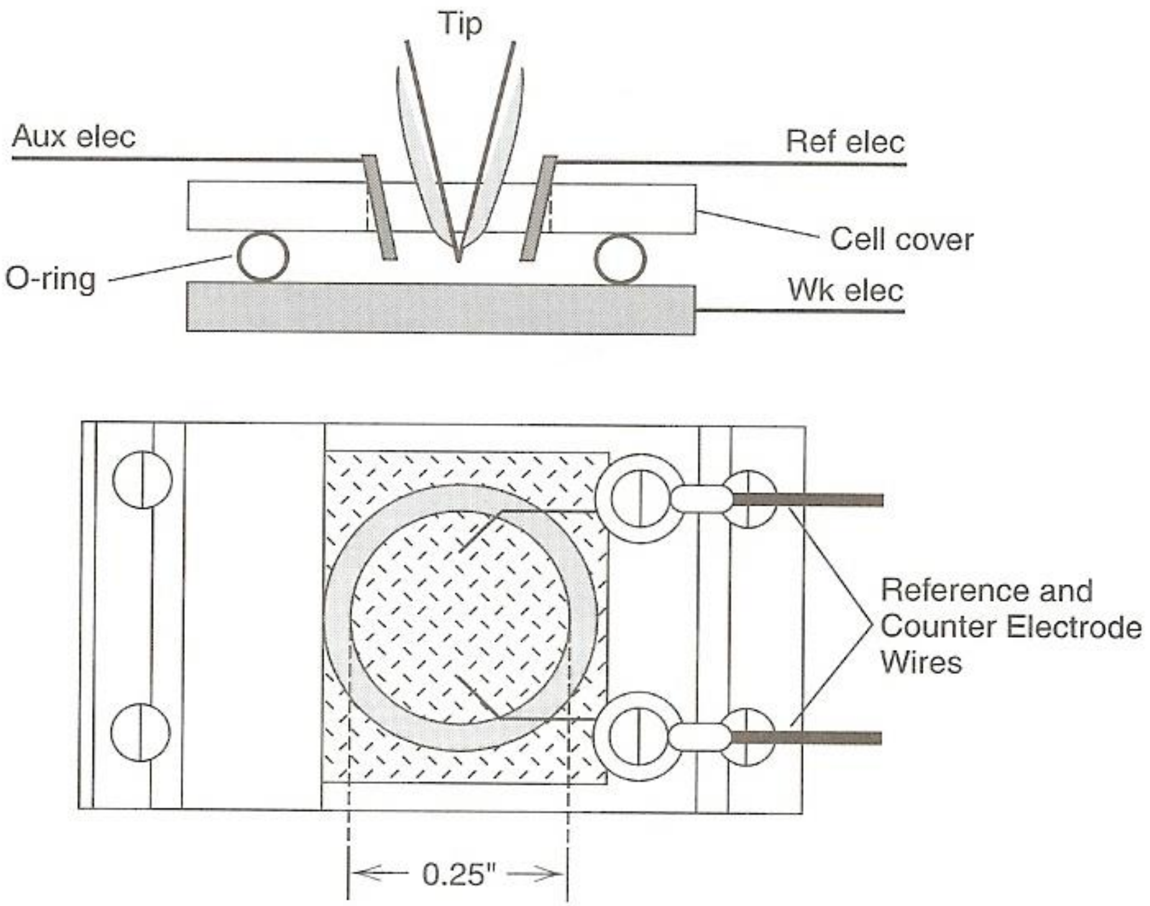


e.g) proton transfer reaction
STM (scanning tunnelling microscopy)
AFM (atomic force microscopy)

