Lecture Note #9

Scanning probe techniques (ch. 16)

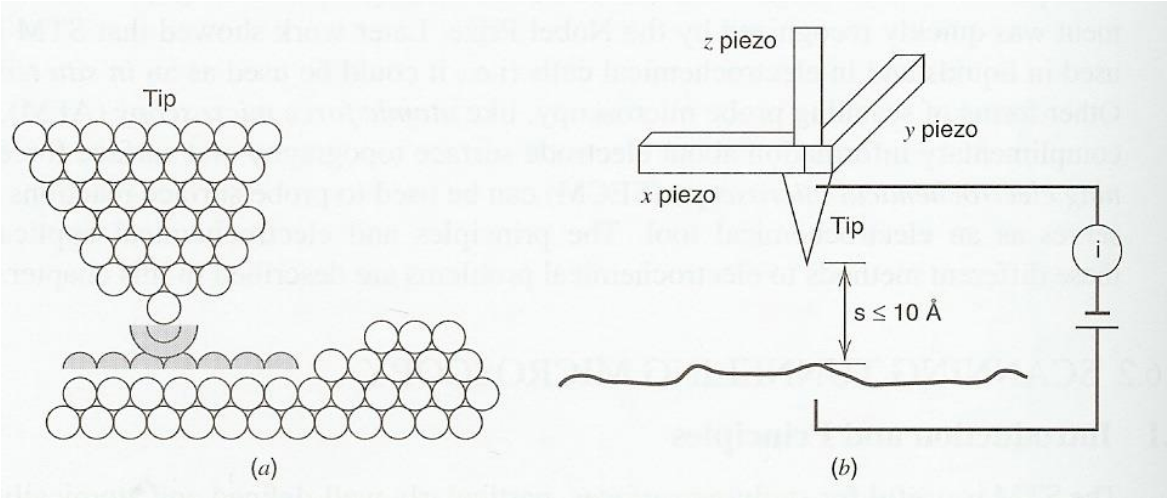
Scanning tunneling microscopy (STM)
Atomic force microscopy (AFM)
Scanning electrochemical microscopy (SECM)

Bard, ch. 16

Scanning probe techniques

Microscopy: optical → scanning electron or force → STM, AFM
in situ vs. ex situ techniques

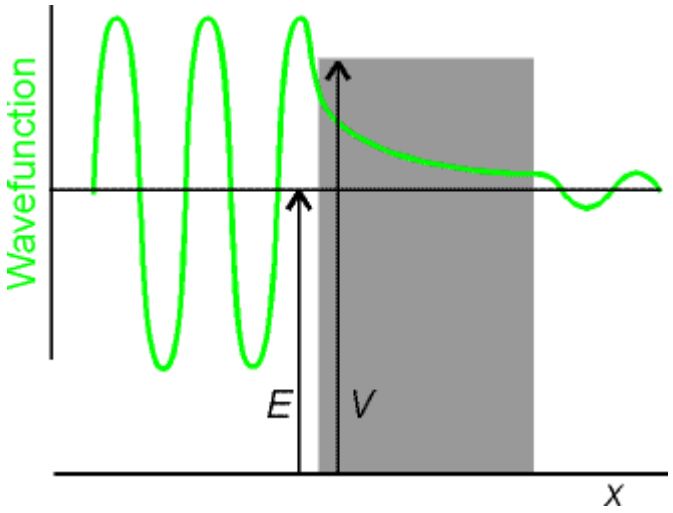
Scanning tunneling microsocpy (STM)

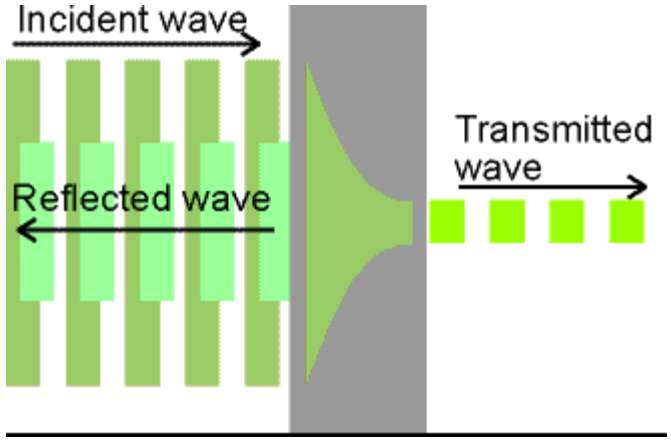


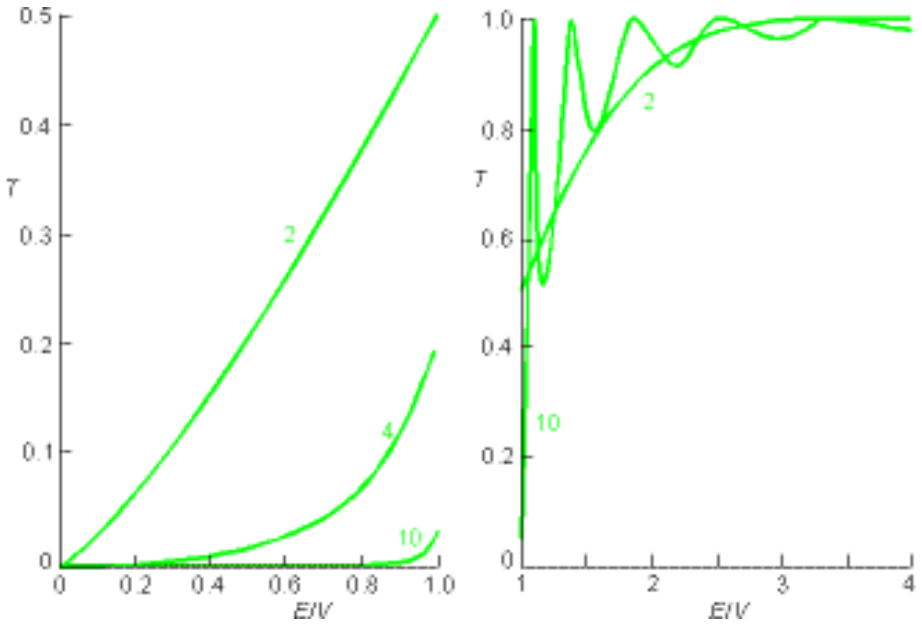
Tunnelling

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

cf) C.M.: insufficient energy to escape







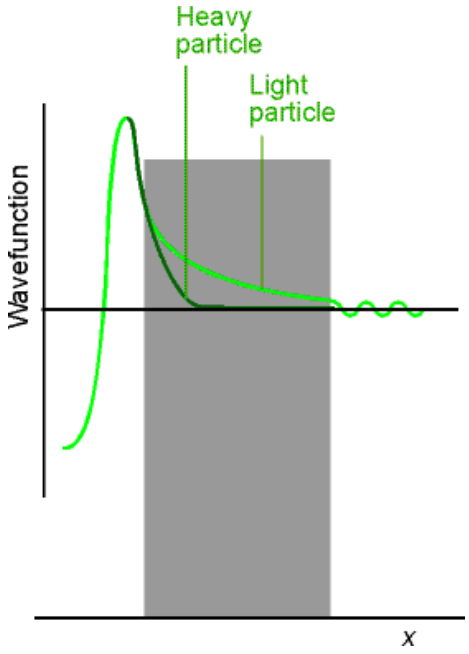
The transition probabilities for passage through a barrier. The horizontal axis is the energy of the incident particle expressed as a multiple of the barrier height. The curves are labelled with the value of $L(2mV)^{1/2}/\hbar$. The graph on the left is for $E<V$ and that on the right for $E>V$. Note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

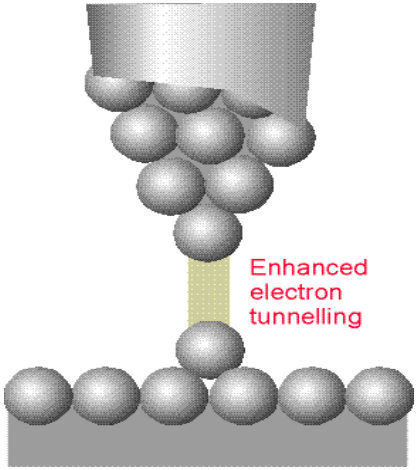
enhanced reflection (antitunnelling)

