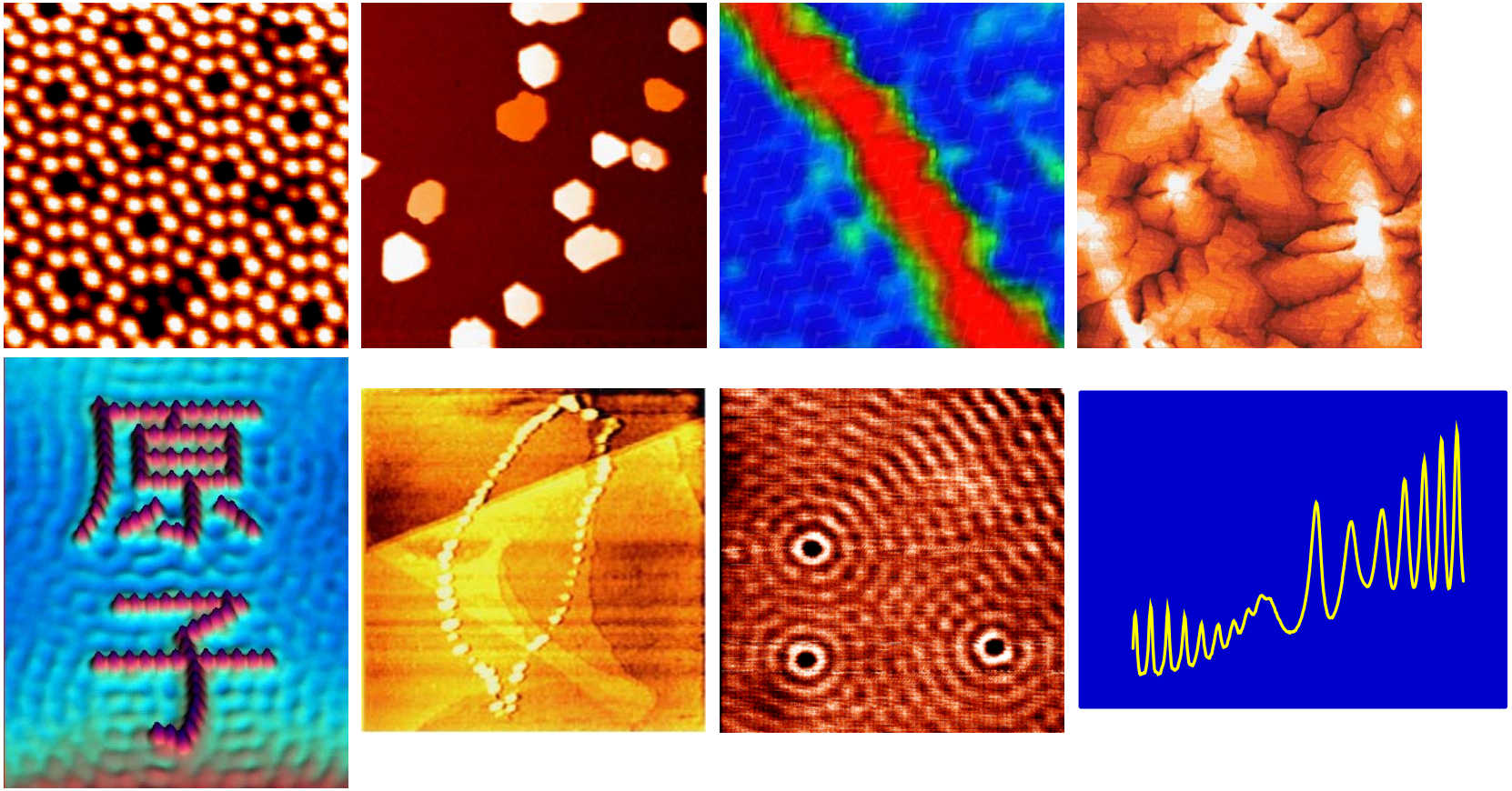
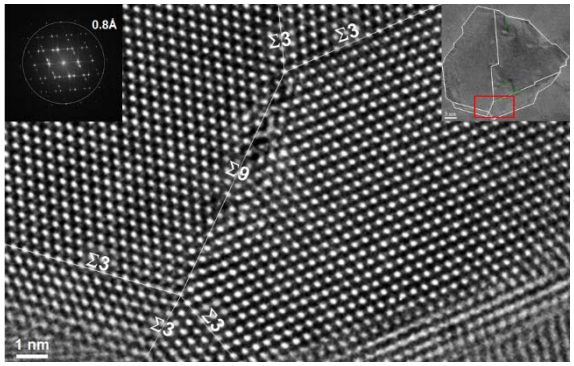
Scanning Tunneling Microscopy

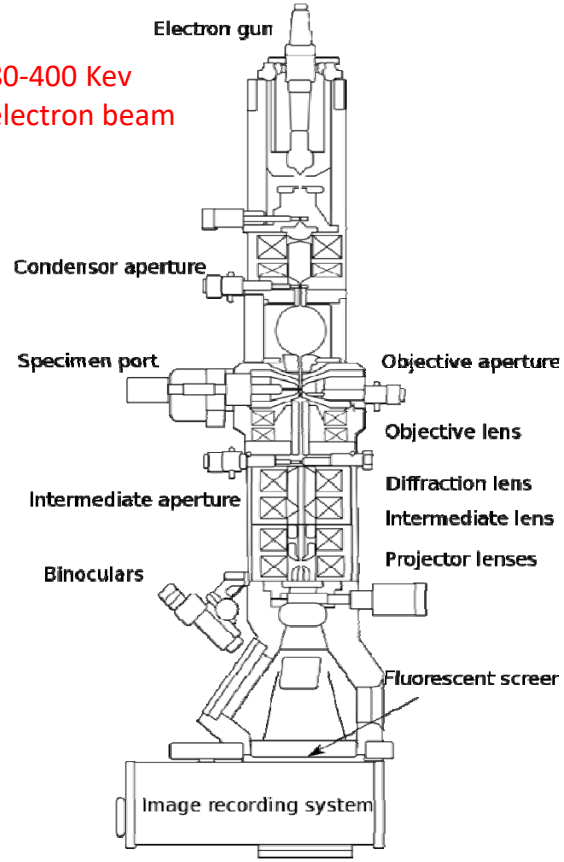
Wei-Bin Su, Institute of Physics, Academia Sinica



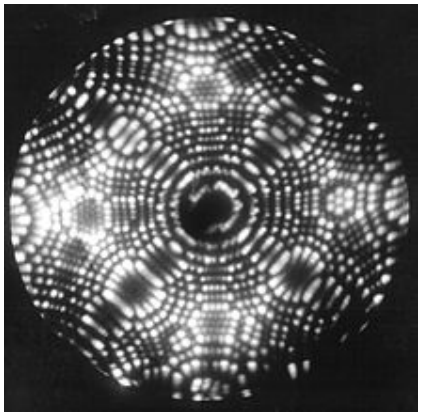
Transmission Electron Microscopy

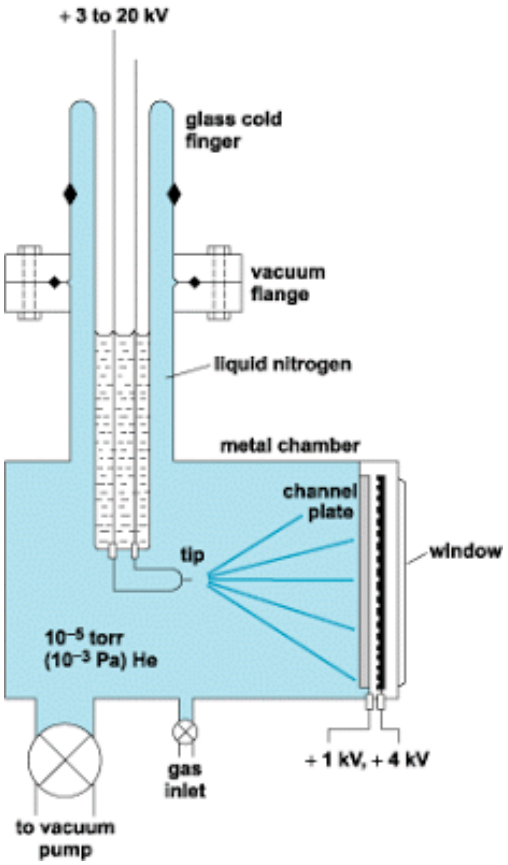


80-400 Kev
electron beam



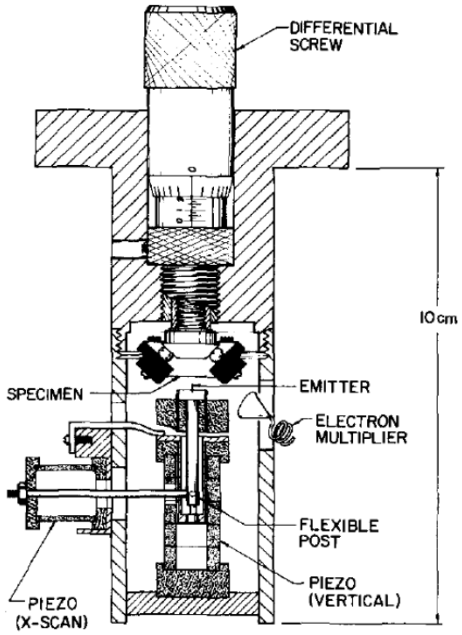
Field Ion Microscopy





Topografiner
1970, Young et al.

A precursor of STM



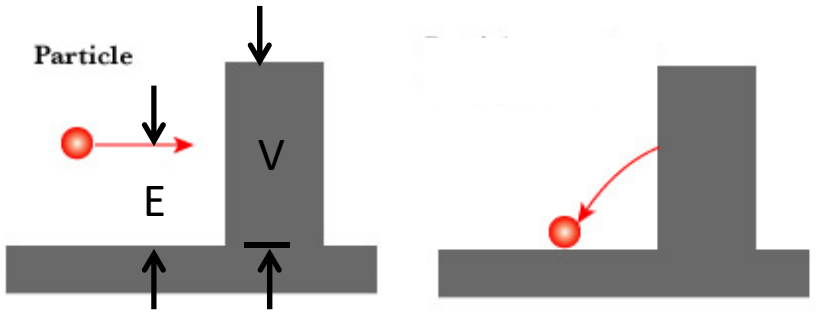
- Included most of the elements of an STM
- Resolution: 500 nm