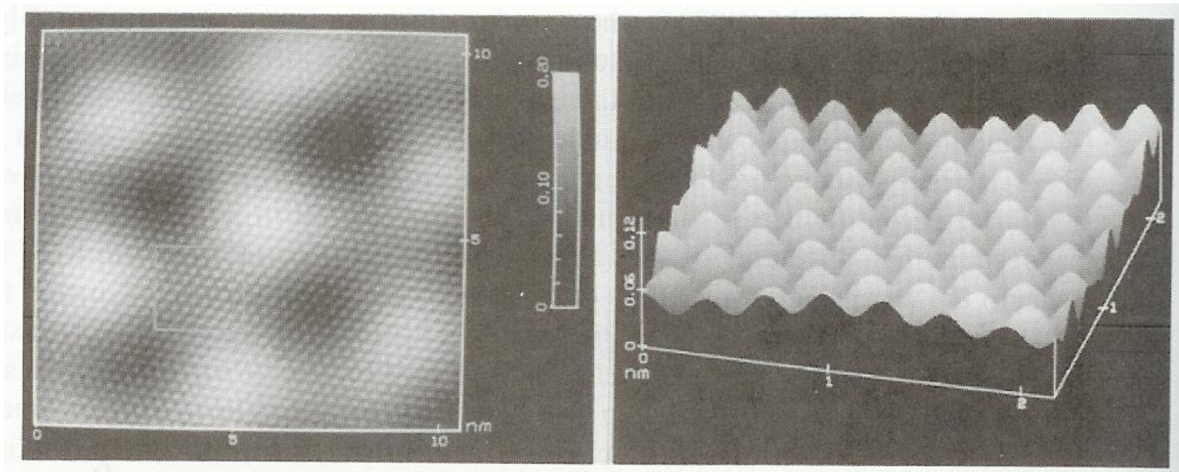
Au(111) at 0.7 V vs. NHE in HCl



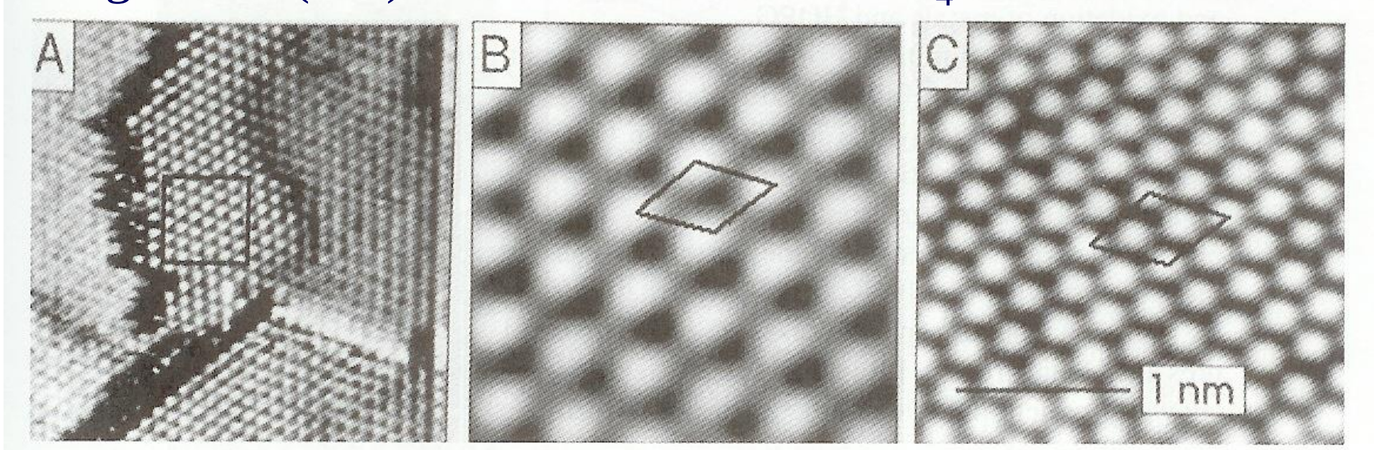
Electrochemical STM



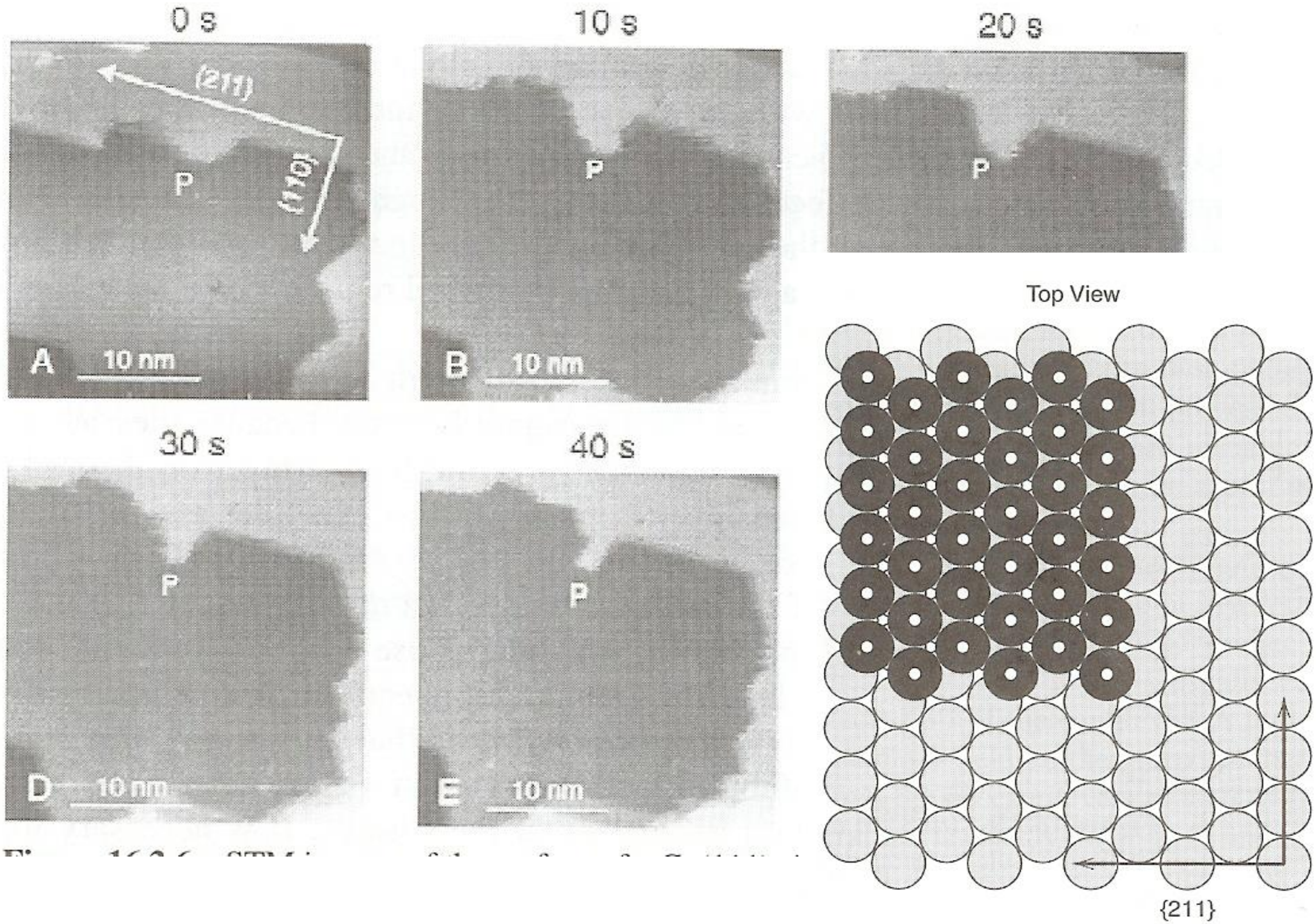
STM images of HOPG

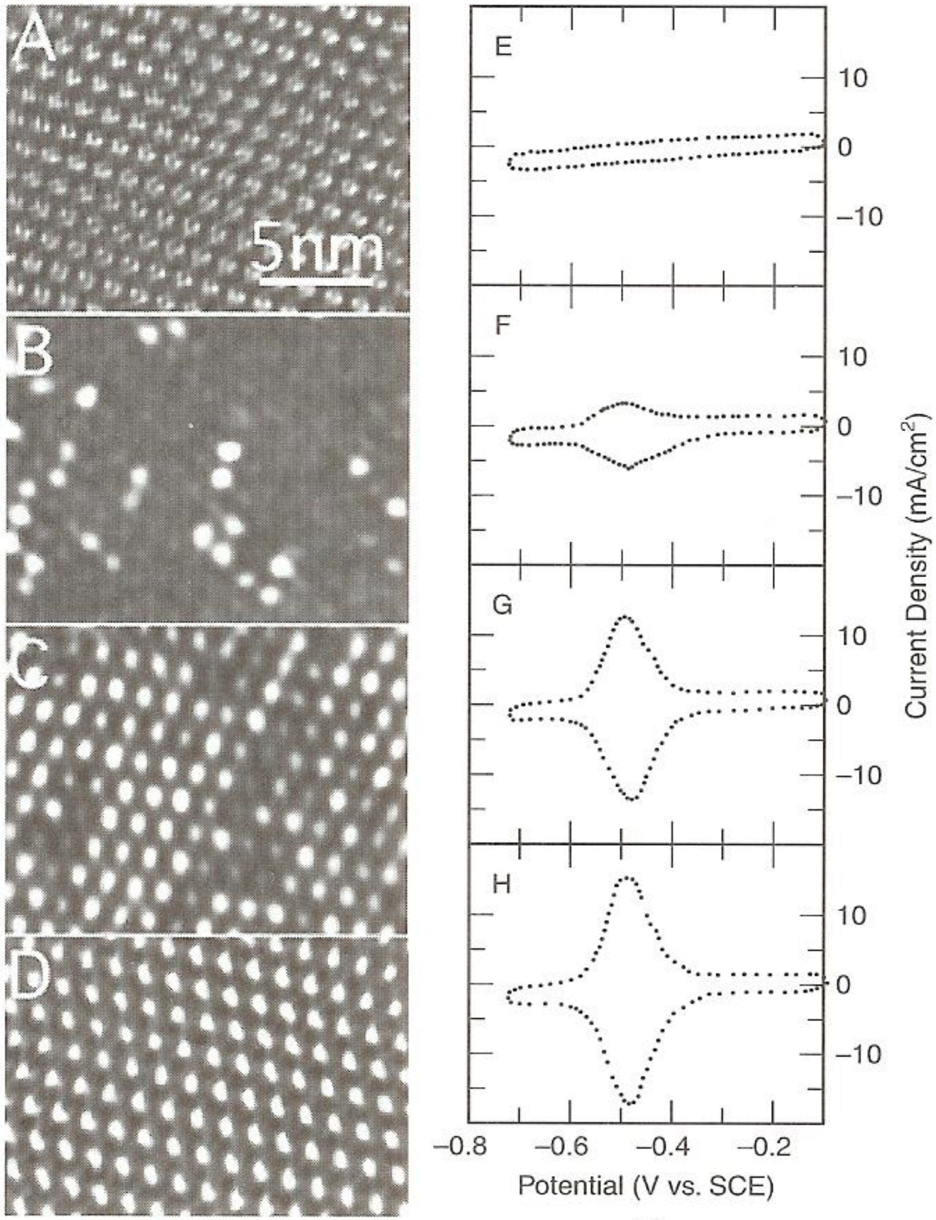


STM images of Pt(111) with I-adlattice in $HClO_4$