- 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



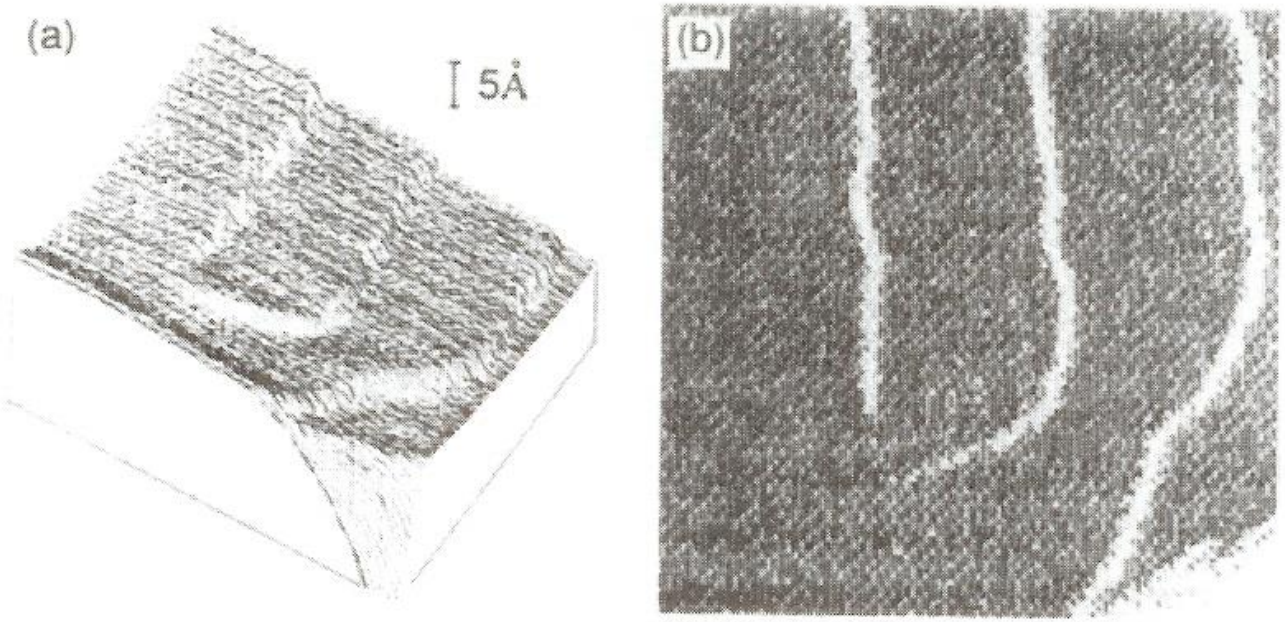


e.g) proton transfer reaction

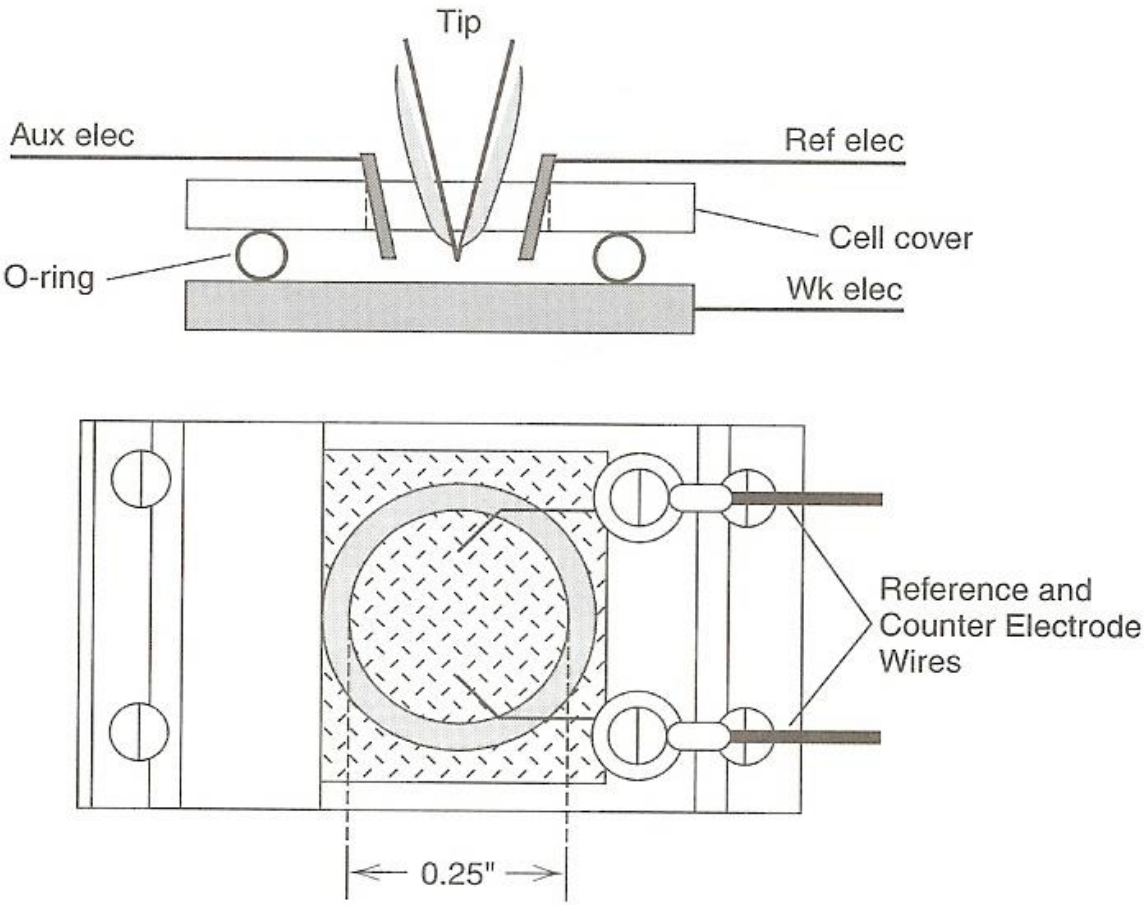
STM (scanning tunnelling microscopy)

AFM (atomic force microscopy)