Problems were overcome by Gerd Binnig and Heinrich Rohrer at the IBM in 1980

The Nobel Prize in Physics 1986

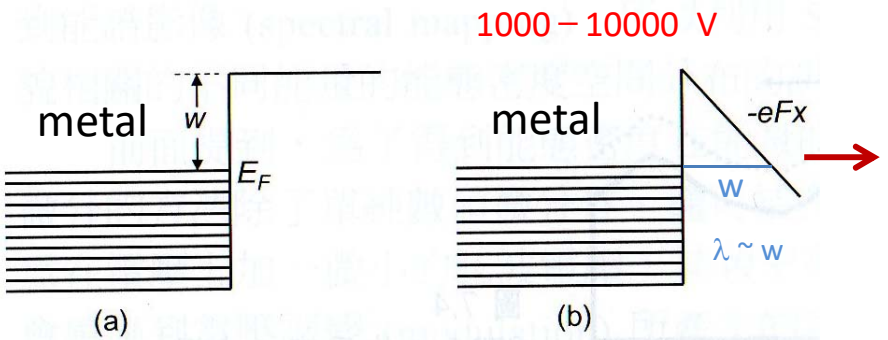
Tunneling effect

classical mechanics

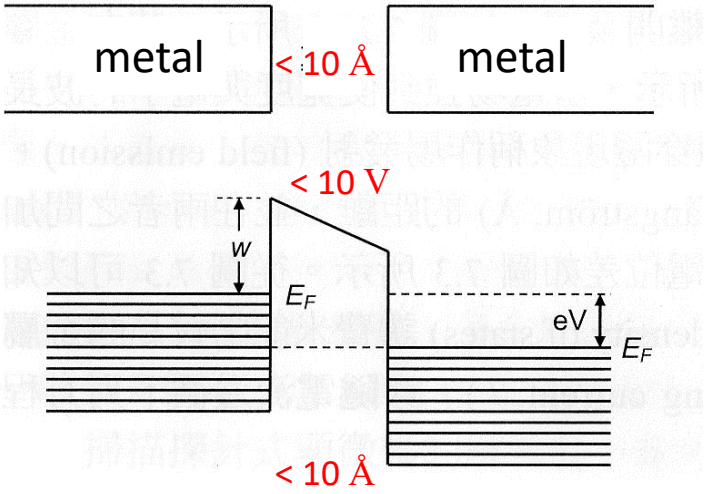


quantum mechanics

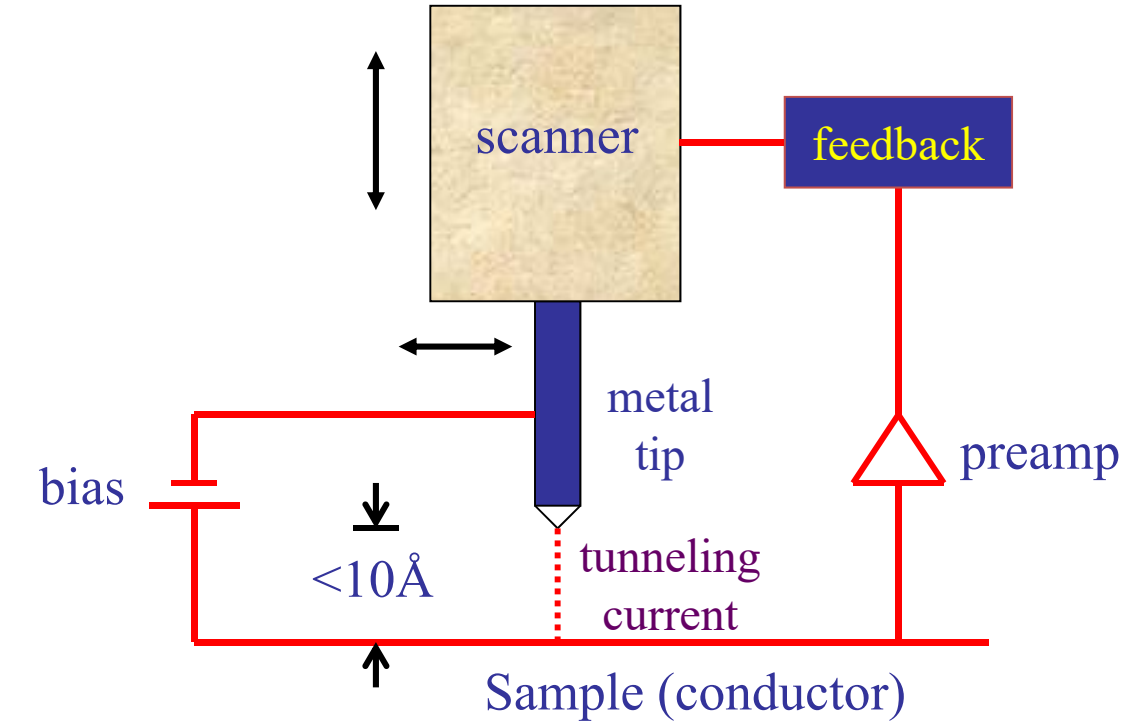
Field emission

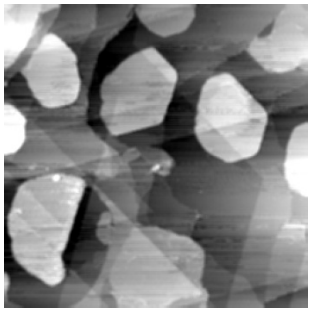


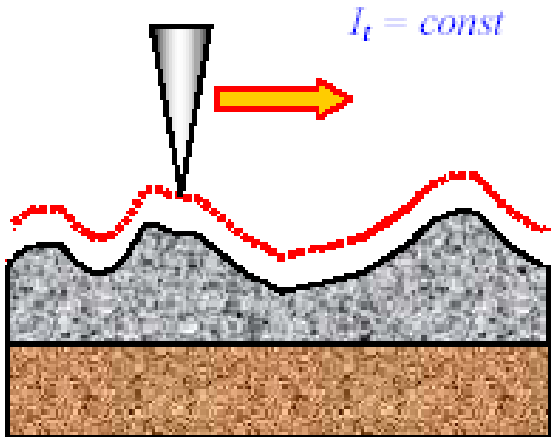
metal-vacuum-metal tunneling



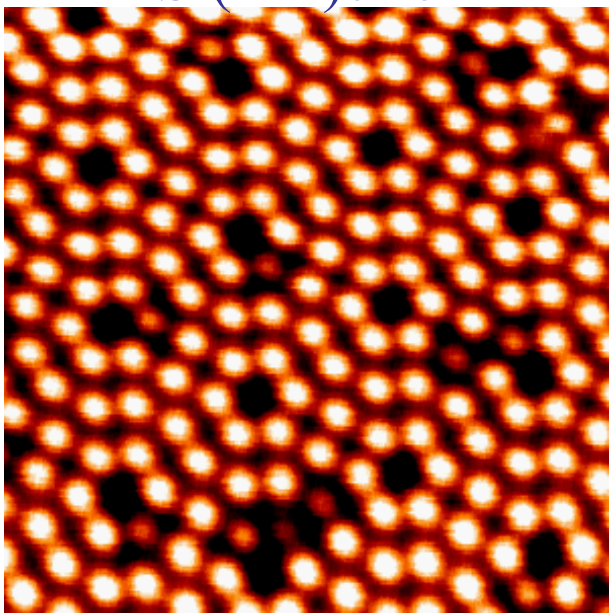
Scanning Tunneling Microscopy (STM)



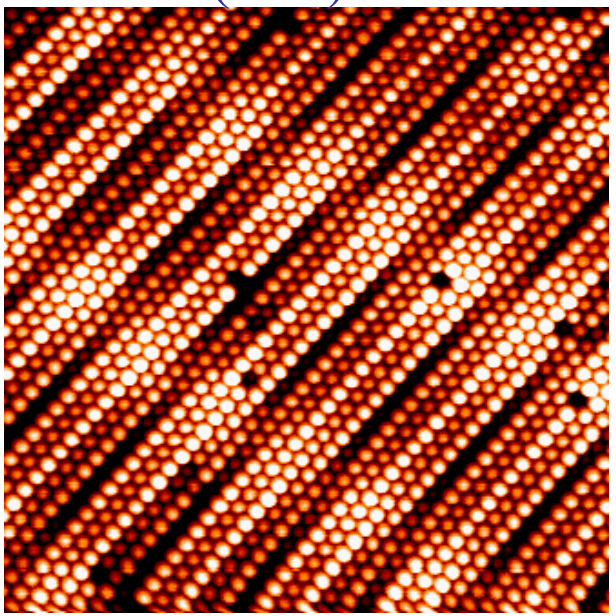


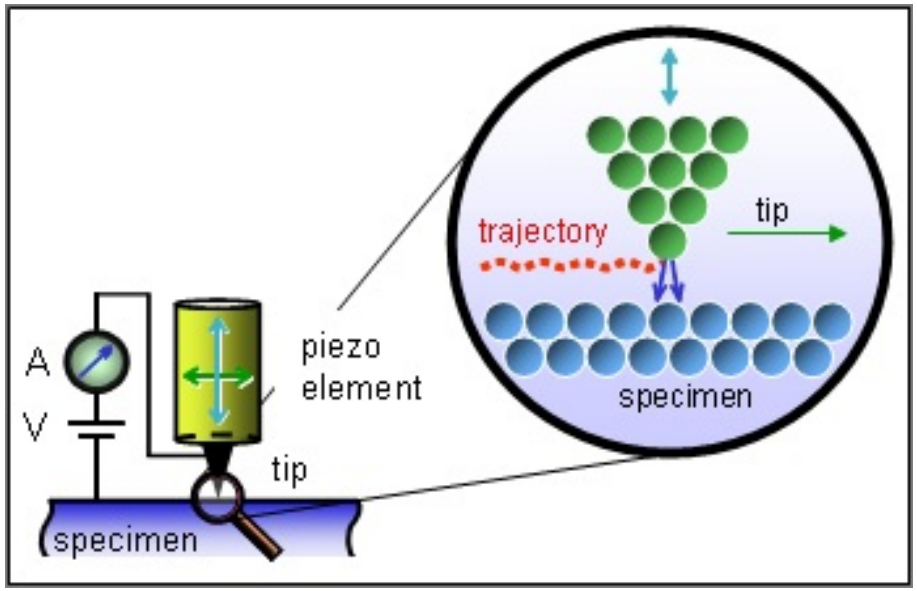


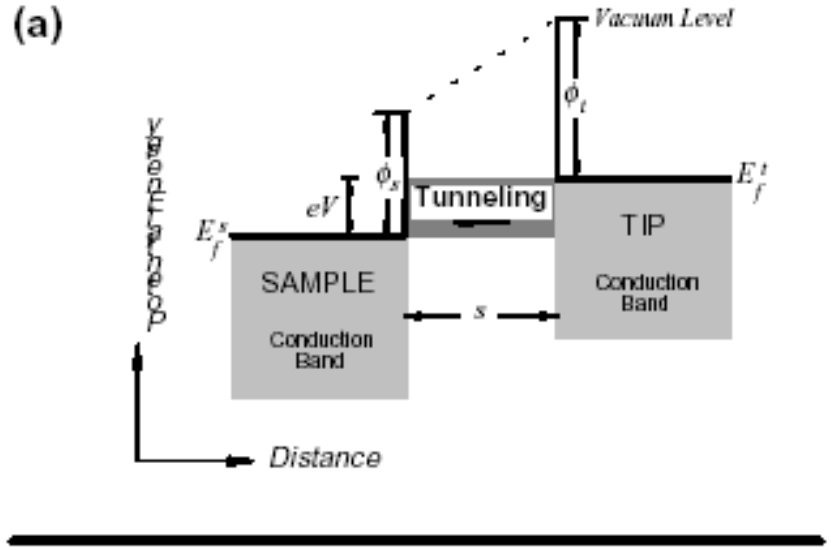
Si(111)7×7



Pt(100)-R0.7^0





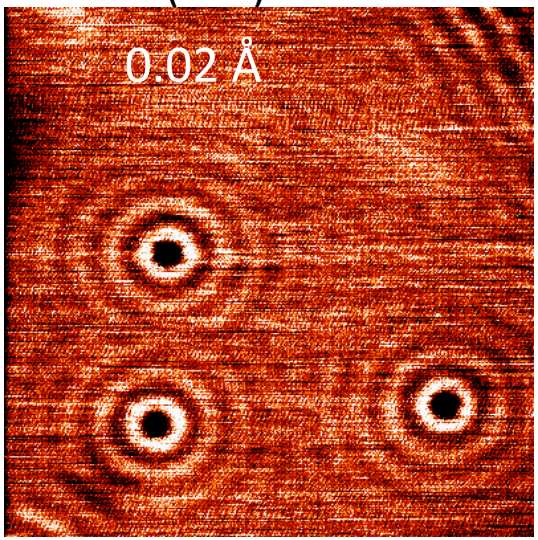


average work function

$I \sim \exp(-2\kappa s)$; $\kappa = (2m\phi/\hbar^2)^{1/2}$; $\phi = (\phi_t + \phi_s)/2$