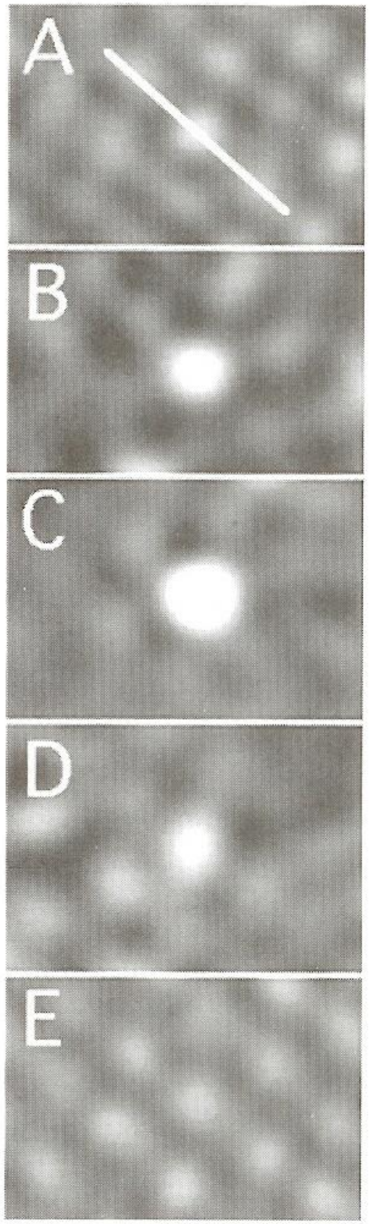
STM images of Cu(111): effect of etching



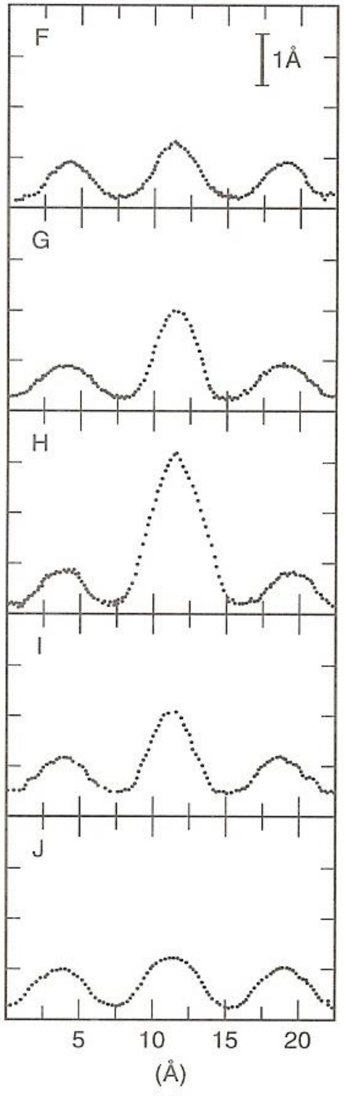


A
5nm
B
C
D
E
F
G
H
10
0
−10
−0.8
−0.6
−0.4
−0.2
Potential (V vs. SCE)
Current Density (mA/cm²)

(*a*) (*b*)



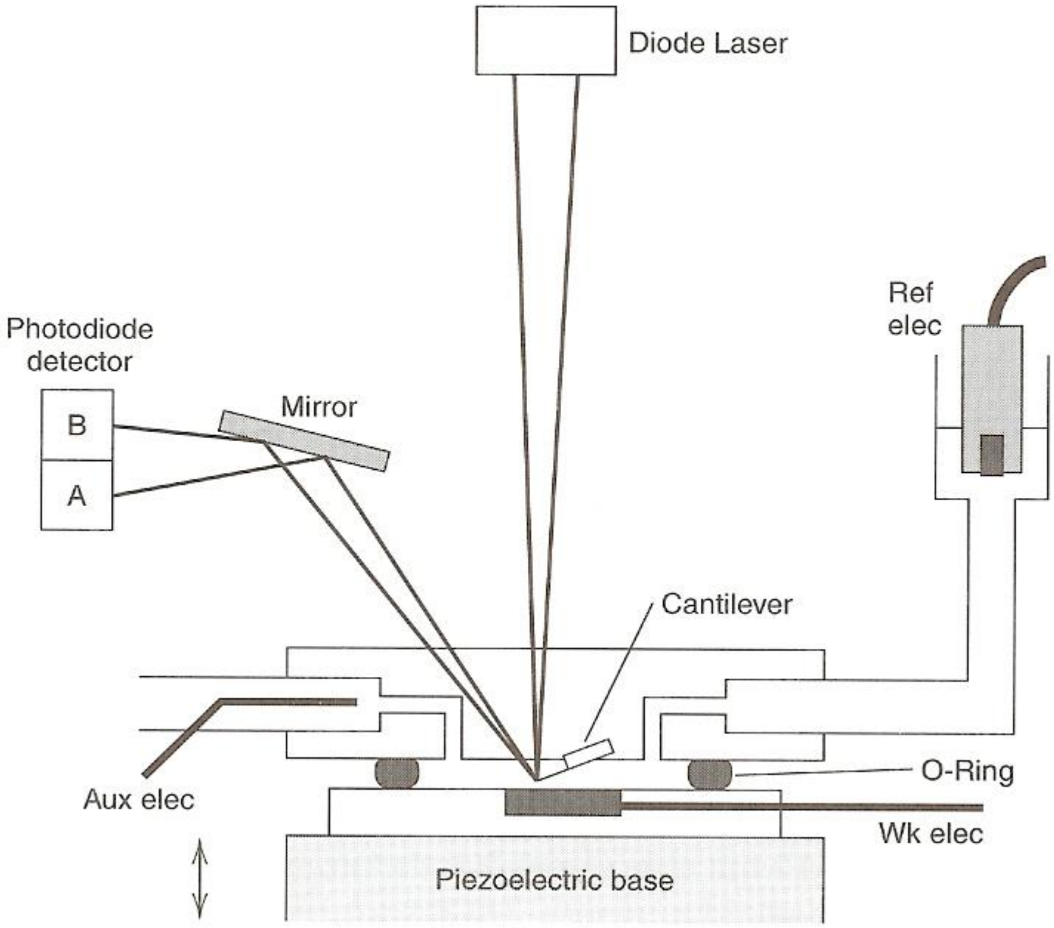
(*a*)