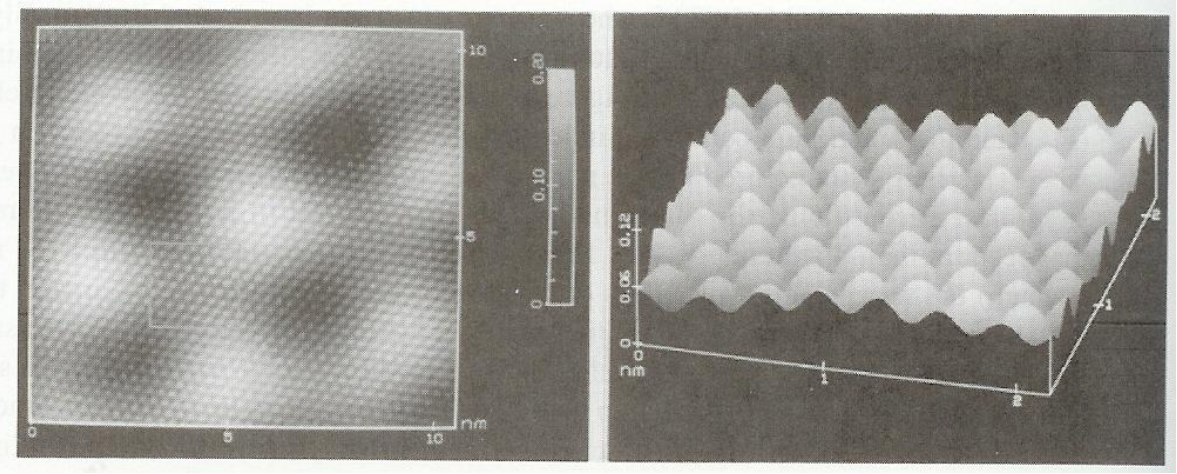
Au(111) at 0.7 V vs. NHE in HCl



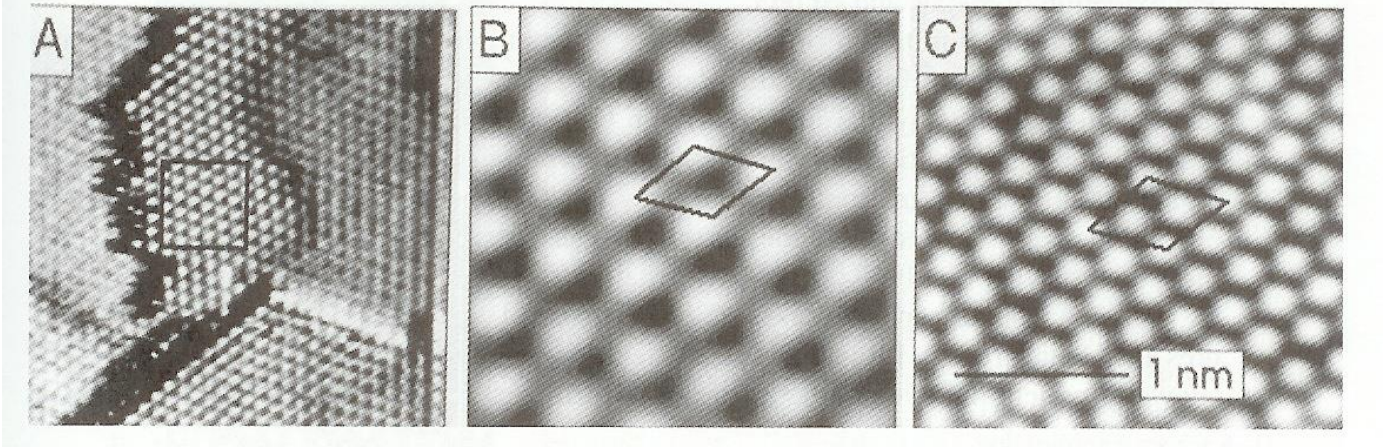
Electrochemical STM



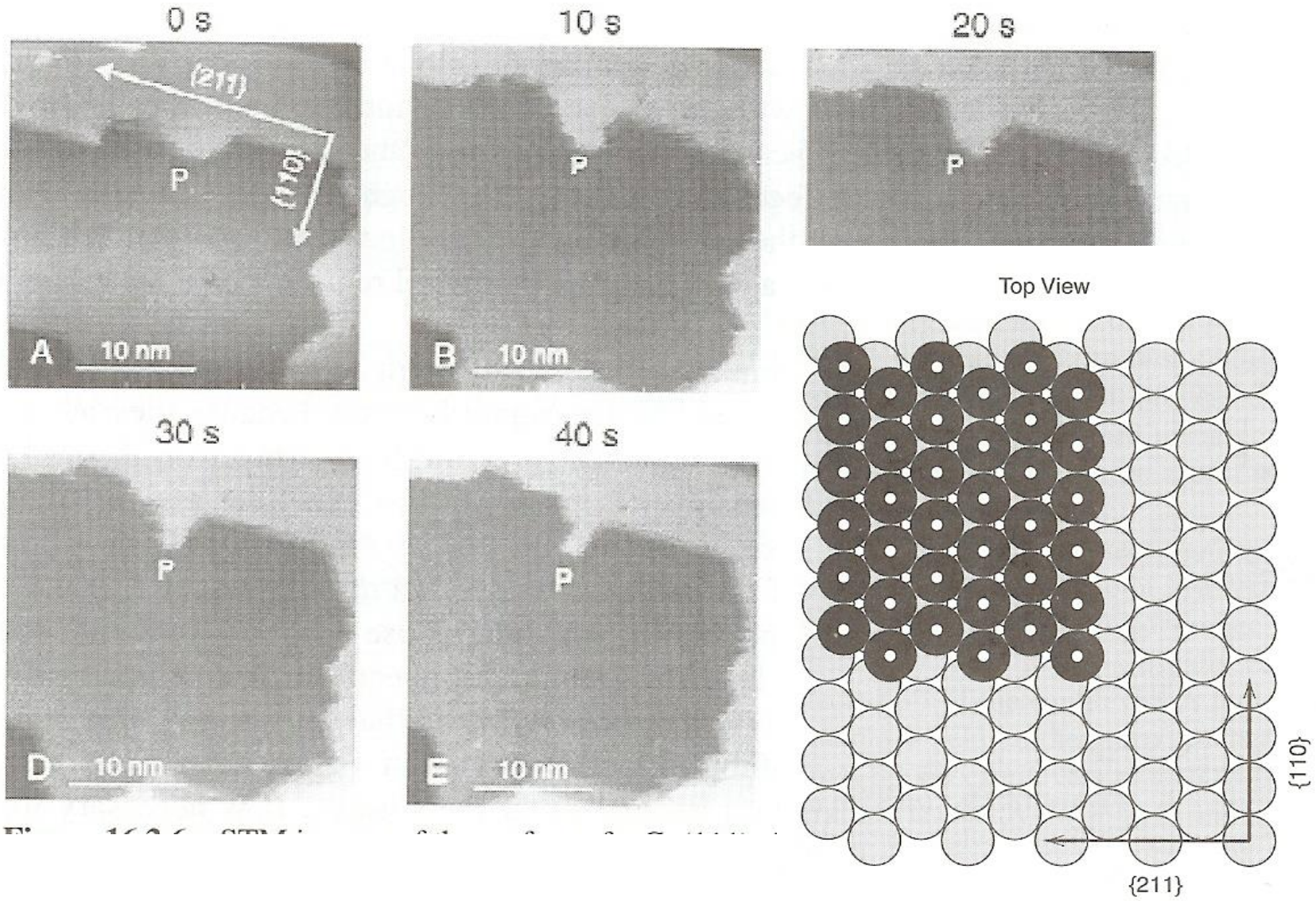
STM images of HOPG

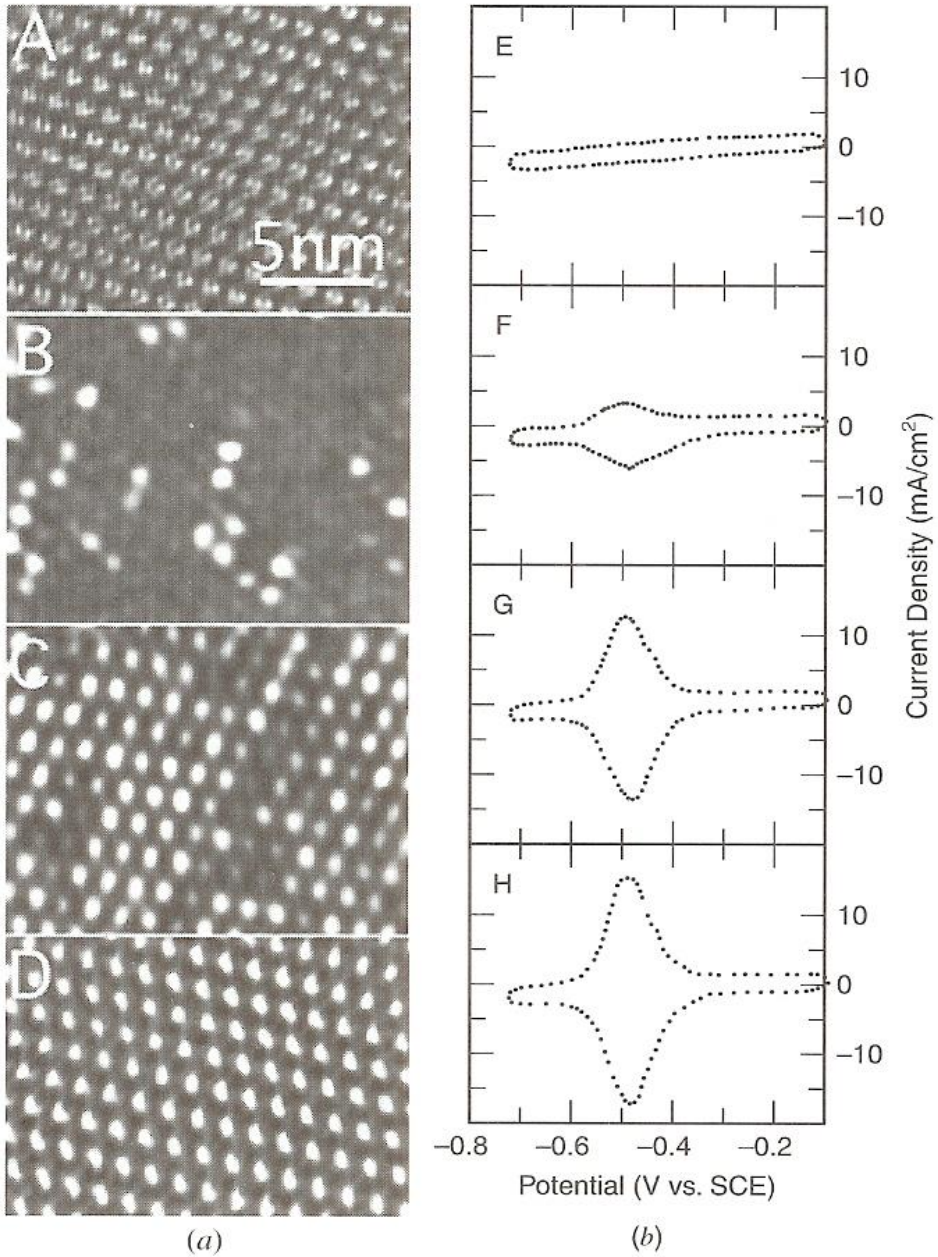


STM images of Pt(111) with I-adlattice in $HClO_4$