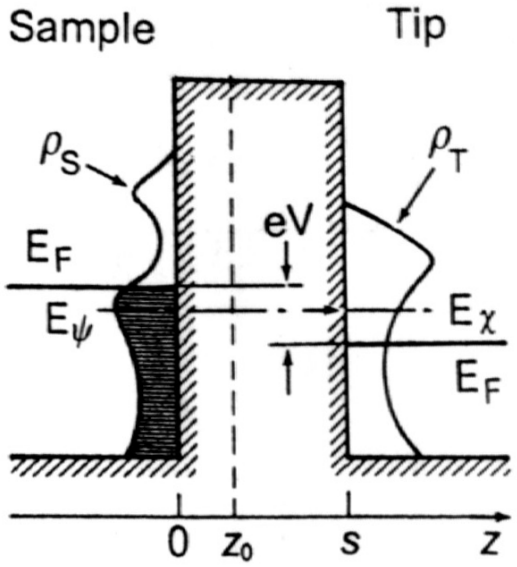
$\kappa \sim 1$ Å^{-1} → the current decays about $e \approx 7.4$ times when s increases by 1 Å

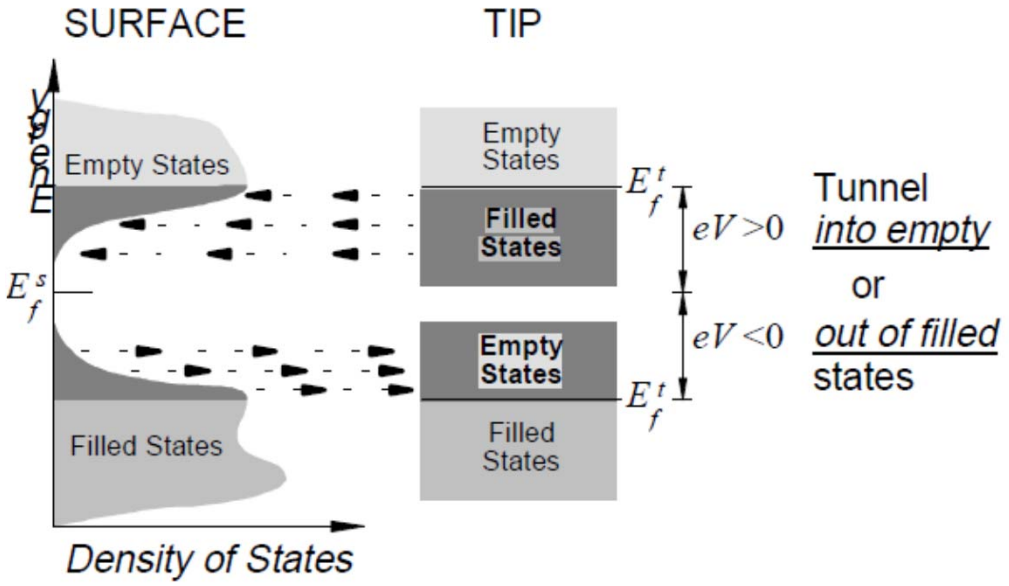
(b) Cu(111) surface



Tunneling current

$$I \propto \int_0^{eV} \rho_s(E_F\text{-}eV+\varepsilon)\, \rho_T(E_F+\varepsilon)\, d\varepsilon \;\; \exp(-2\kappa s)$$



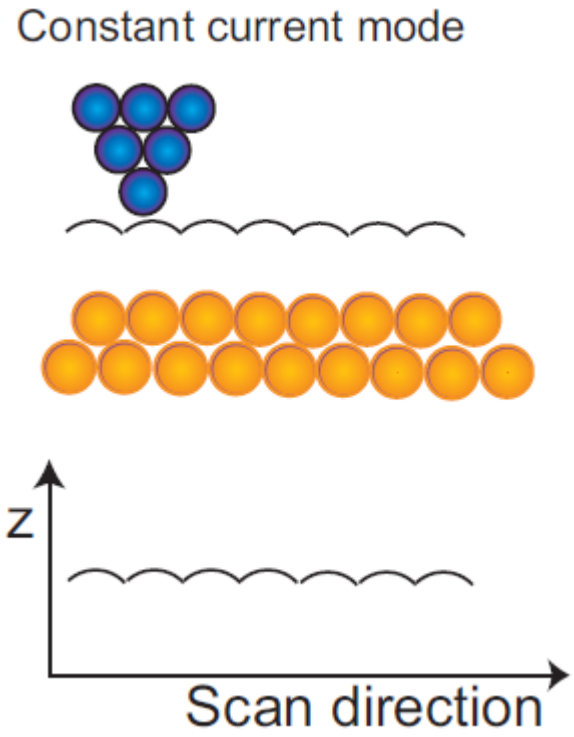


ρ_T is constant

$\Rightarrow dI/dV \propto \rho_s(E_F\text{-}eV)$

Modes of Operation

1. **Constant Current Mode**
   By using a feedback loop the tip is vertically adjusted in such a way that the current always stays constant.



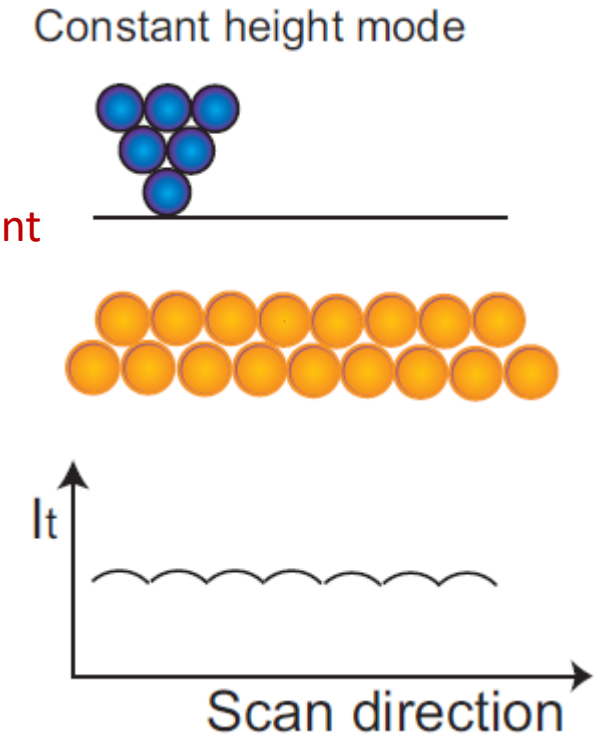
constant

$$I \propto \int_0^{eV} \rho_s(E_F\text{-}eV+\varepsilon)\, \rho_T(E_F+\varepsilon) d\varepsilon \exp(-2\kappa s)$$

$\rho_s \uparrow$ $s \uparrow$

2. Constant Height Mode

In this mode the vertical position of the tip is not changed, equivalent to a slow or disabled feedback. The current as a function of lateral position represents the surface image. This mode is only appropriate for atomically flat surfaces as otherwise a tip crash would be inevitable. One of its advantages is that it can be used at high scanning frequencies (up to 10 kHz). In comparison, the scanning frequency in the constant current mode is about
1 image per second or
even per several minutes.

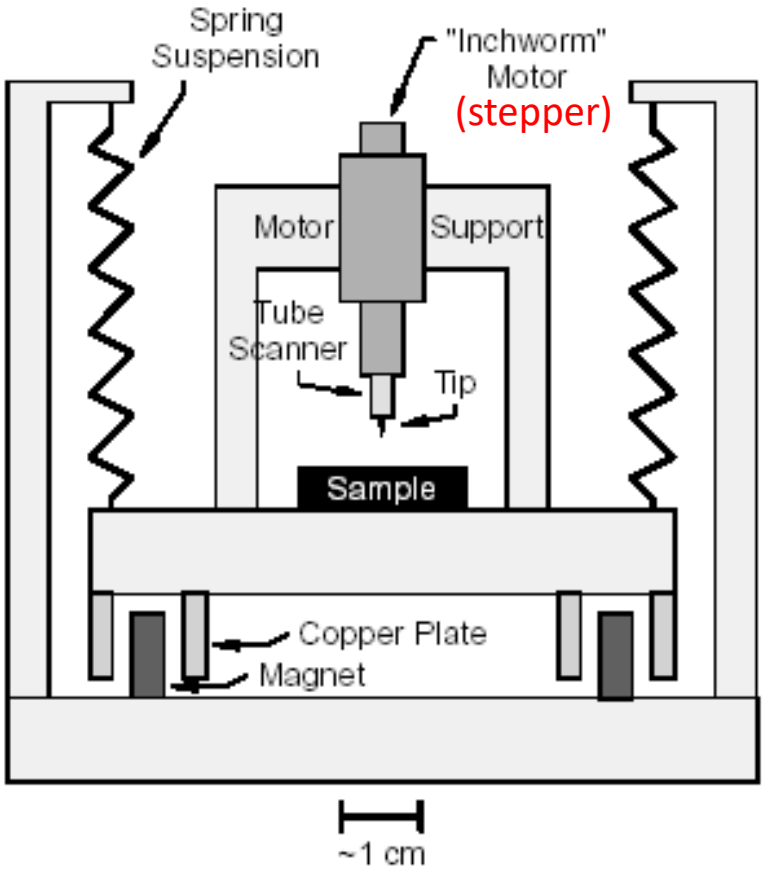


$$I \propto \int_0^{eV} \rho_s(E_F\text{-}eV+\varepsilon)\, \rho_T(E_F+\varepsilon) d\,\varepsilon \exp(-2\kappa s)$$

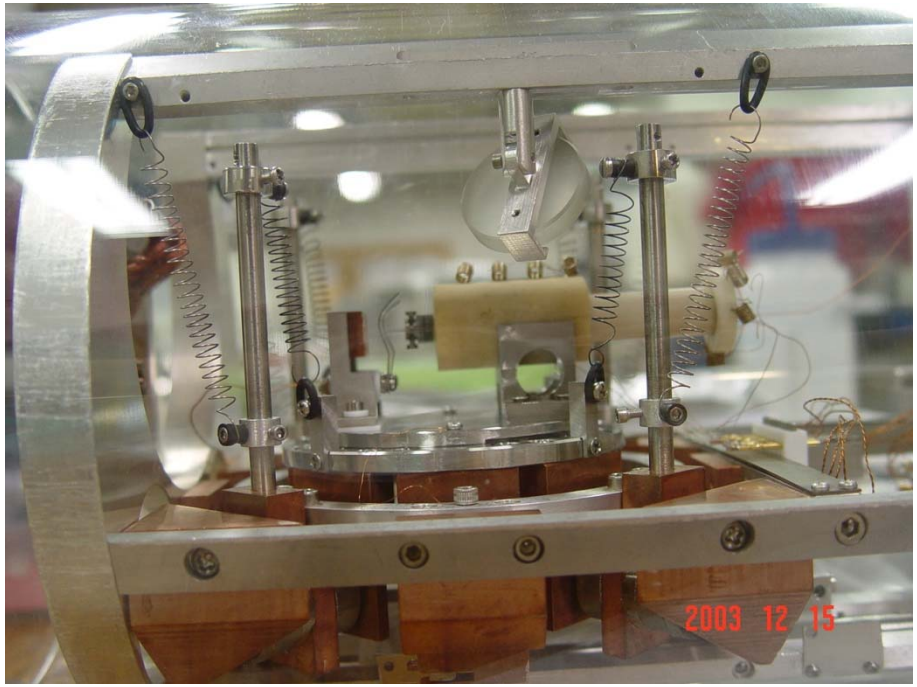
Not suitable to observe surface morphology

Suitable to observe dynamics phenomenon such as diffusion of surface atom.