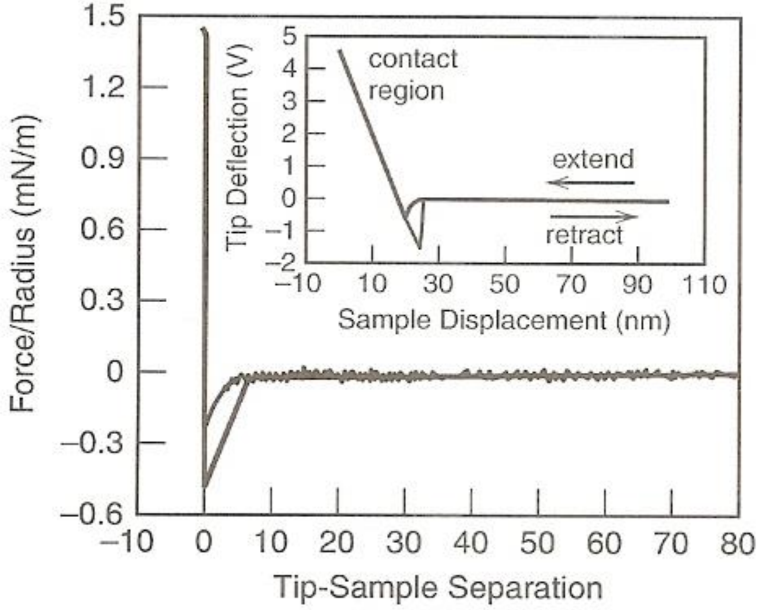
(*b*)

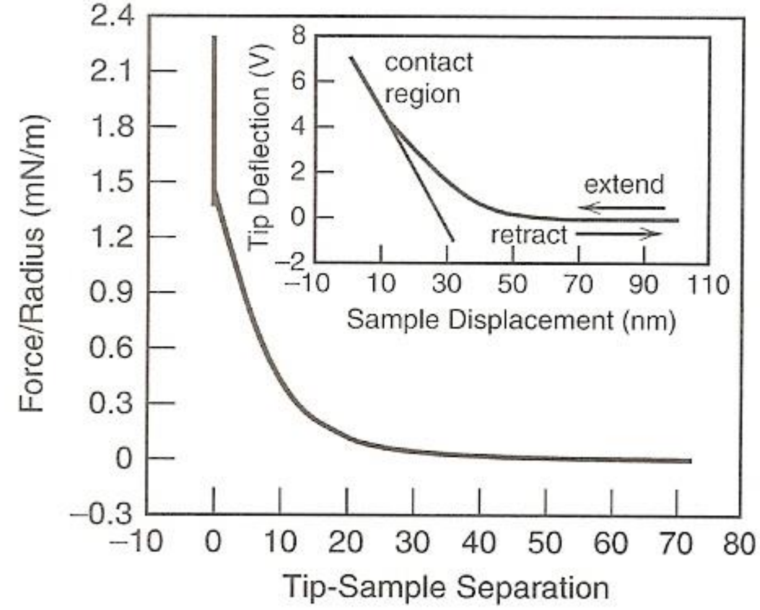
Scanning tunneling spectroscopy (STS)

Atomic force microscopy (AFM)



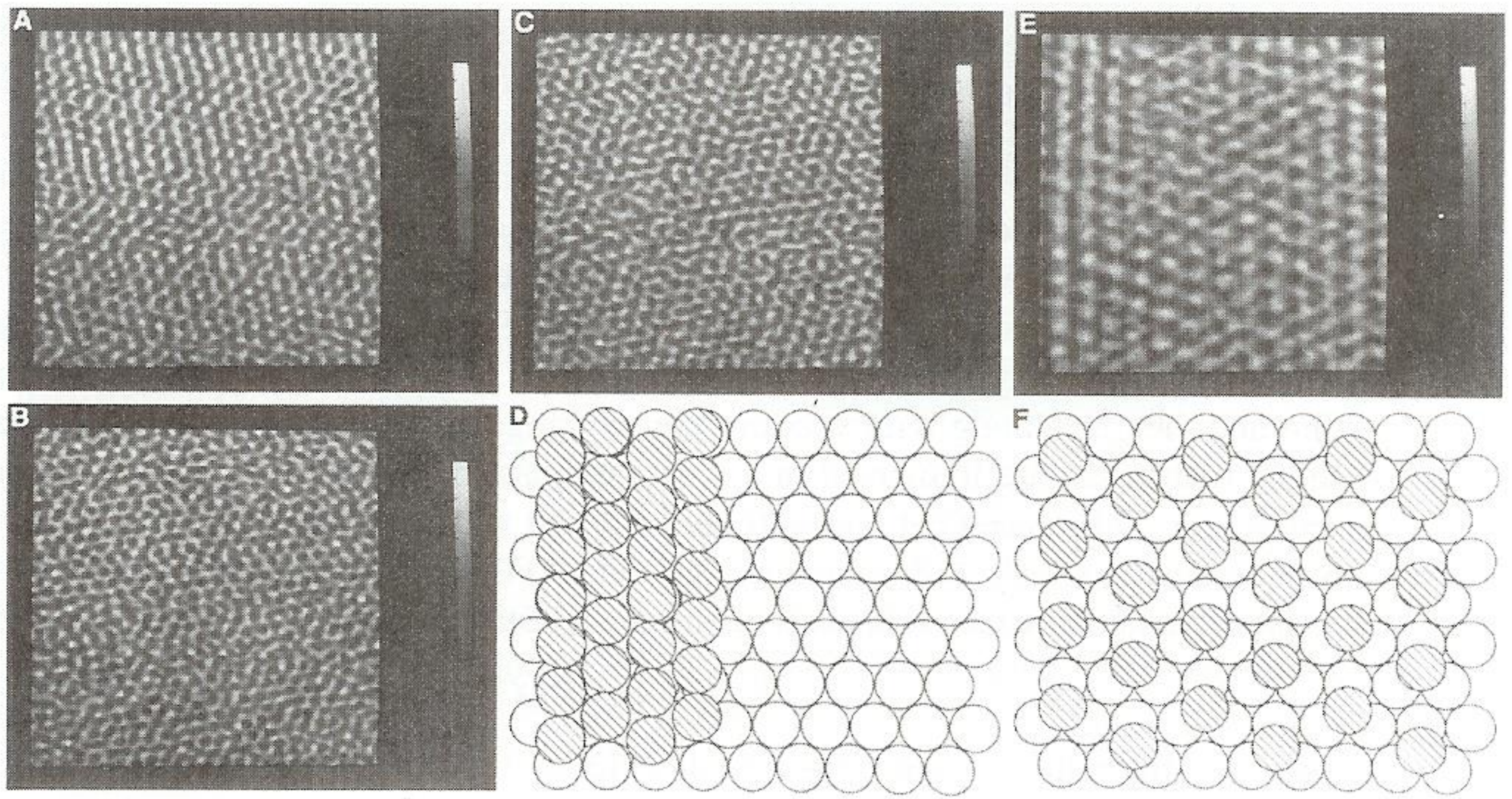
Cantilever displacement vs. z-deflection for (left) attractive interaction and (right) repulsive interaction