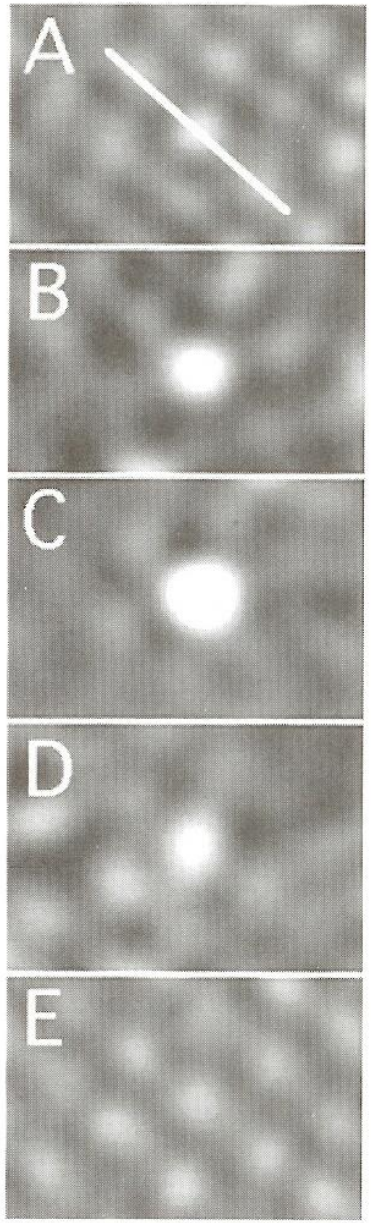


STM images of Cu(111): effect of etching

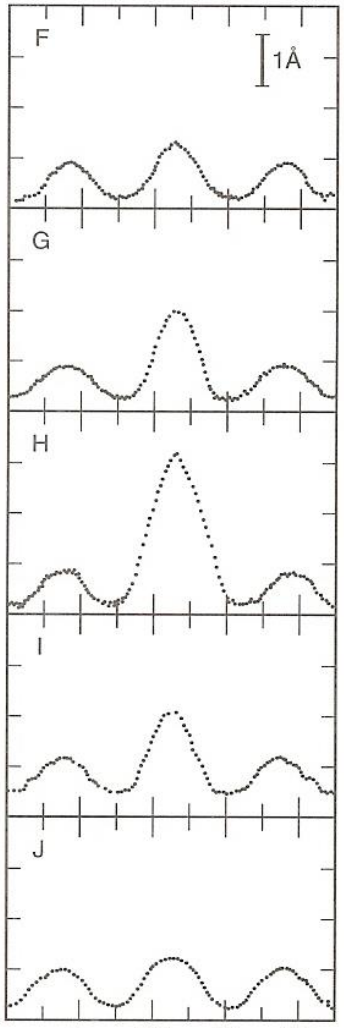



A
5nm
B
C
D
E
F
G
H
10
0
−10
−0.8
−0.6
−0.4
−0.2
Potential (V vs. SCE)
Current Density (mA/cm²)

(*a*) (*b*)



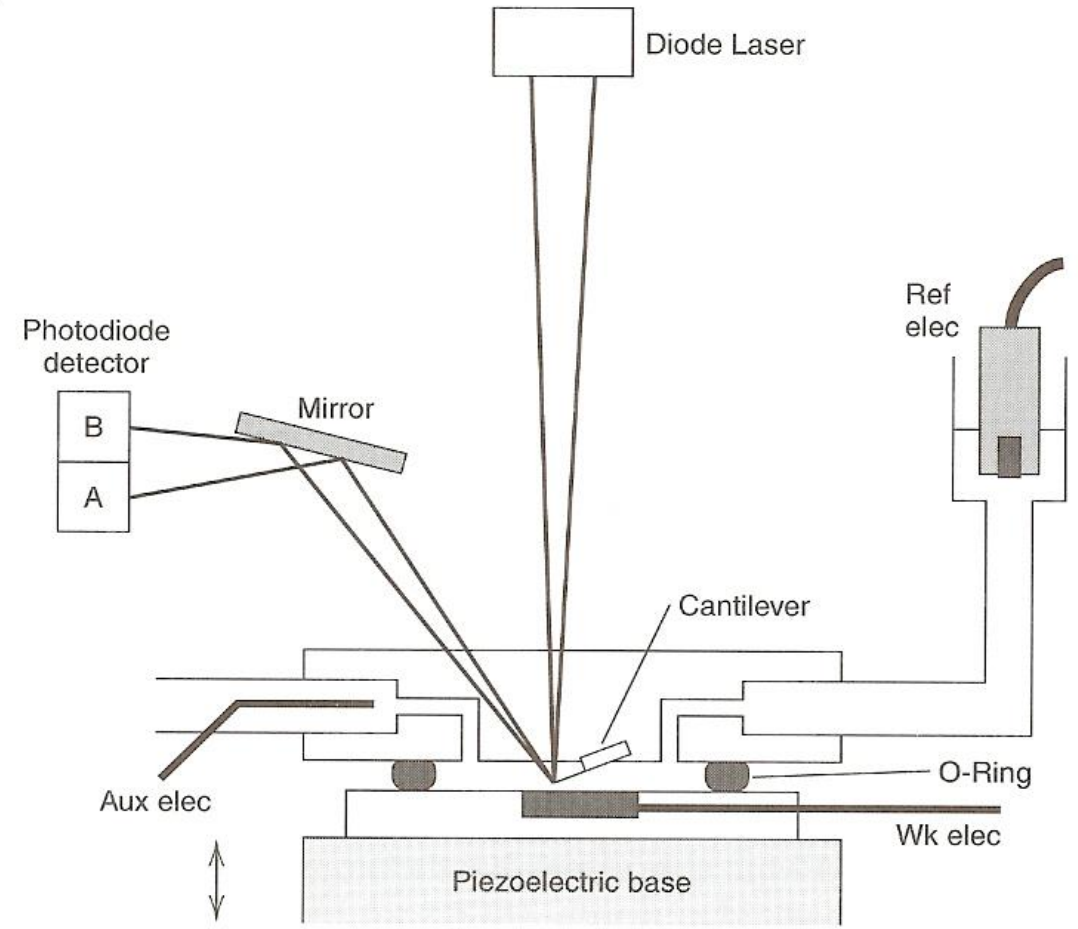
(a)



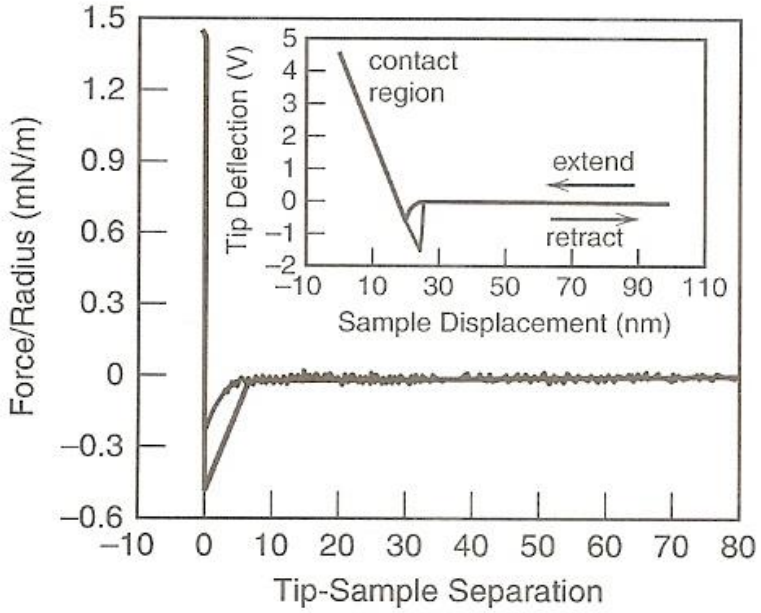
(b)