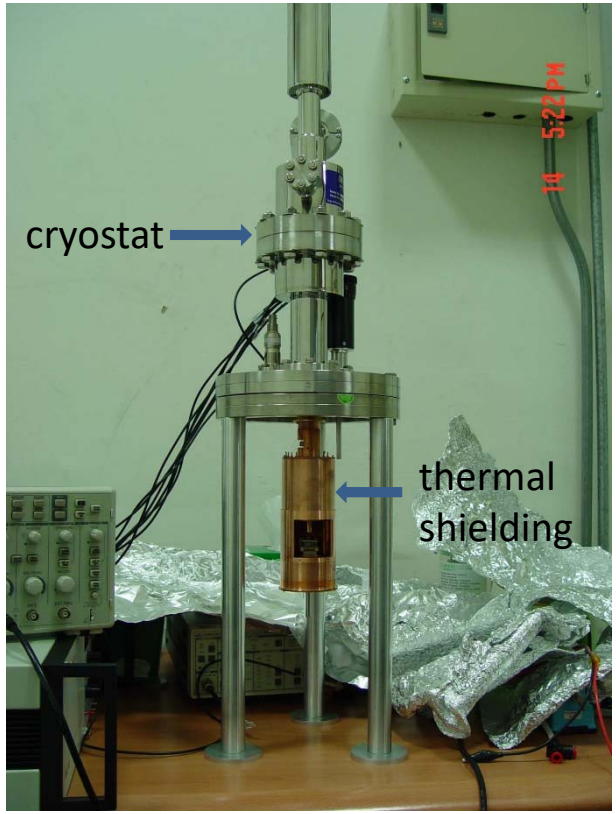
Structure of STM

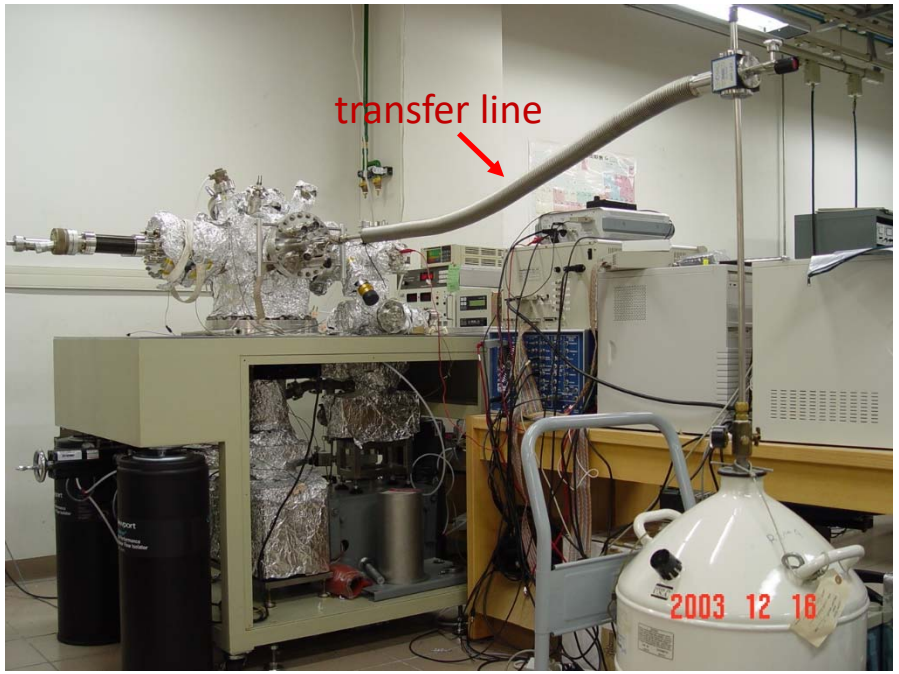


RT UHV STM



Homemade Low Temperature STM

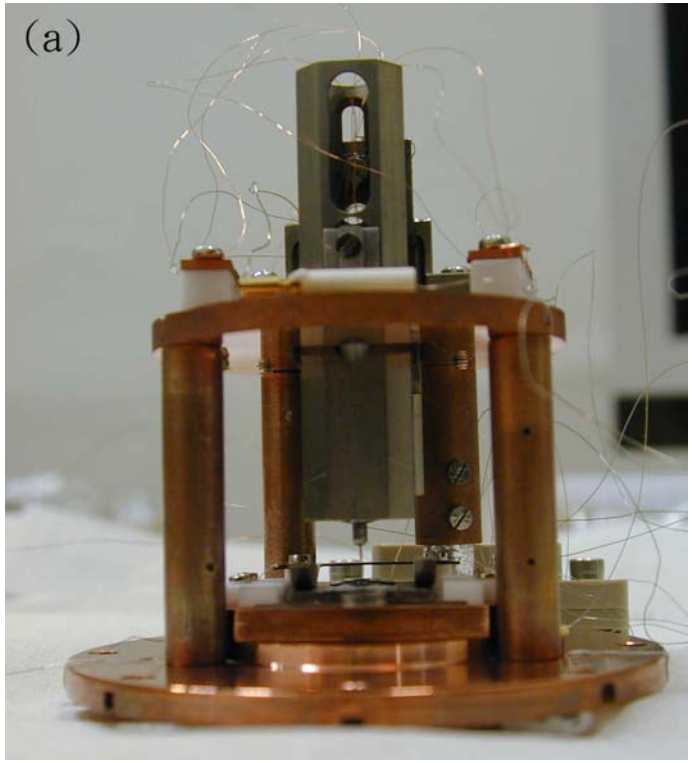


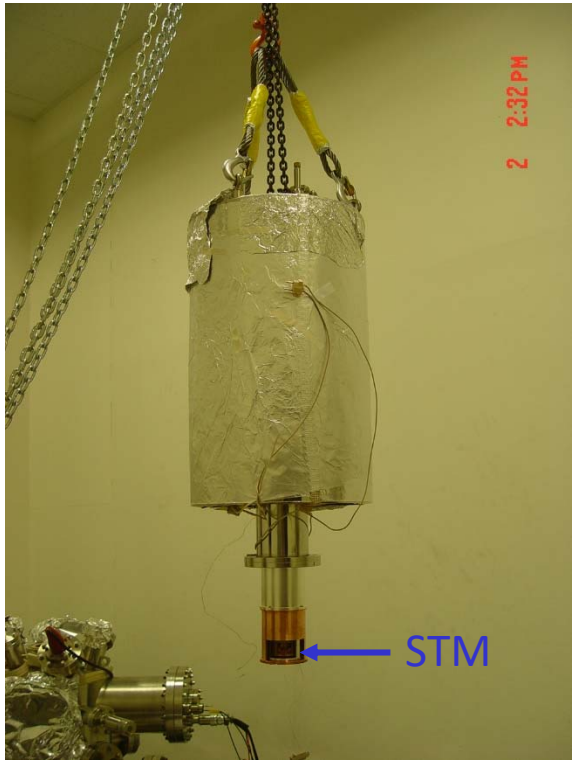


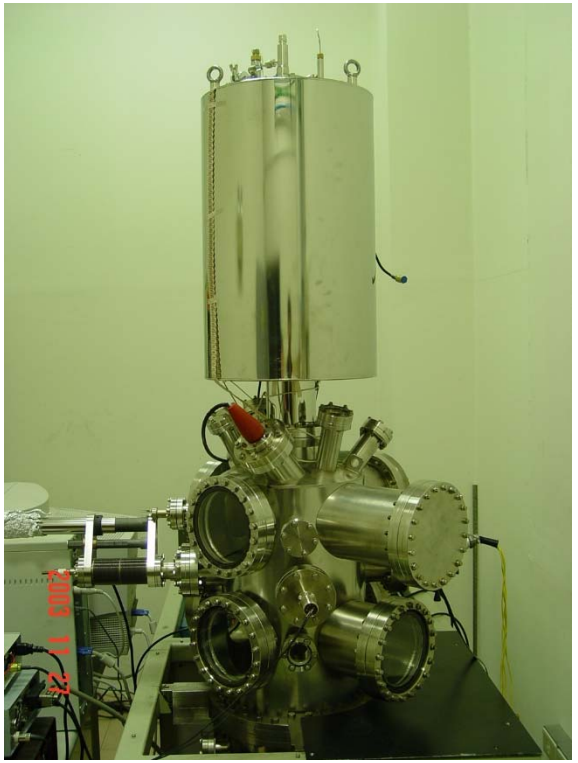
Home made LT UHV STM

Homemade STM

UHV-compatible
LHe Cryostat







Lowest temperature ~ 5 K

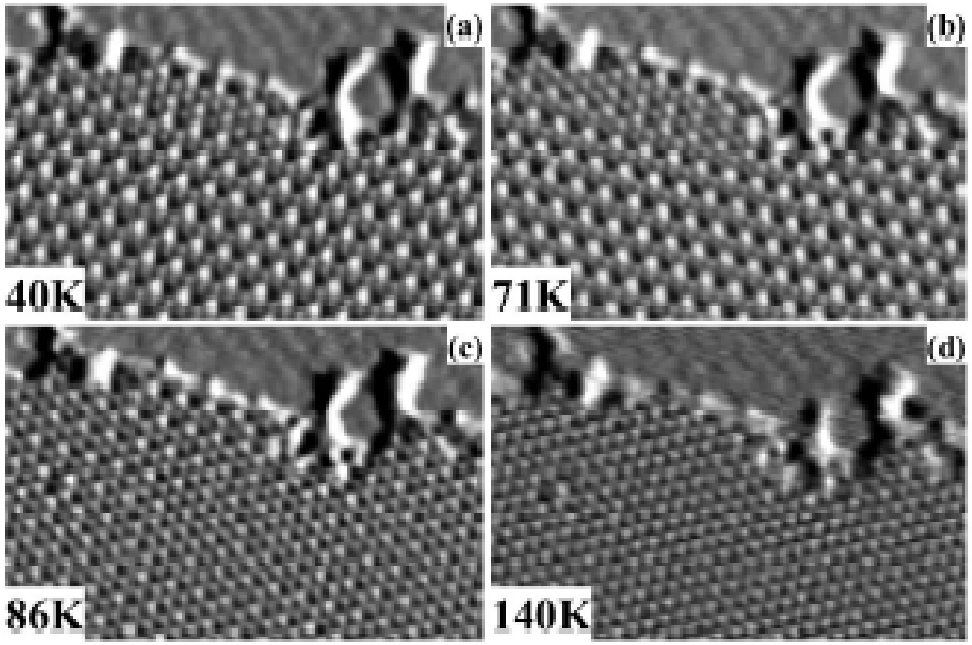
LHe consumption rate ~12 liter/37hours

Thermal drift ~ 6 Å/ hour

Merits of LT STM

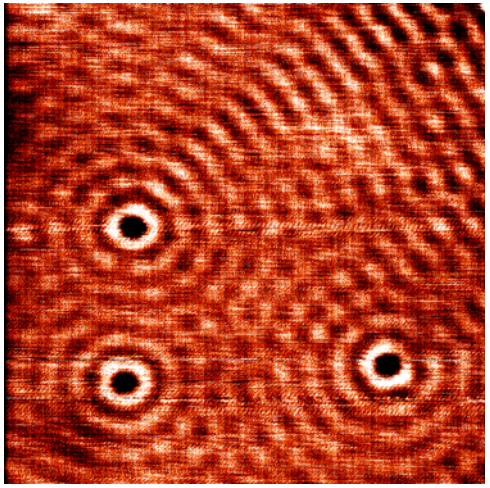
Phase transition

(3 x3)Pb/Si(111) → (√3 x √3)Pb/Si(111)