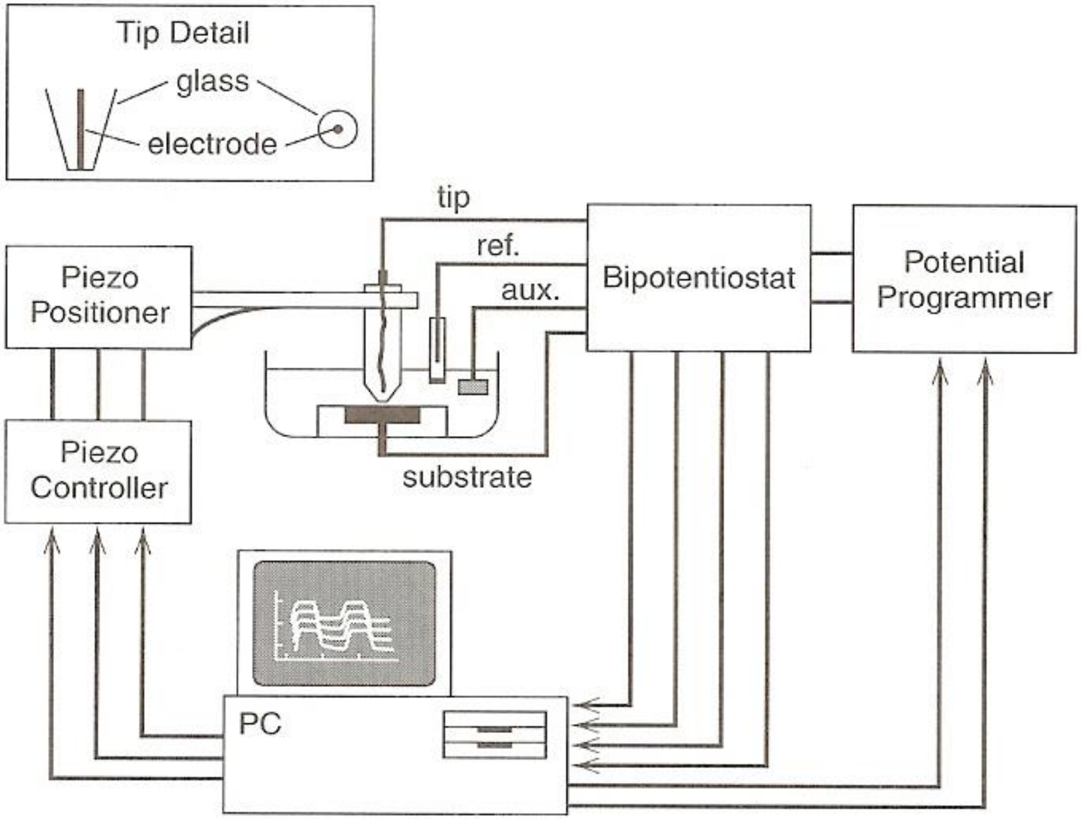


Electrochemical AFM

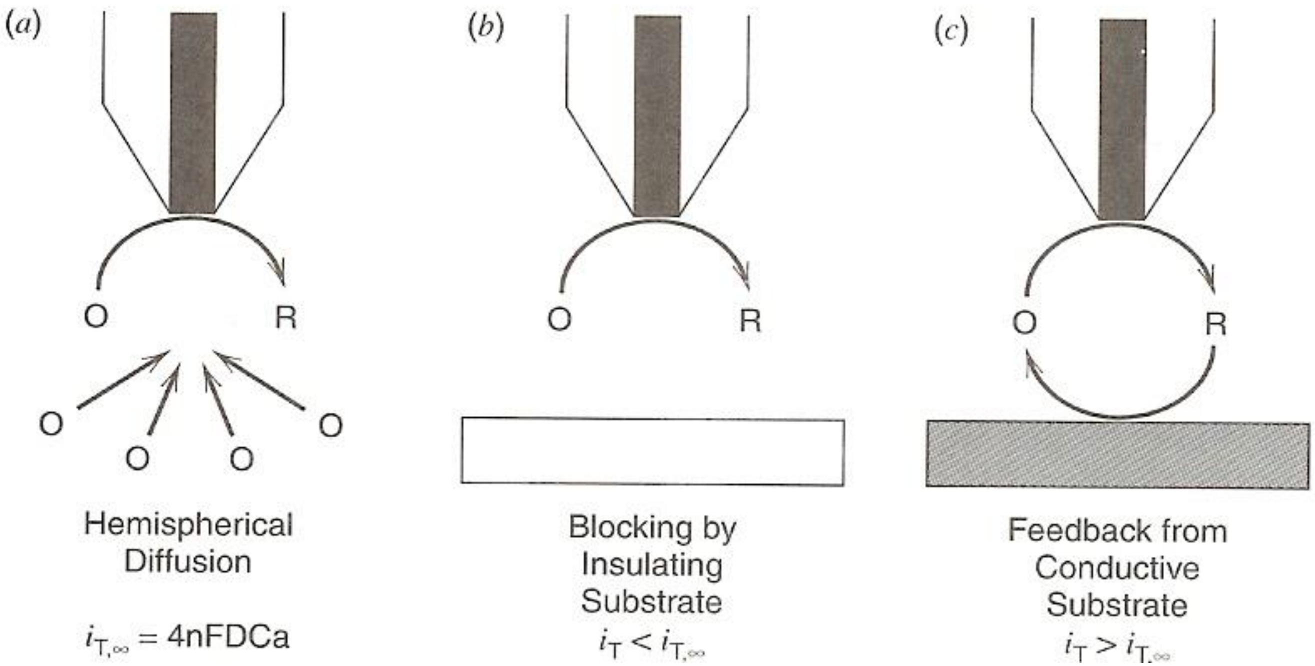
AFM of Cu underpotential deposition (UPD) on Au(111)