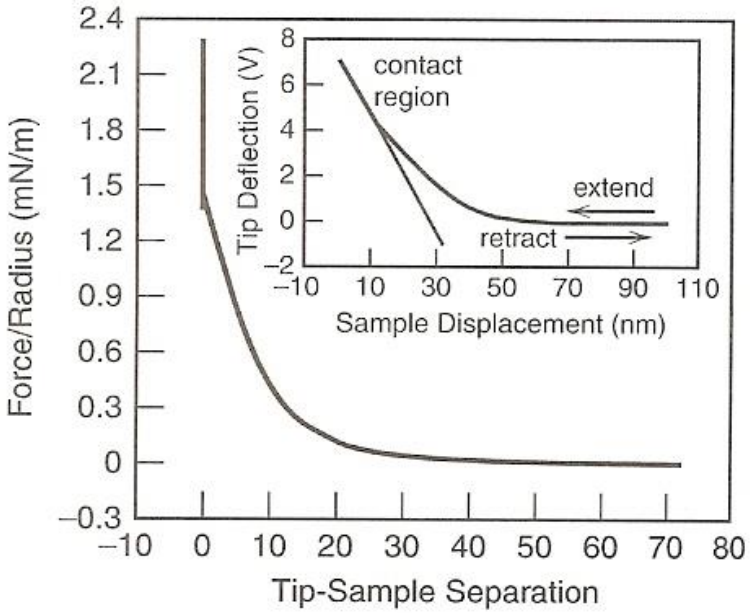
Scanning tunneling spectroscopy (STS)

Atomic force microscopy (AFM)



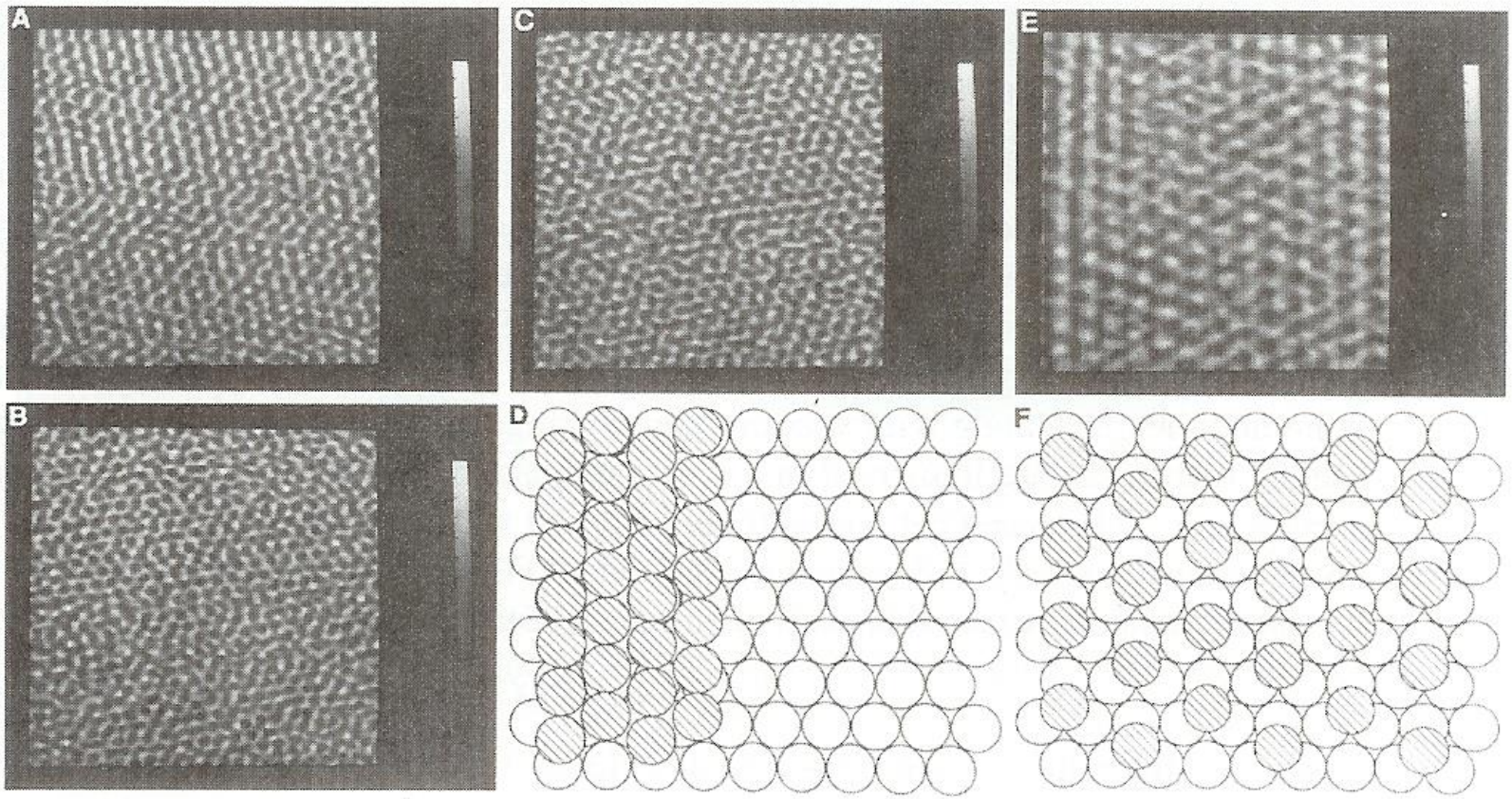
Cantilever displacement vs. z-deflection for (left) attractive interaction and (right) repulsive interaction