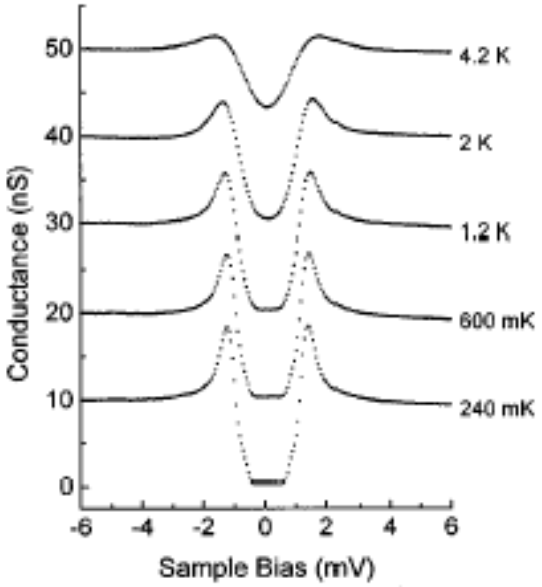


I. Brihuega et al. Phys. Rev. Lett. **94**, 046101 (2005)

Interference wave of surface state



Superconducting gap

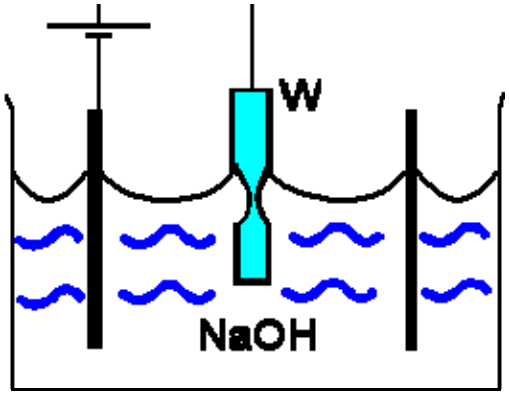


Tip

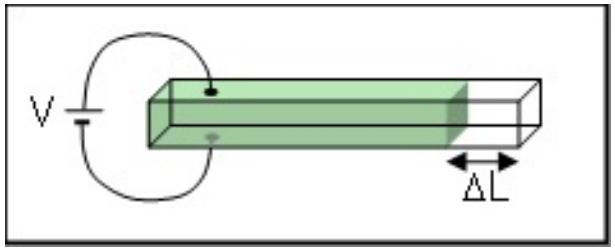
The tip is the trickiest part in the STM experiment. It needs a small curvature to resolve coarse structures. For atomic resolution a minitip with a one atomic end is necessary. Tips typically are made out of tungsten or Pt-Ir wire.

A sharp tip can be produced by:

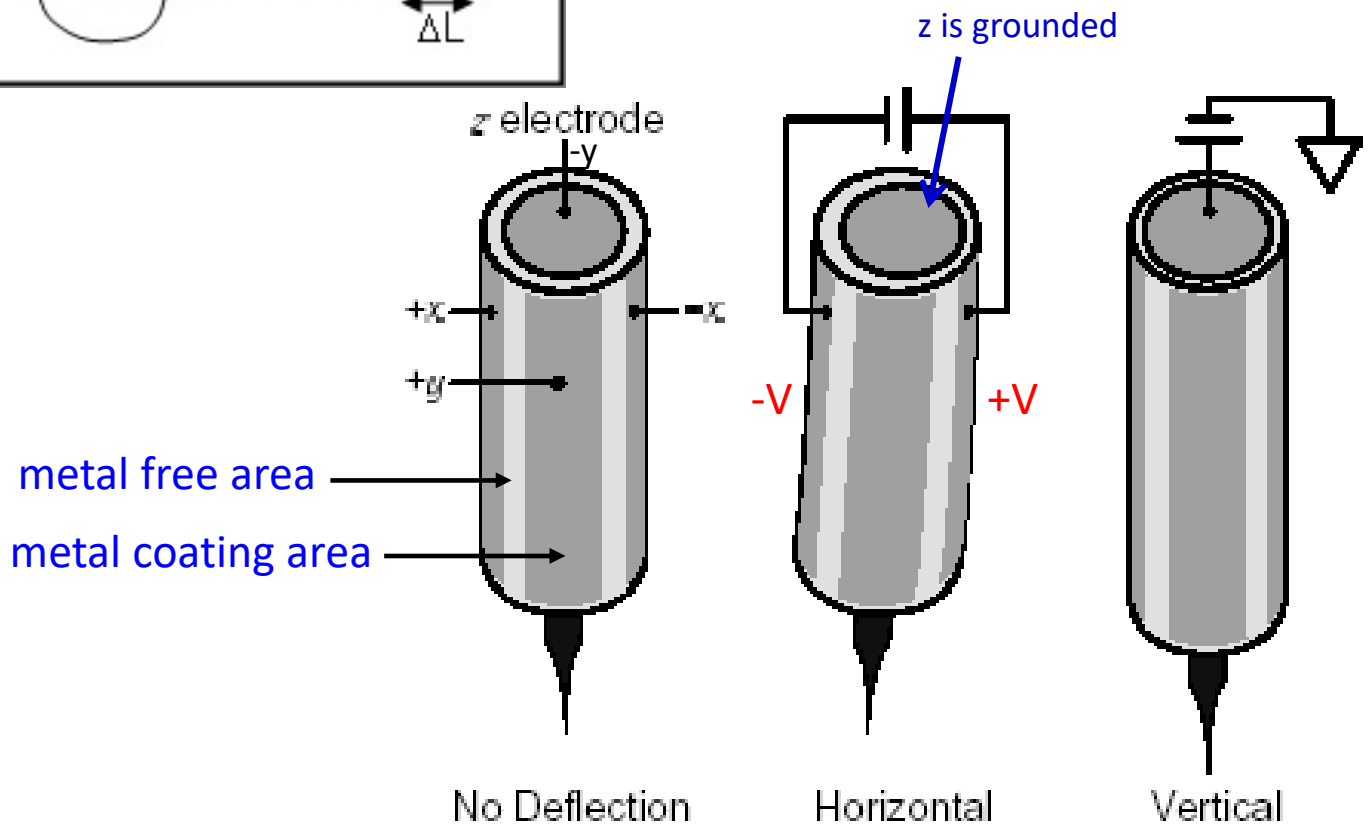
- Cutting and grinding (Pt-Ir)
- Electrochemical etching (W)

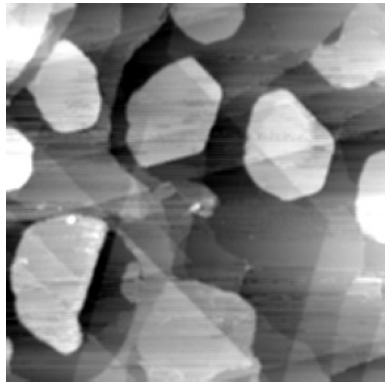


Most often the tip is covered with an oxide layer and contaminations from the etchant and is also not sharp enough. Thus other treatments to the tip, like annealing or field evaporation are necessary.



Tube Scanner





The contrast in STM image is the variation of voltage on z electrode.

Piezoelectric ceramic PZT [$Pb(Zr,Ti)O_3$]

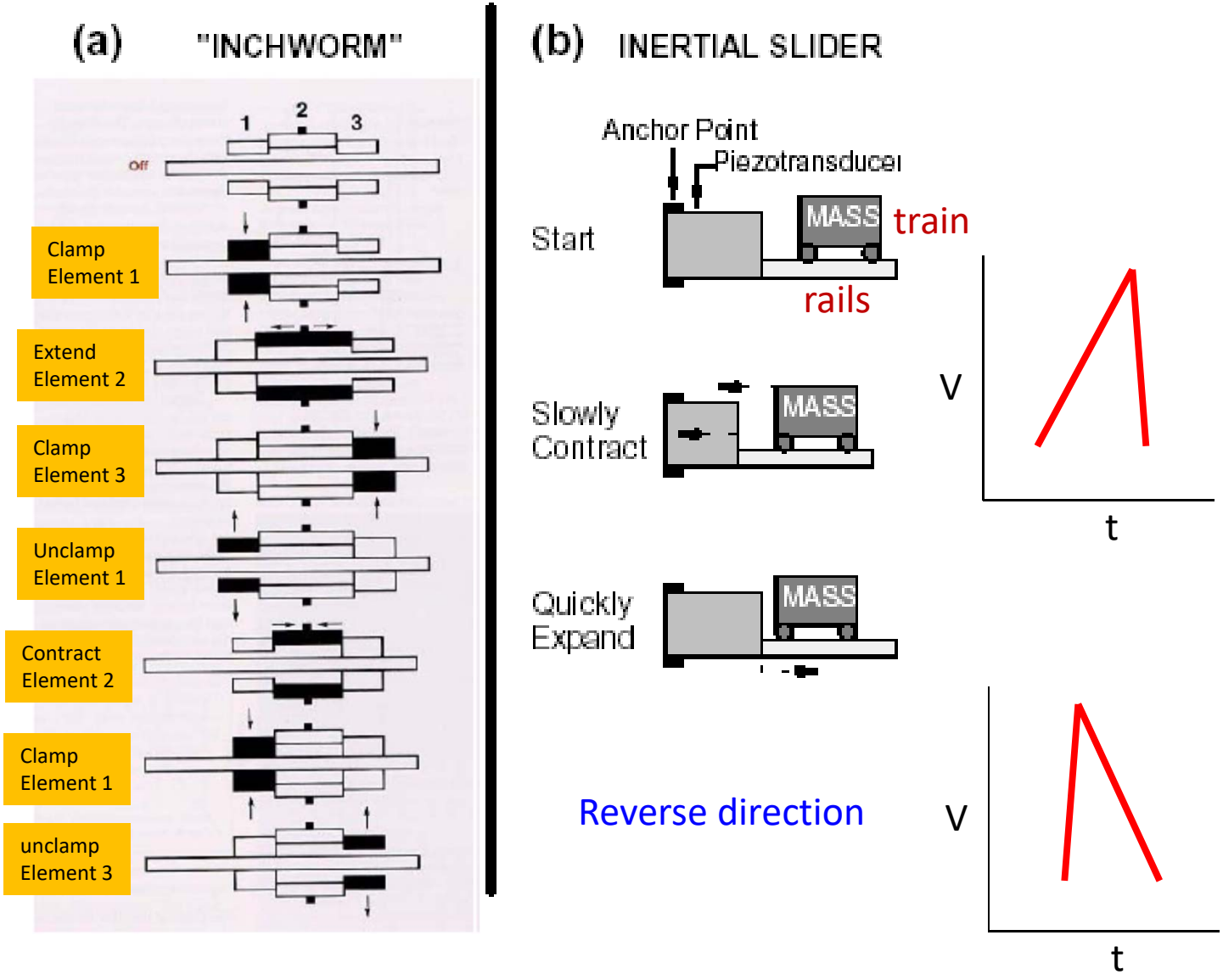
(piezo)