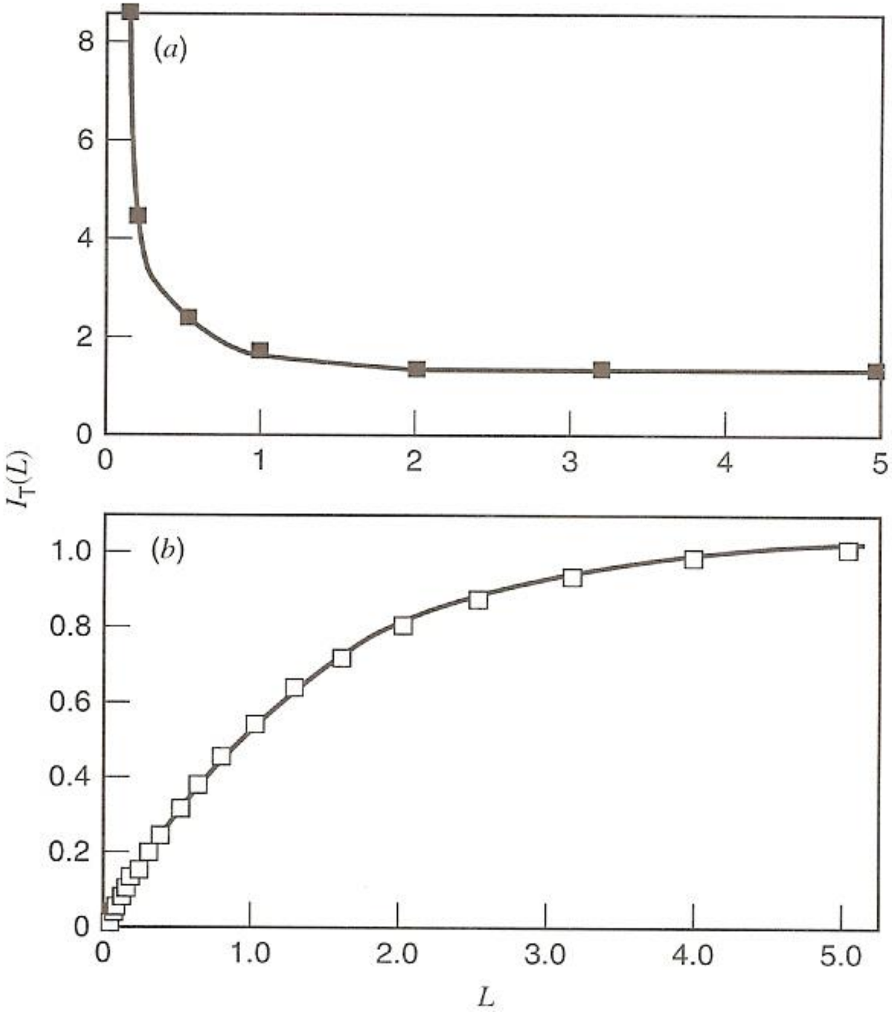
Scanning electrochemical microscopy (SECM)