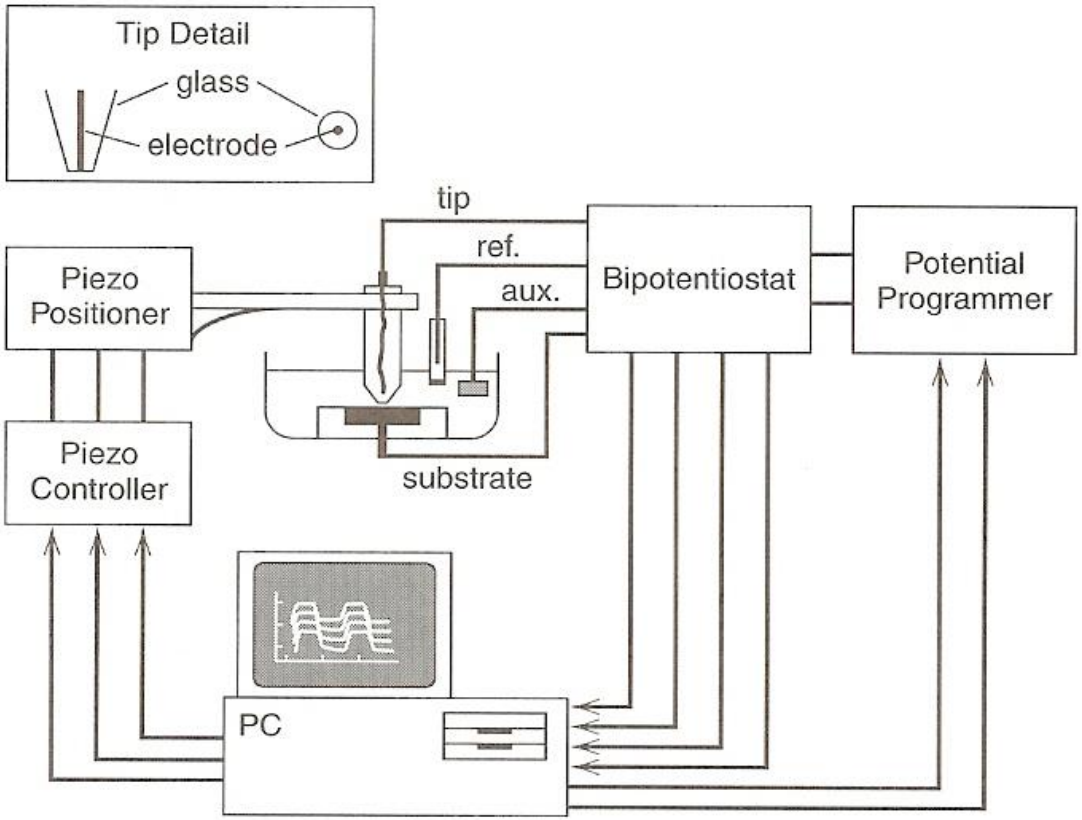


Electrochemical AFM

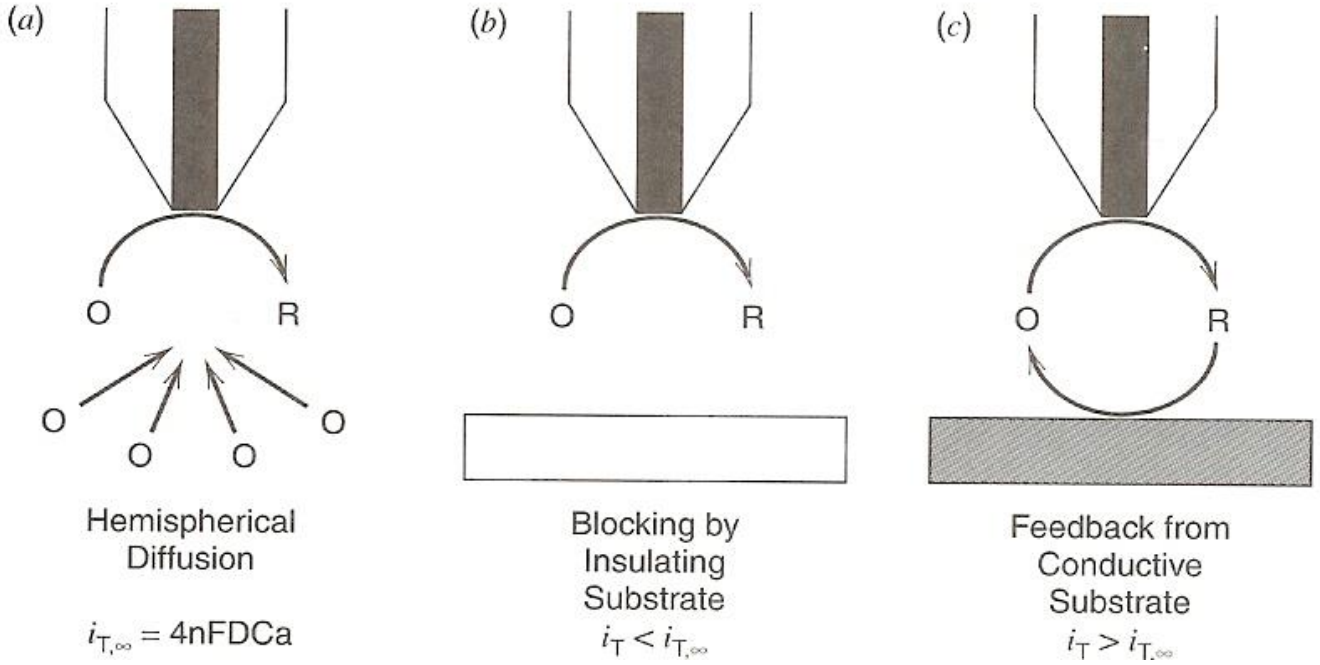
AFM of Cu underpotential deposition (UPD) on Au(111)



Scanning electrochemical microscopy (SECM)