can be deformed by applying voltage

Stepper

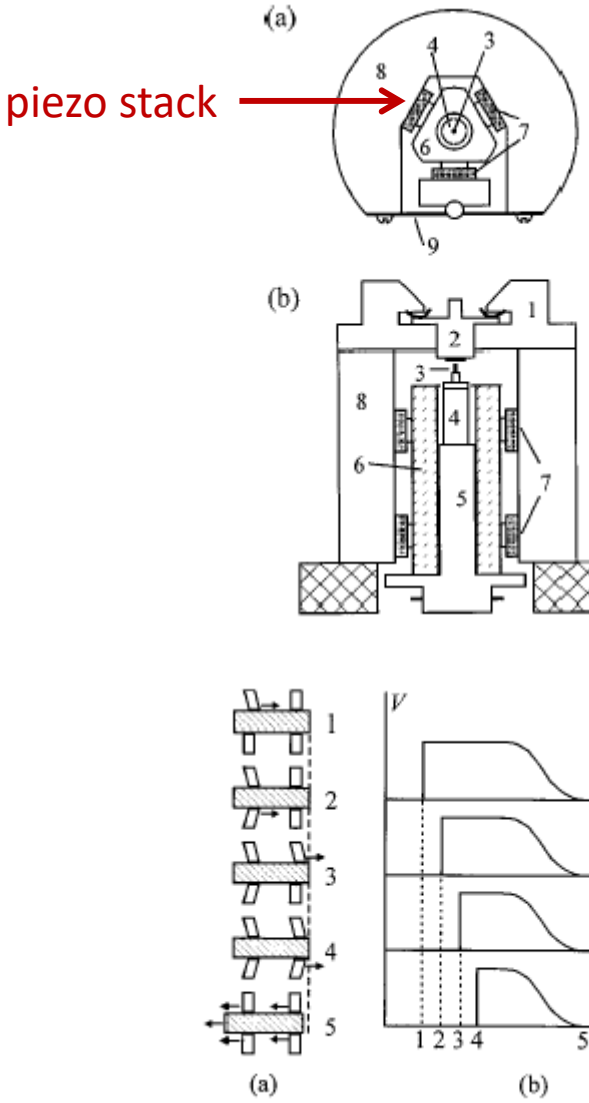
1,3: Piezo-clamp

2: Piezo-tube

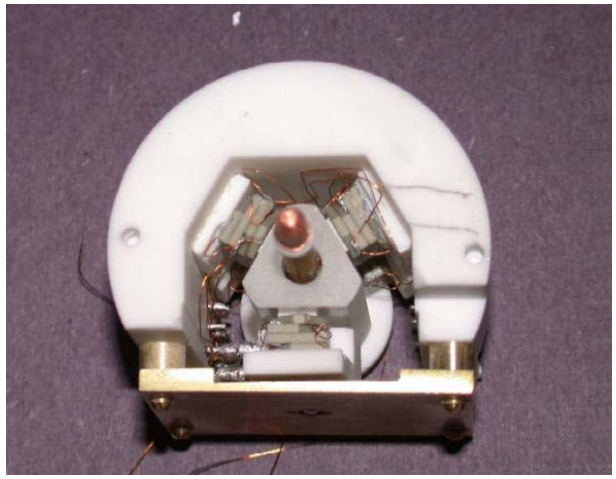


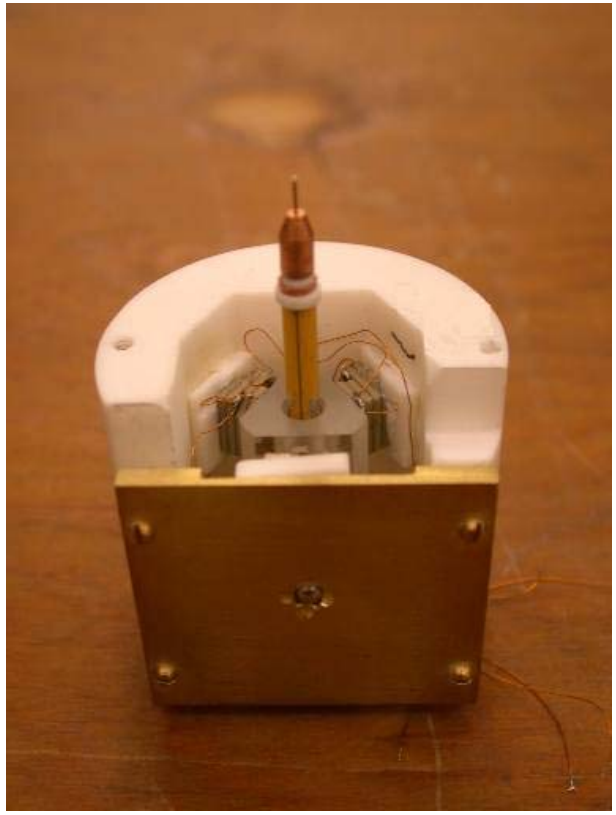
Pan-style Stepper invented by S. H. Pan

piezo stack



High rigidity





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Vibration damping

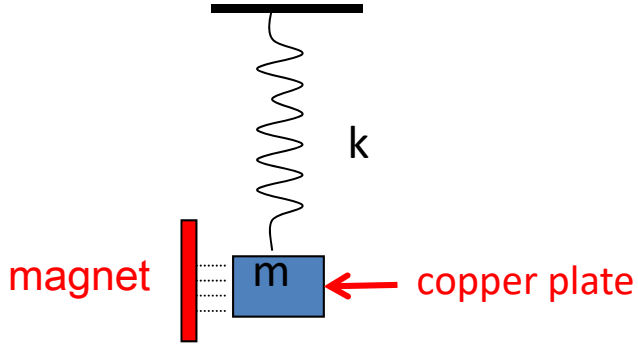
The tip-sample distance must be kept constant within 0.01Å to get good atomic resolution. Therefore it is absolutely necessary to reduce inner vibrations and to isolate the system from external vibrations.
Environmental vibrations are caused by:

- Vibration of the building 15 - 20 Hz
- Running people 2 - 4 Hz
- Vacuum pumps
- Sound

Vibration damping can be done by

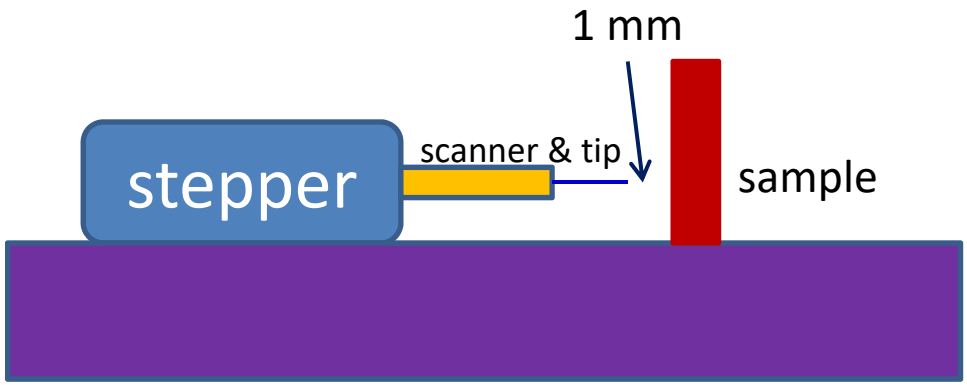
- Suspension with springs (including additional eddy current dampers)
- Pneumatic systems