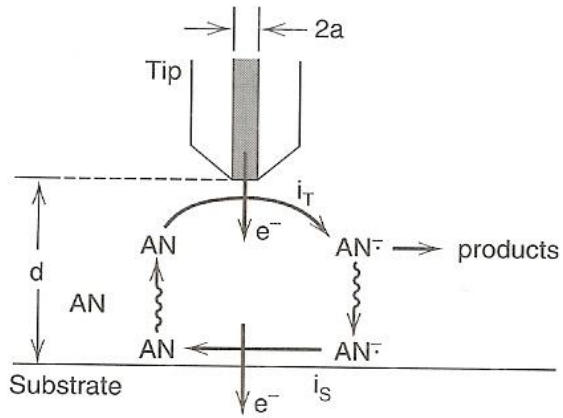


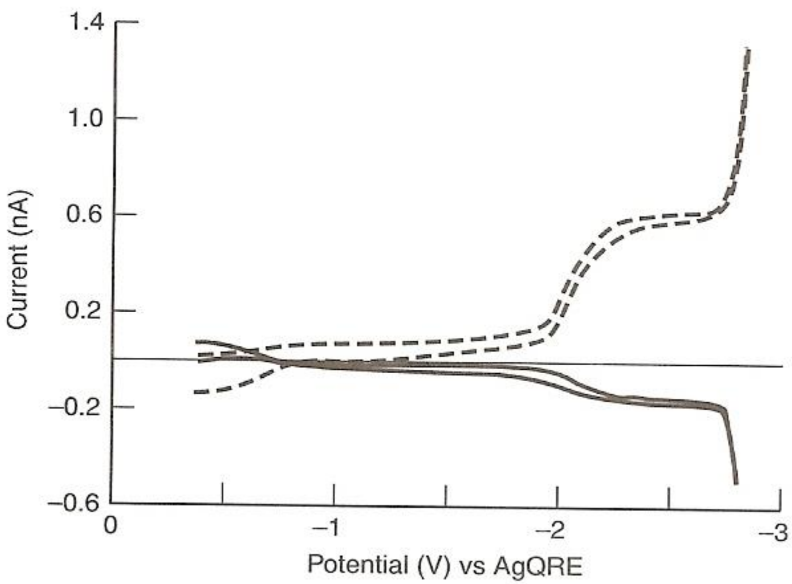
Principles of SECM



SECM appoach curves for steady-state currents

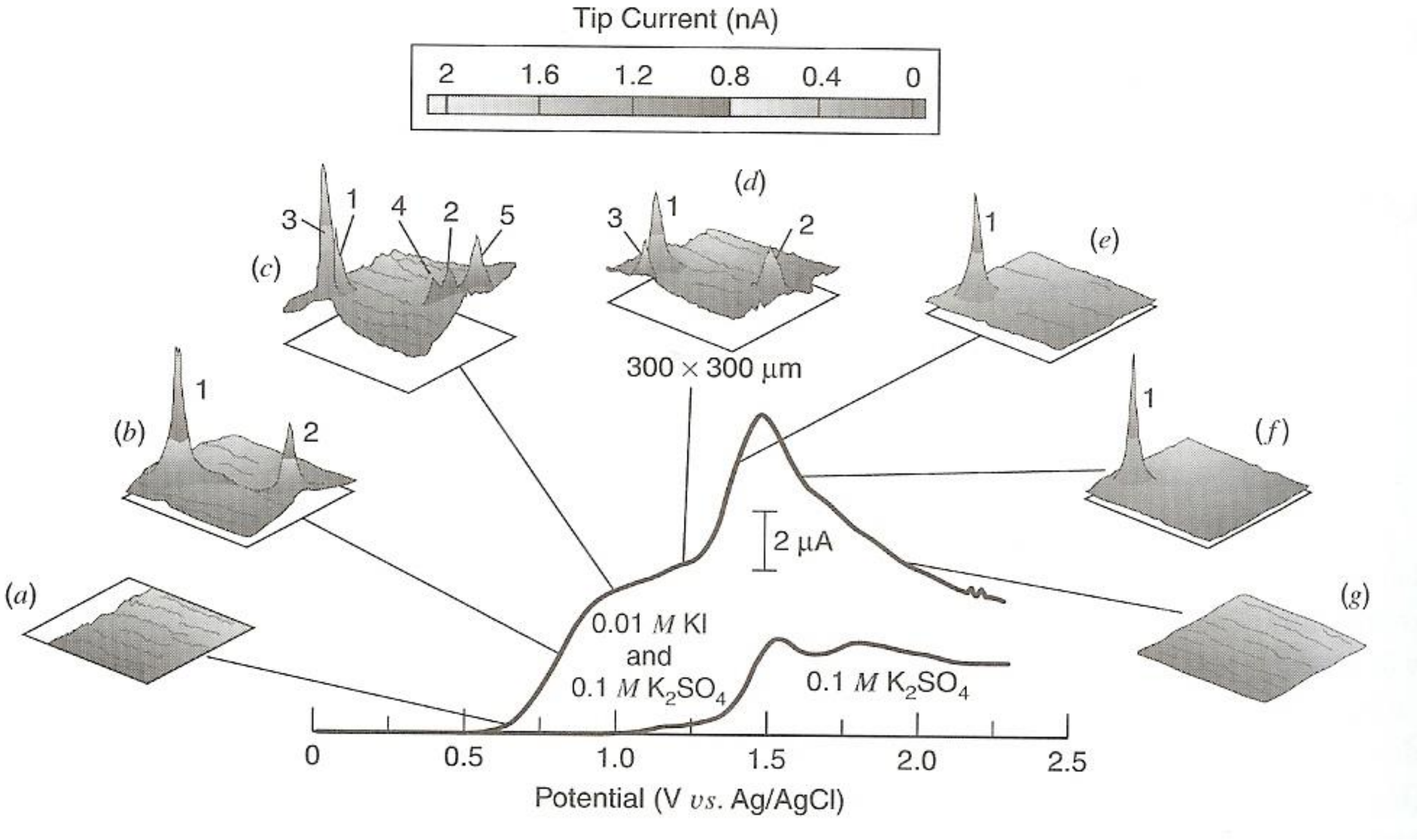


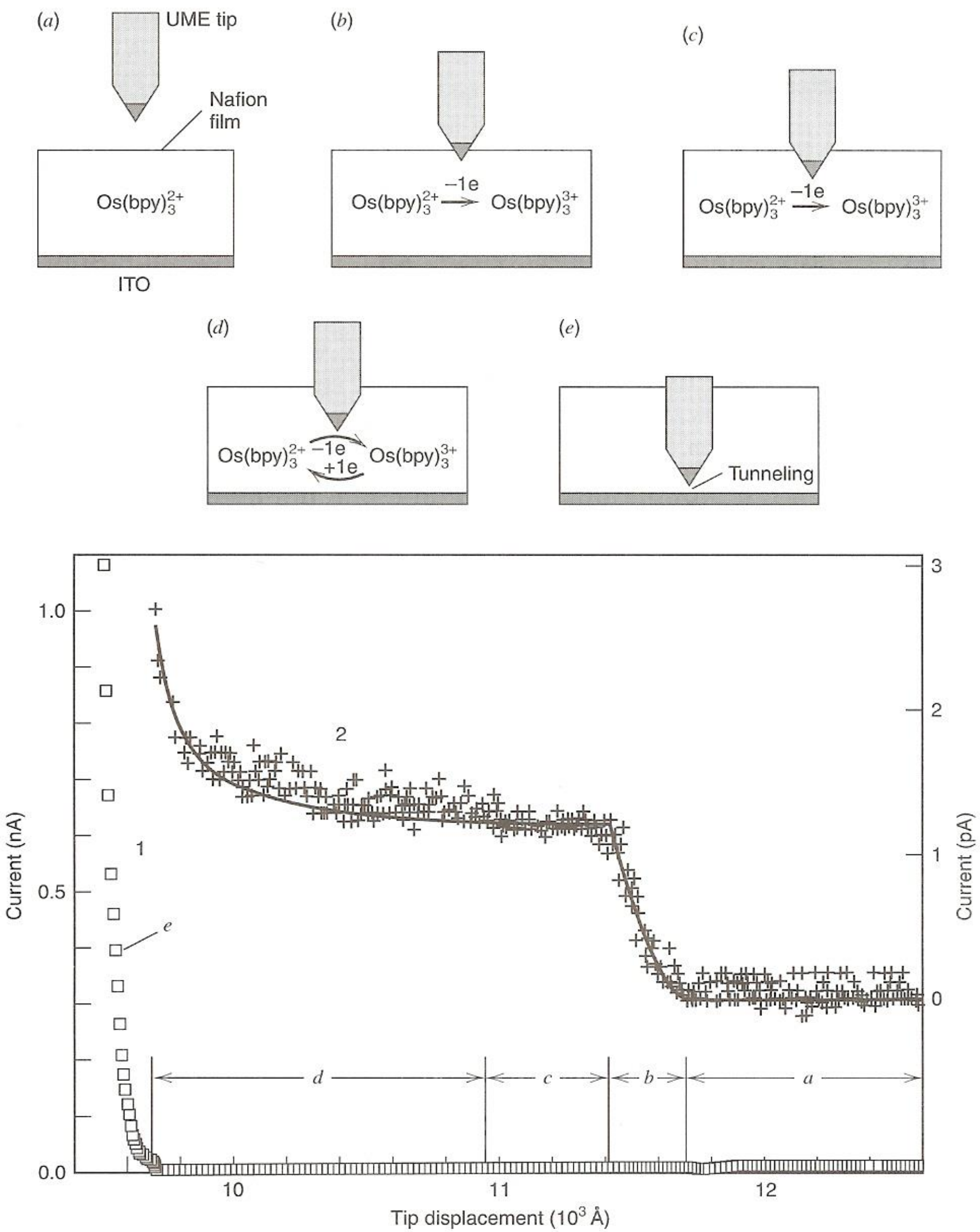

2a
Tip
i_T
e^-
AN
$AN^{\bar{\cdot}}$
products
d
AN
AN
$AN^{\bar{\cdot}}$
Substrate
e^-
i_S