Principles of SECM



Hemispherical Diffusion

$i_{T,\infty} = 4nFDCa$

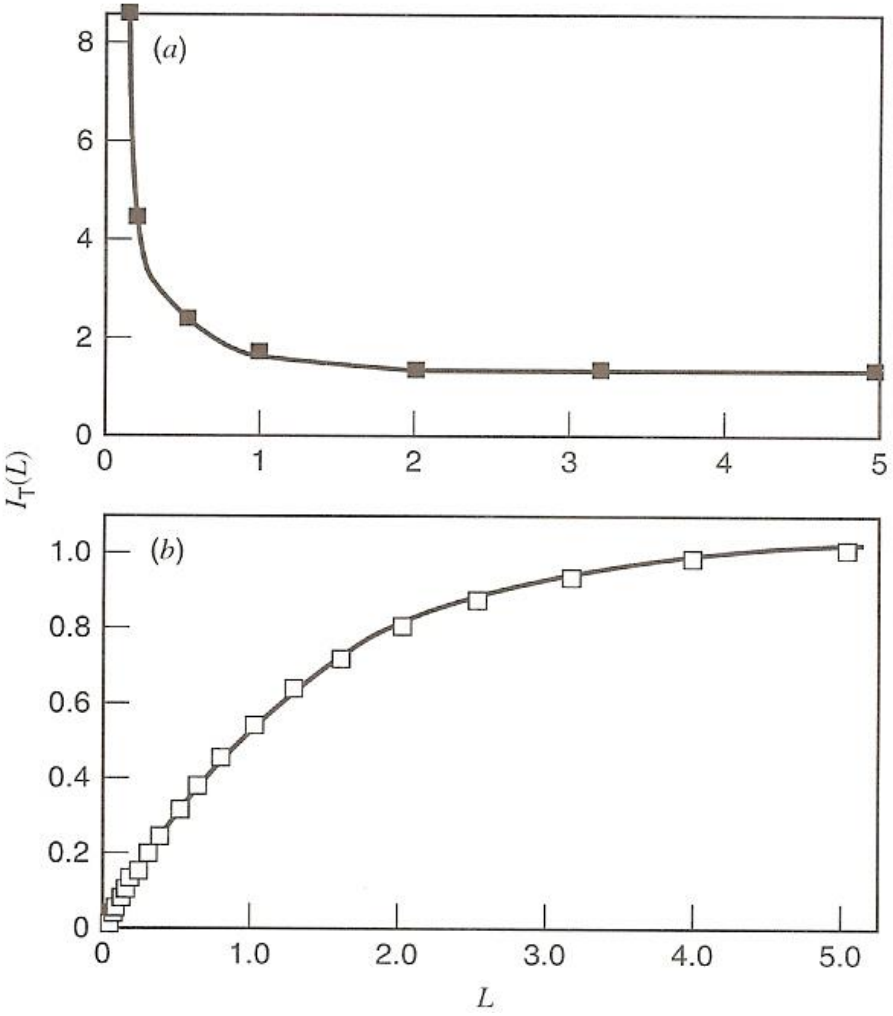
Blocking by Insulating Substrate

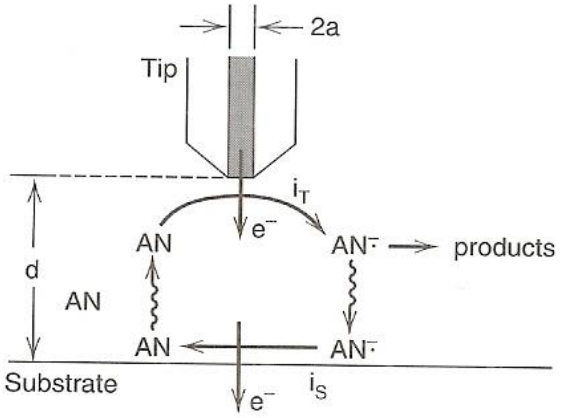
$i_T < i_{T,\infty}$

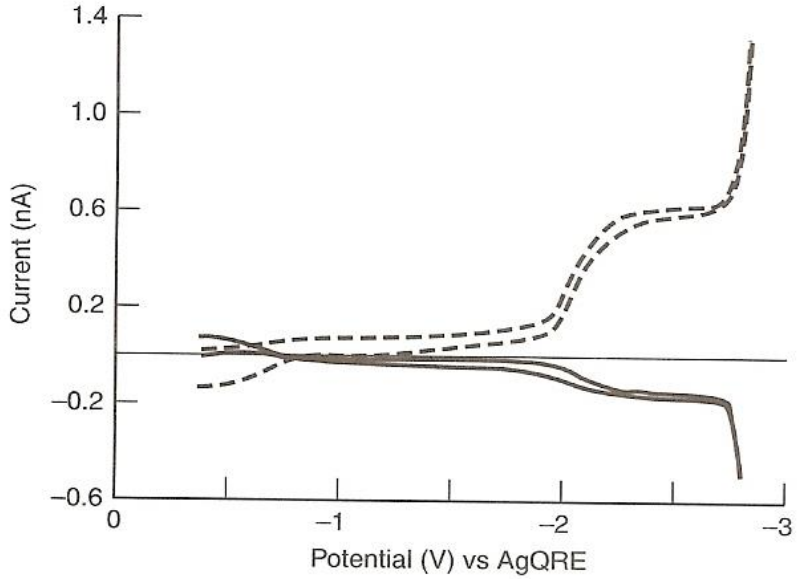
Feedback from Conductive Substrate

$i_T > i_{T,\infty}$

SECM appoach curves for steady-state currents

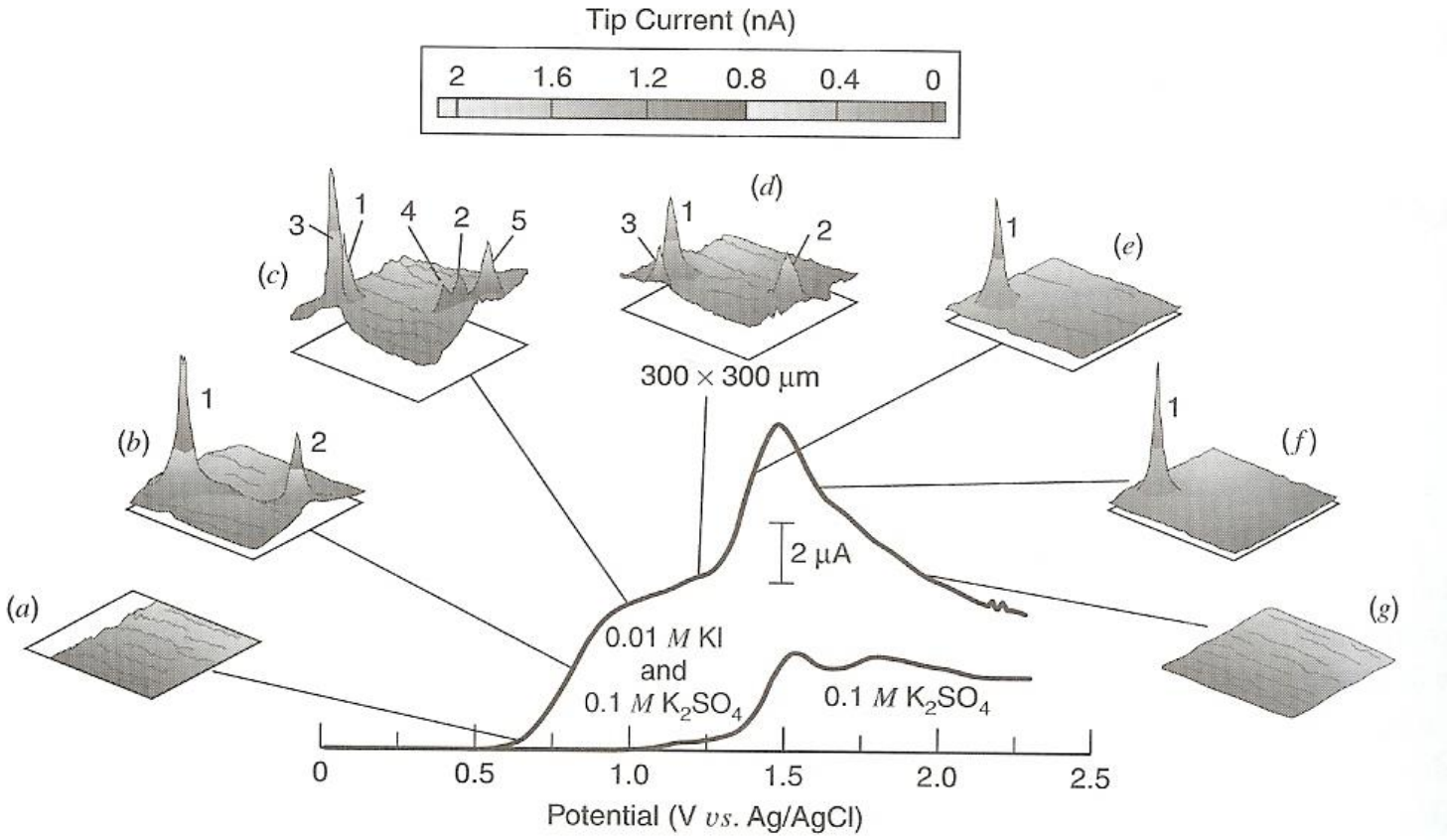


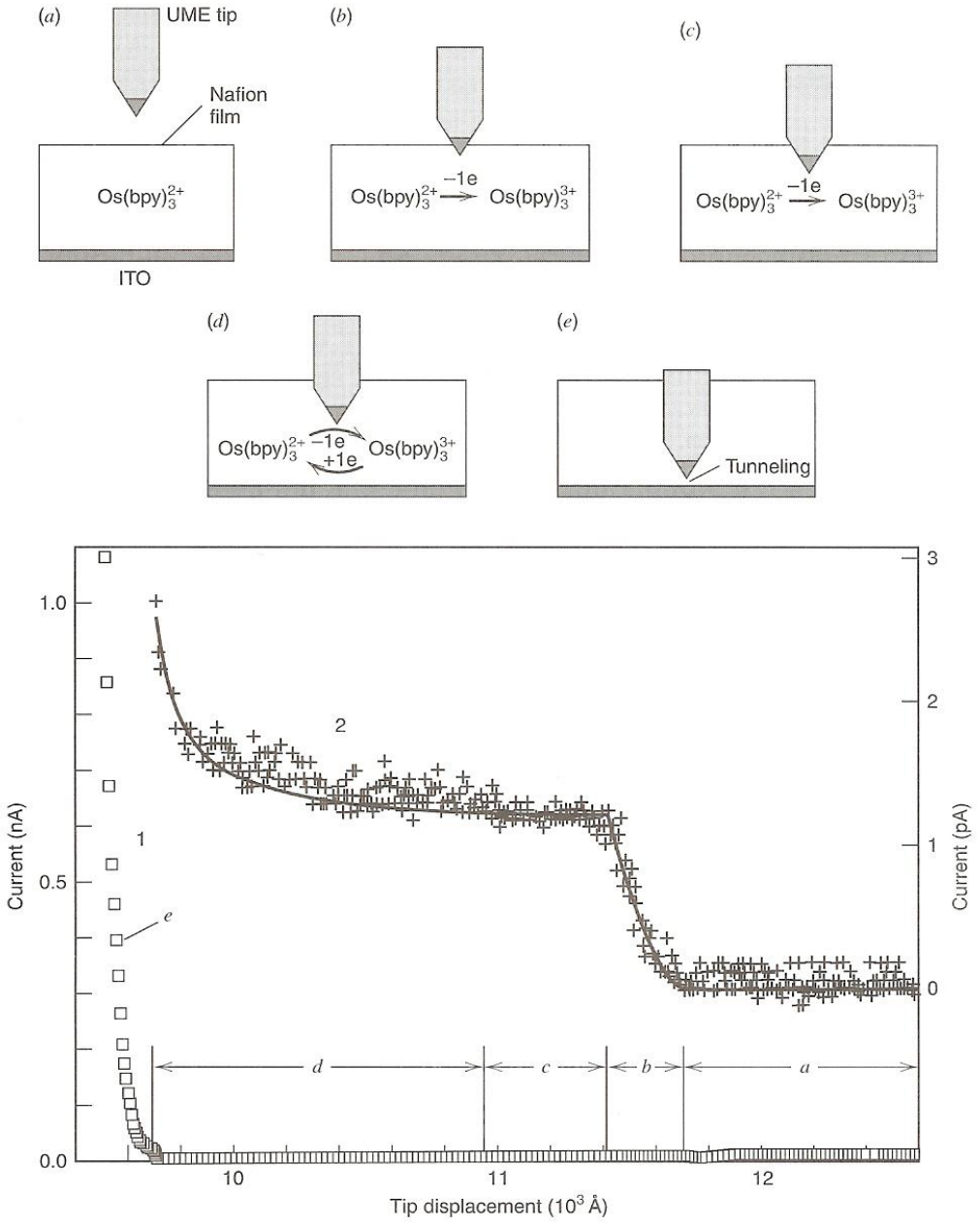

2a
Tip
i_T
e^-
AN
$AN^{\cdot-}$
products
d
AN
AN
$AN^{\cdot-}$
Substrate
e^-
i_S


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