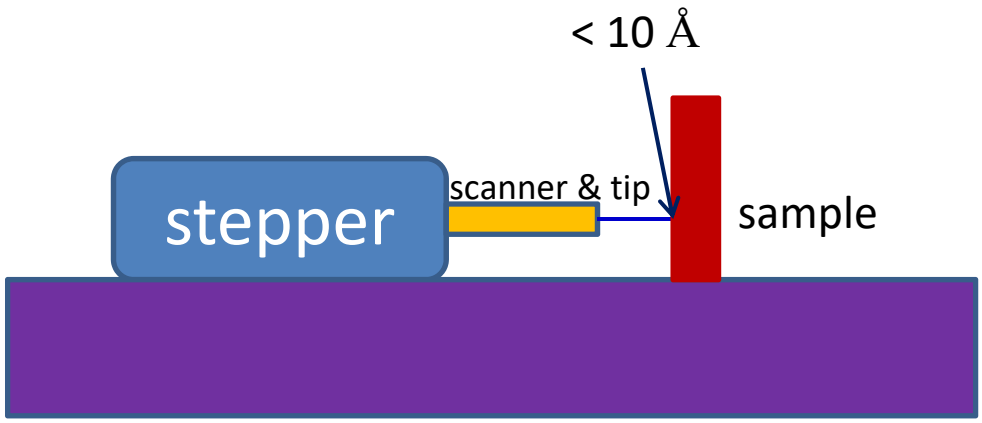
magnets and copper plates

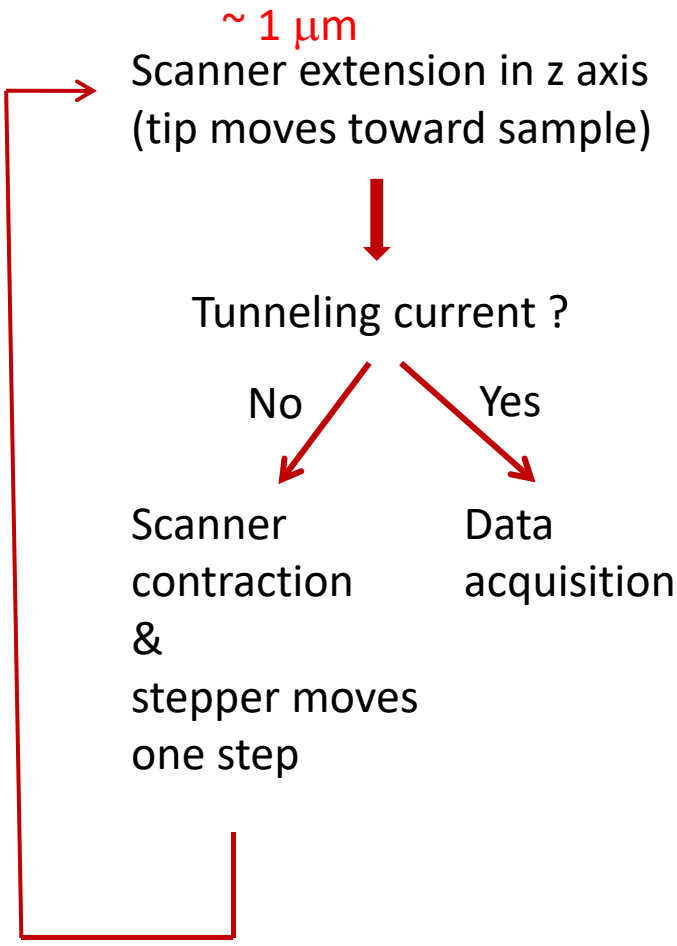


STM electronics

1. Auto approach



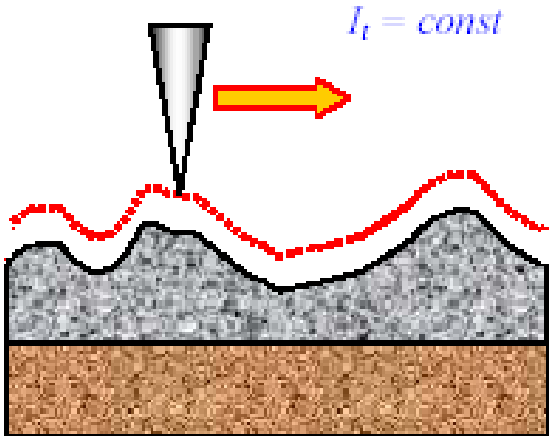


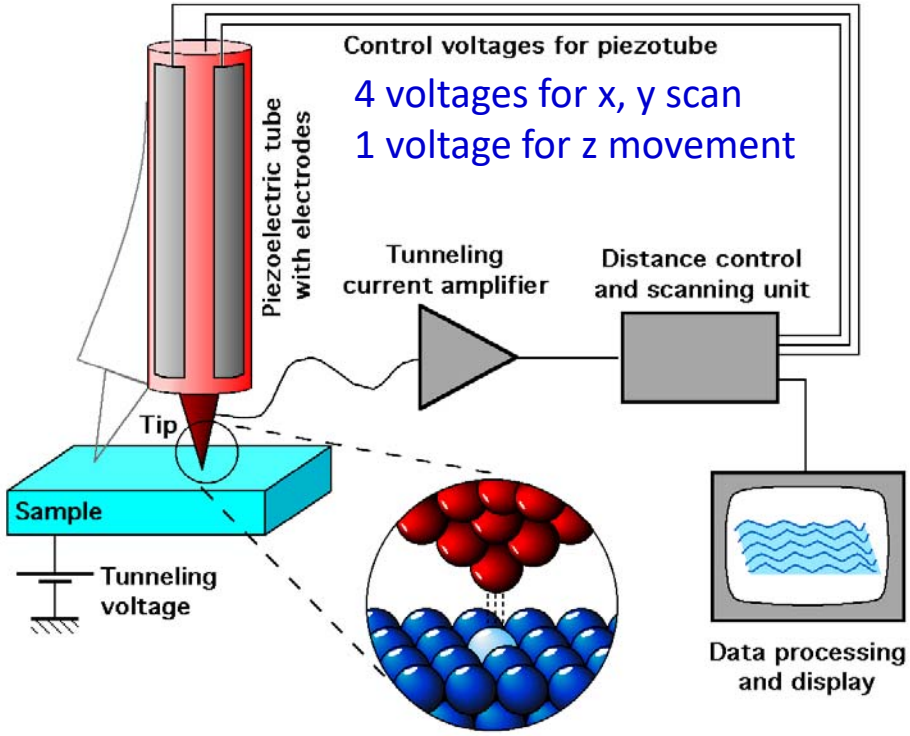


Extension in z axis > one step of stepper

STM electronics

2. Data acquisition





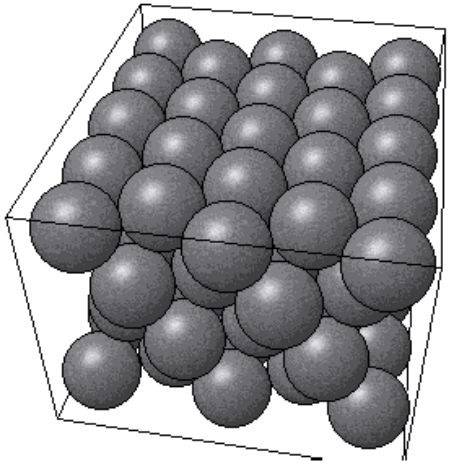
V_z : voltage on z electrode V_z (x,y) under the same current

The tunneling current (0.01nA-50nA) is converted into a voltage by a current amplifier. To get a linear response with respect to the tunneling gap (the current is exponentially dependant on the tip-sample distance) the signal is processed by a logarithmic amplifier. The output of the logarithmic amplifier is compared with a predetermined voltage which is used as a reference current. The error signal is passed to feedback electronics, which applies a voltage to the z piezo to keep the difference between the current set point and the tunneling current small. Care has to be taken to keep the noise signal ratio on a low level. Also the response time of the feedback has to be minimized without loosing accuracy.

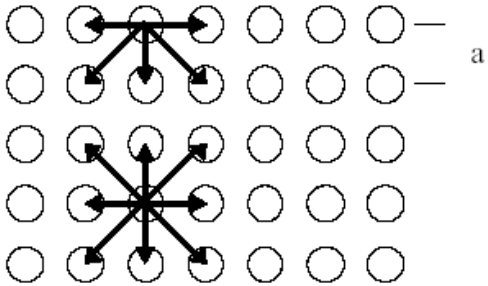
Applications of scanning tunneling microscopy

Surface reconstruction

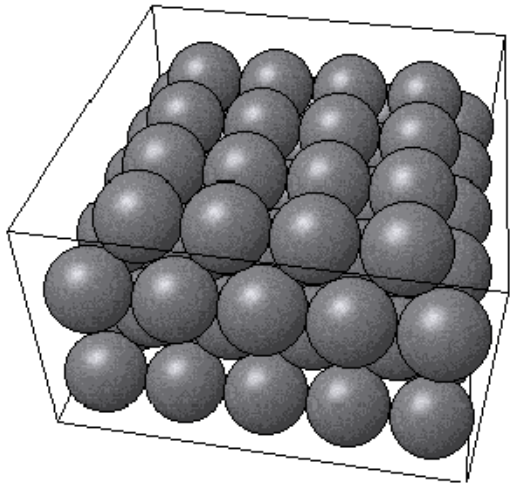
FCC(111)

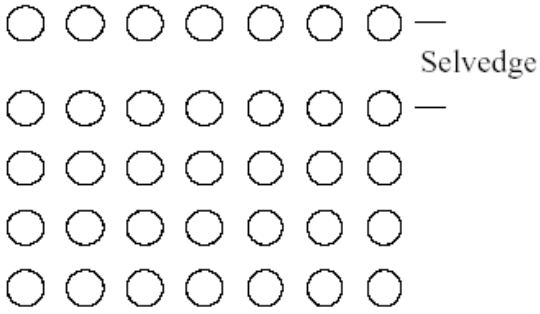


Atoms at surface experience different bonding environment than bulk - causes *relaxation* and *reconstruction*

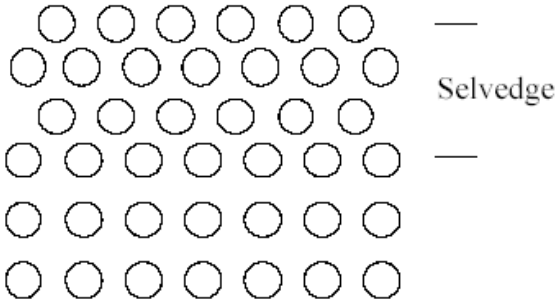


FCC(100)