1.4
1.0
0.6
0.2
−0.2
−0.6
Current (nA)
0
−1
−2
−3
Potential (V) vs AgQRE

Imaging surface topography & reactivity

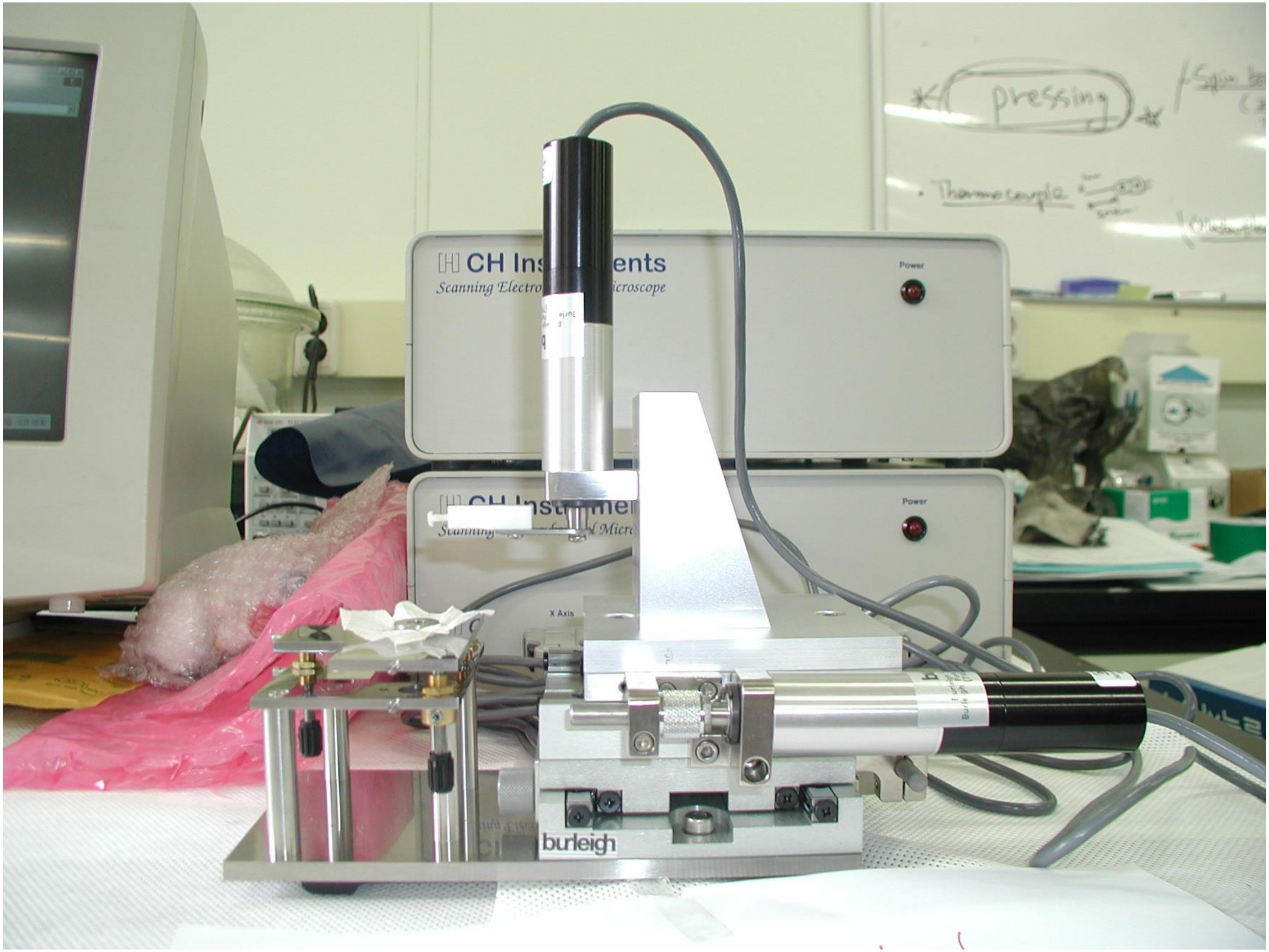
Ta oxide formation on Ta



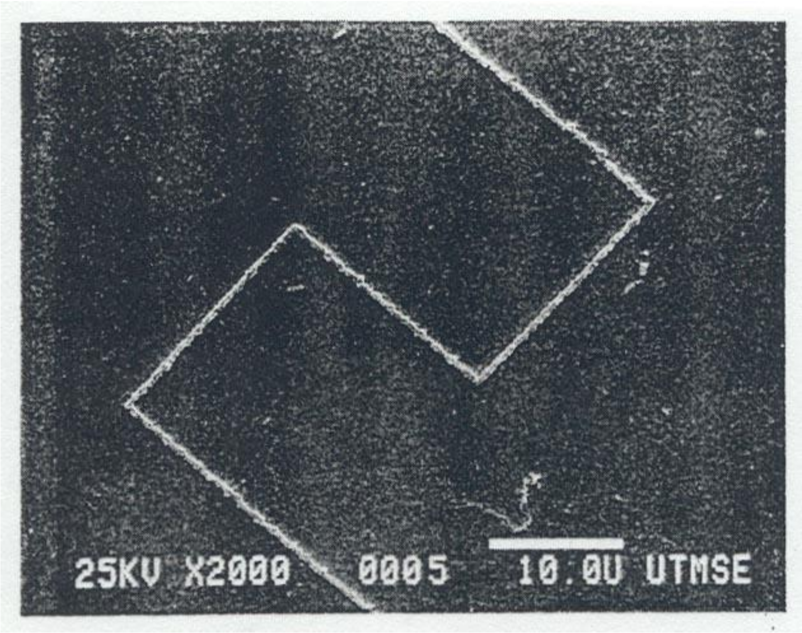


(a)
UME tip
Nafion film
Os(bpy)$_3^{2+}$
ITO
(b)
Os(bpy)$_3^{2+}$ $\xrightarrow{-1e}$ Os(bpy)$_3^{3+}$
(c)
Os(bpy)$_3^{2+}$ $\xrightarrow{-1e}$ Os(bpy)$_3^{3+}$
(d)
Os(bpy)$_3^{2+}$ −1e +1e Os(bpy)$_3^{3+}$
(e)
Tunneling
1.0
0.5
0.0
Current (nA)
3
2
1
0
Current (pA)
1
2
e
d
c
b
a
10
11
12
Tip displacement (10^3 Å)

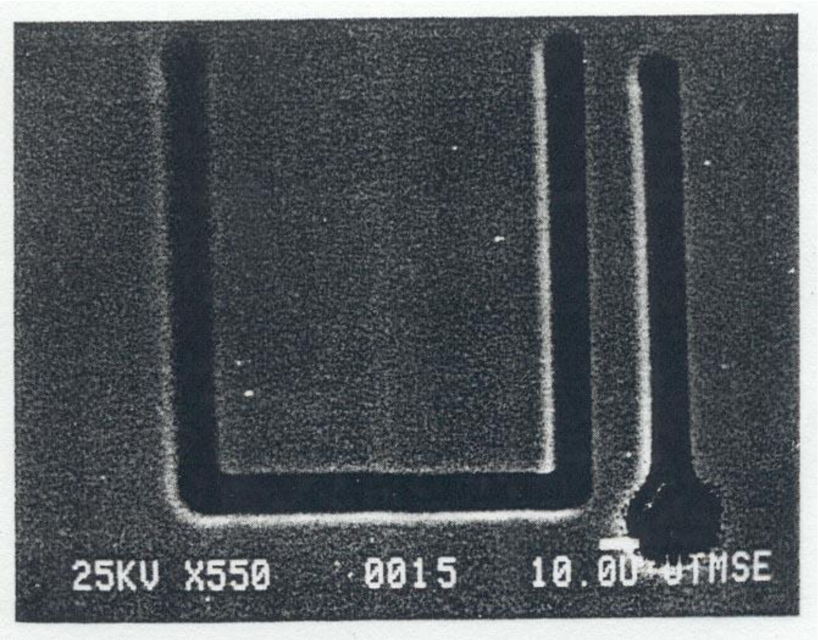
Commercialized SECM



SECM applications



Ag line formation



Electrochemical Cu etching