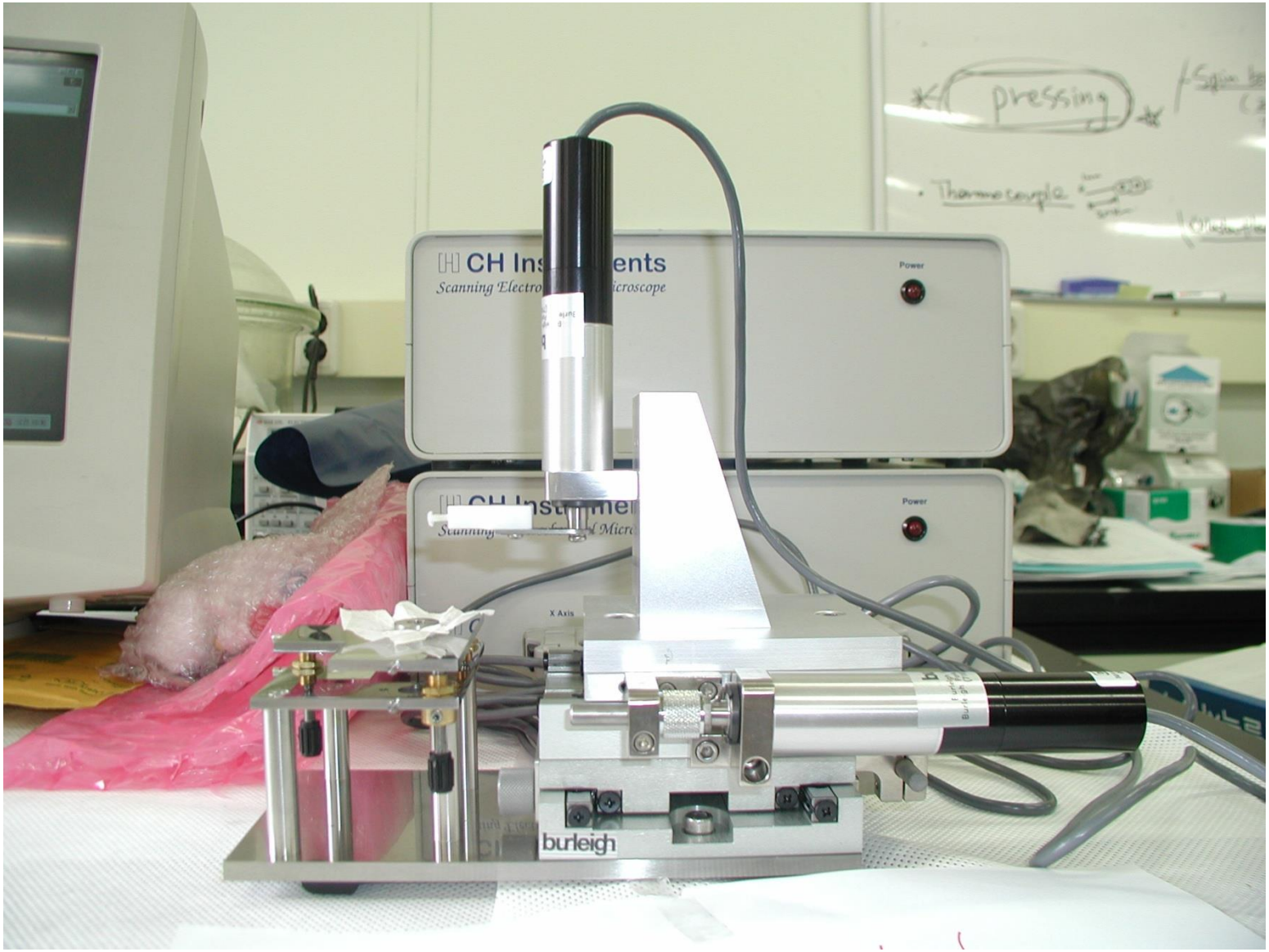
Imaging surface topography & reactivity

Ta oxide formation on Ta

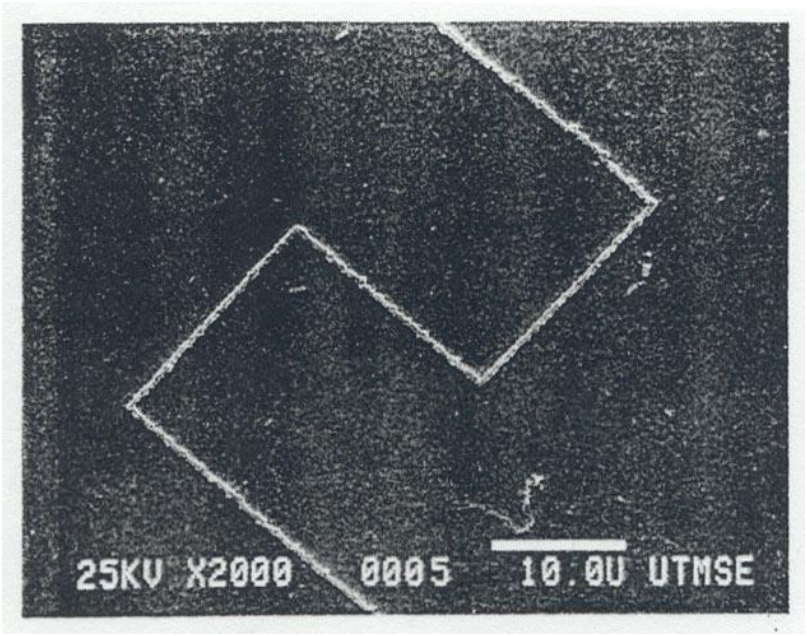



(a)
UME tip
Nafion film
$Os(bpy)_3^{2+}$
ITO
(b)
$Os(bpy)_3^{2+}$ −1e → $Os(bpy)_3^{3+}$
(c)
$Os(bpy)_3^{2+}$ −1e → $Os(bpy)_3^{3+}$
(d)
$Os(bpy)_3^{2+}$ −1e +1e $Os(bpy)_3^{3+}$
(e)
Tunneling
Current (nA)
Current (pA)
Tip displacement (10^3 Å)
1.0
0.5
0.0
3
2
1
0
10
11
12
1
2
e
d
c
b
a

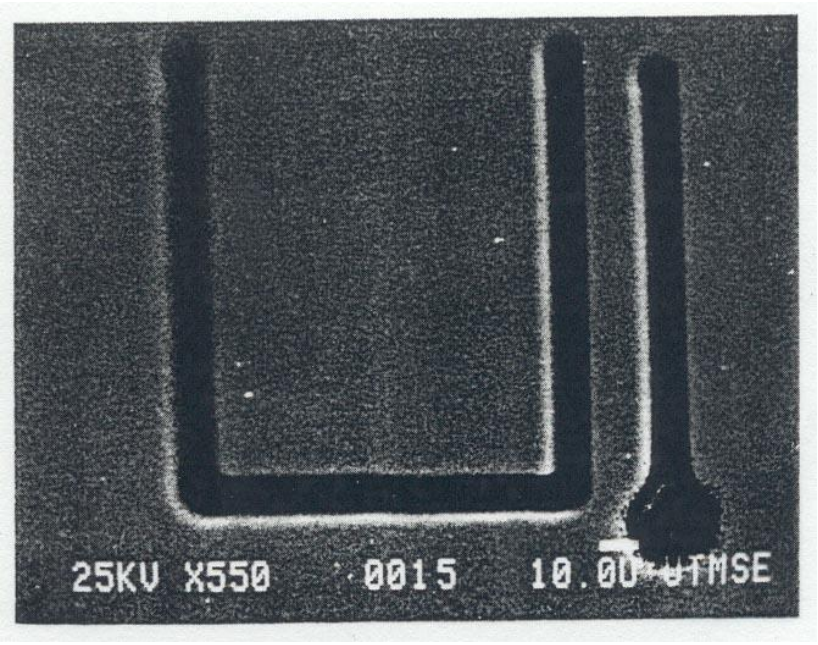
Commercialized SECM



SECM applications



Ag line formation



Electrochemical Cu etching