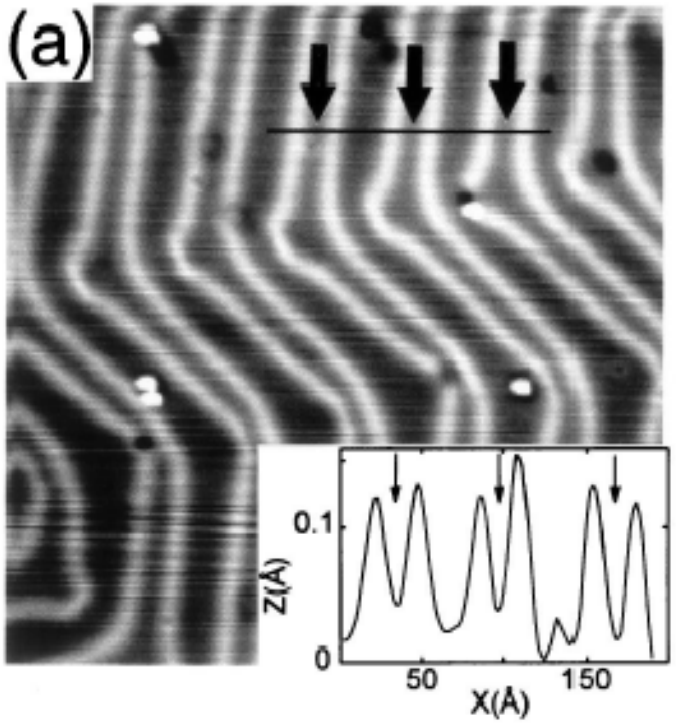


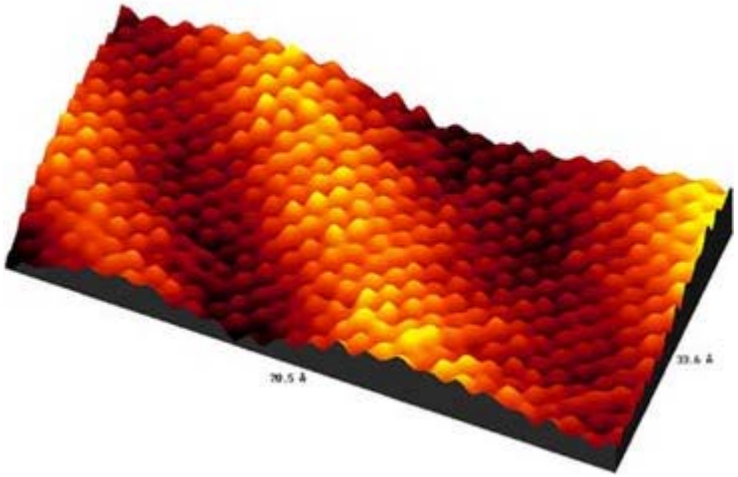
Relaxation

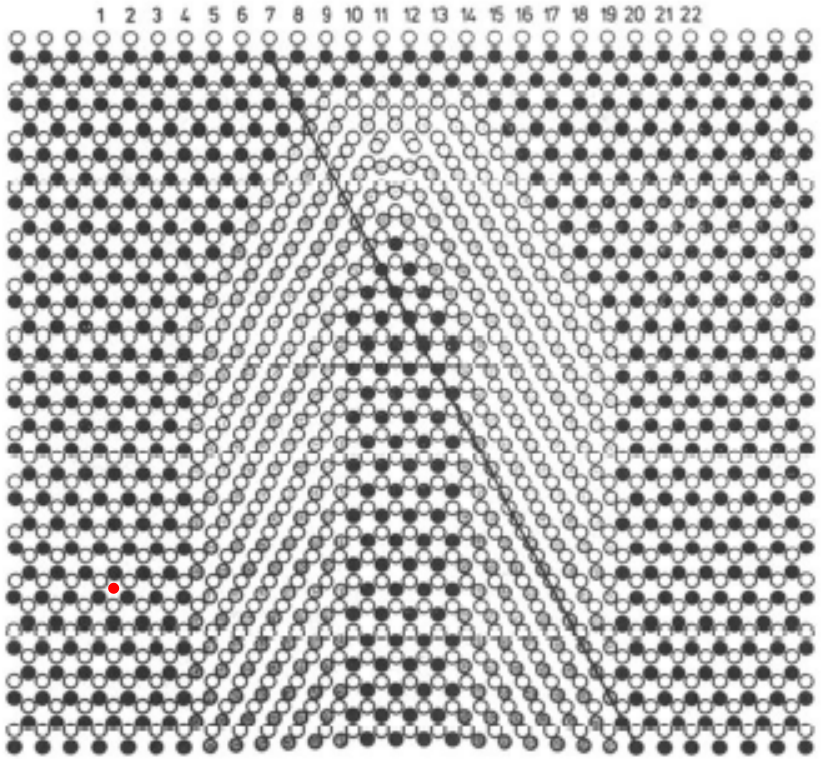


Reconstruction

22×√3 Reconstruction of Au(111) surface



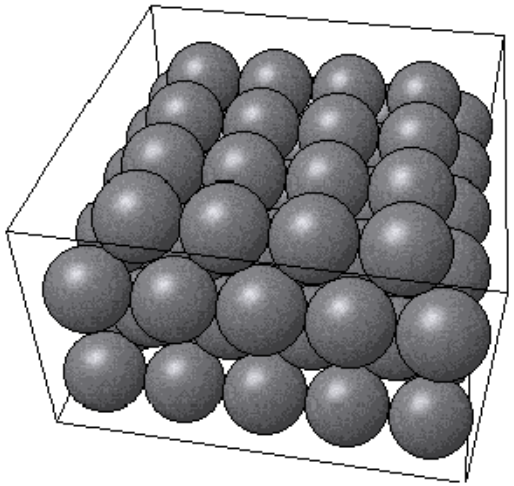


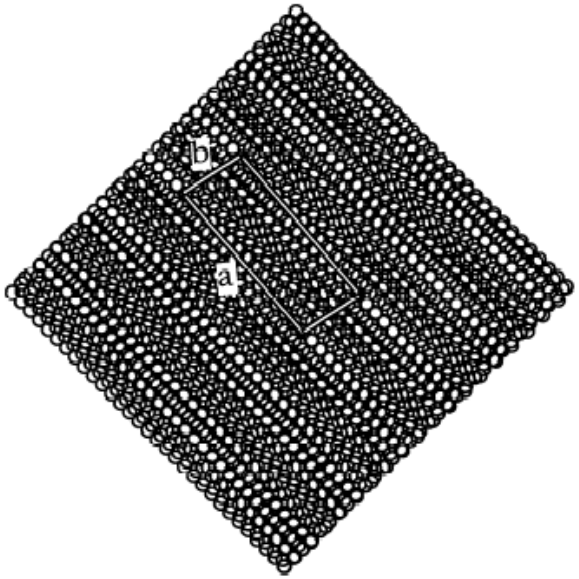


FCC (ABC) ridge HCP (ABA) FCC

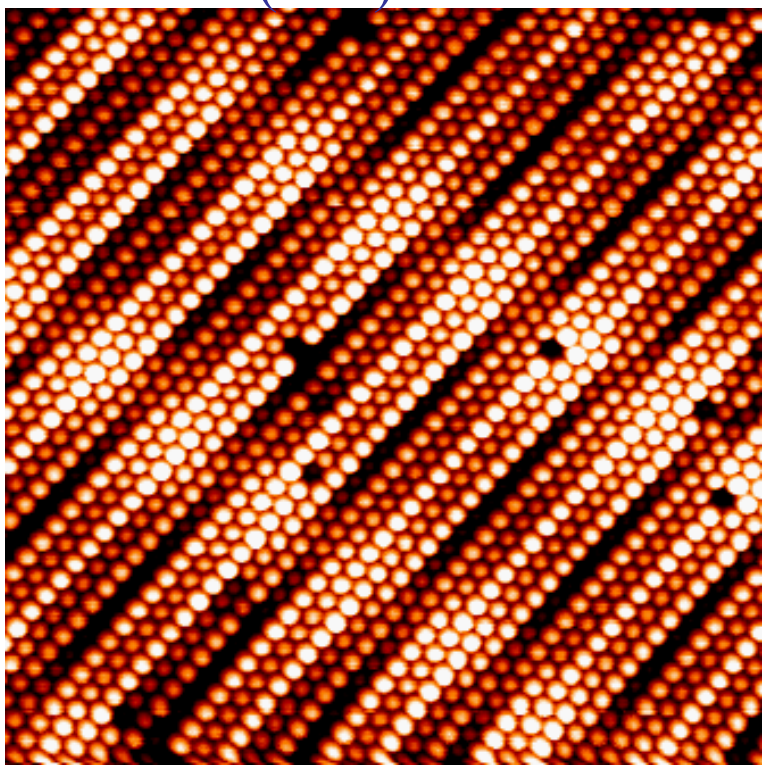
Reconstruction on Pt(100)

FCC(100)





Pt(100)-R0.7^0

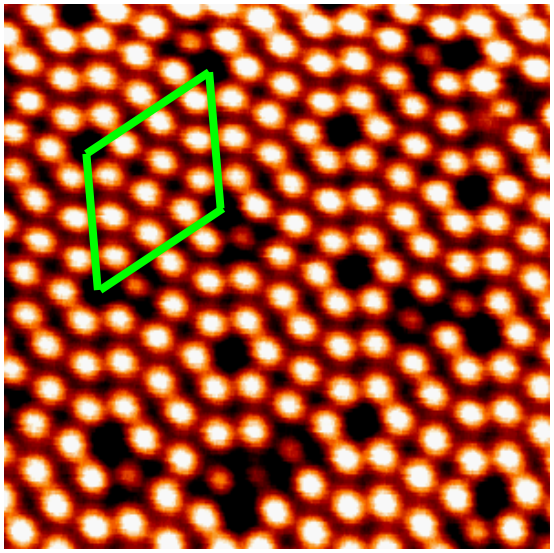


Close packed lattice (0.965 A) / square lattice (A)

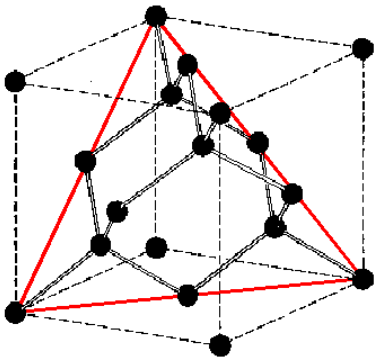
A=lattice constant

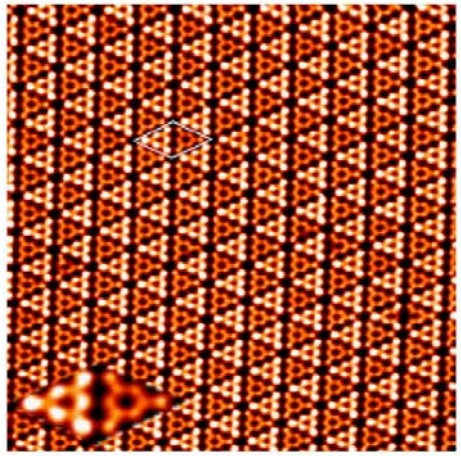
Reconstruction on Si(111)

STM image of Si(111)7×7 (empty state)



Si

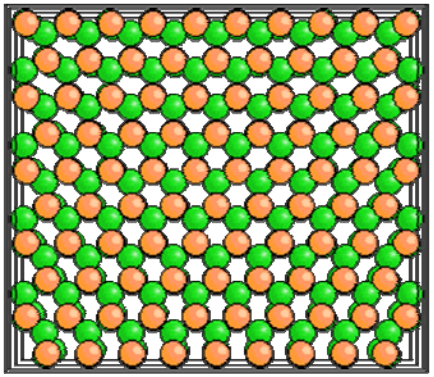




filled state

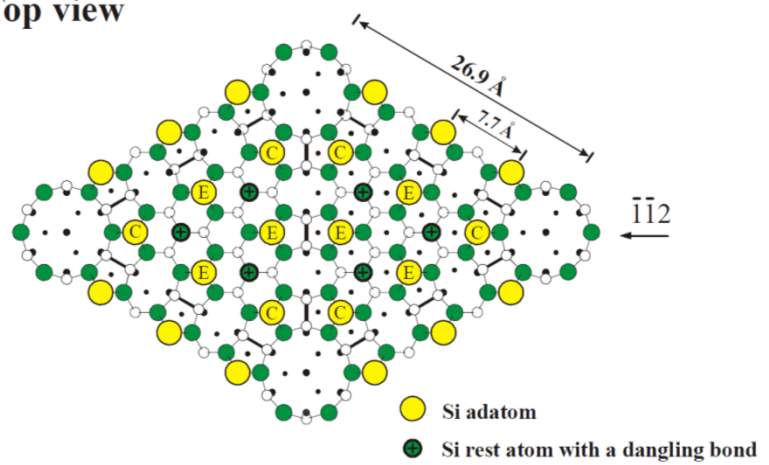
bilayer

Top view

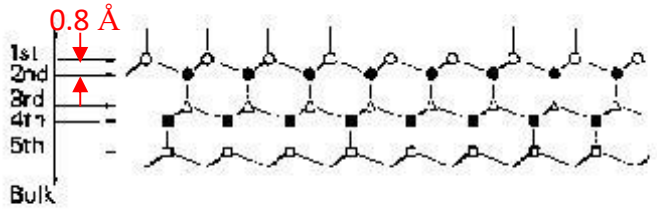


Atomic Model of Si(111)-(7×7)

Top view

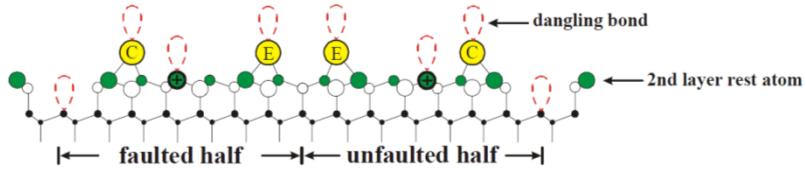


Side view



(a)

Side view



Surface Diffusion

Einstein Equation : $D=\langle x^2\rangle/2\alpha\gamma$

D: diffusion coefficient,

$\langle x^2\rangle$: mean square displacement of atom

α=1 for one dimensional diffusion

α=2 for two dimensional diffusion ($\langle x^2\rangle+\langle y^2\rangle$)

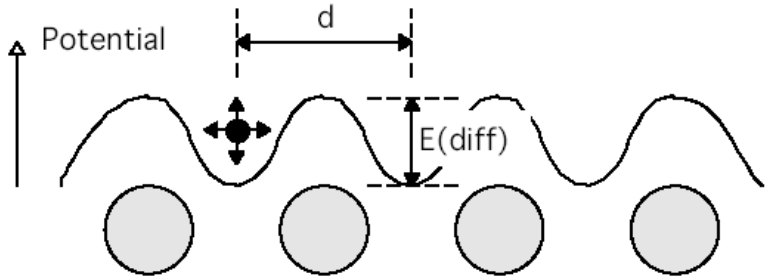
γ: time interval

$\langle x^2\rangle$ can be related to the number of jumps N

According to random walk theory $\langle x^2\rangle=Nd^2$

L: mean jump distance

Γ Is defined as the number of atom jumps per time interval $=N/\gamma$



$D=d^2\Gamma/2$

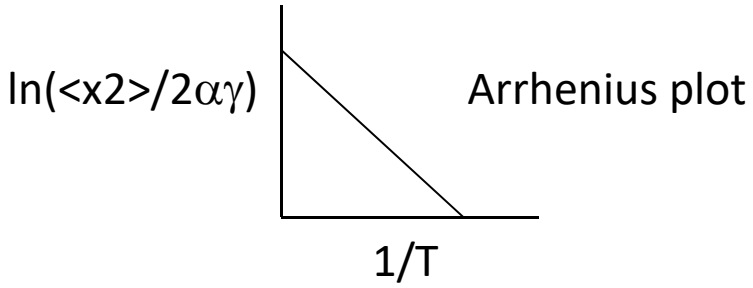
$\Gamma=\nu_0 \exp(-E_d/kT)$

ν_0 is vibration frequency,
E_d is activation energy

$D=D_0\exp(-E_d/kT)=\langle x2\rangle/2\alpha\gamma$

D_0 is the diffusivity$=\nu_0 d^2/2$

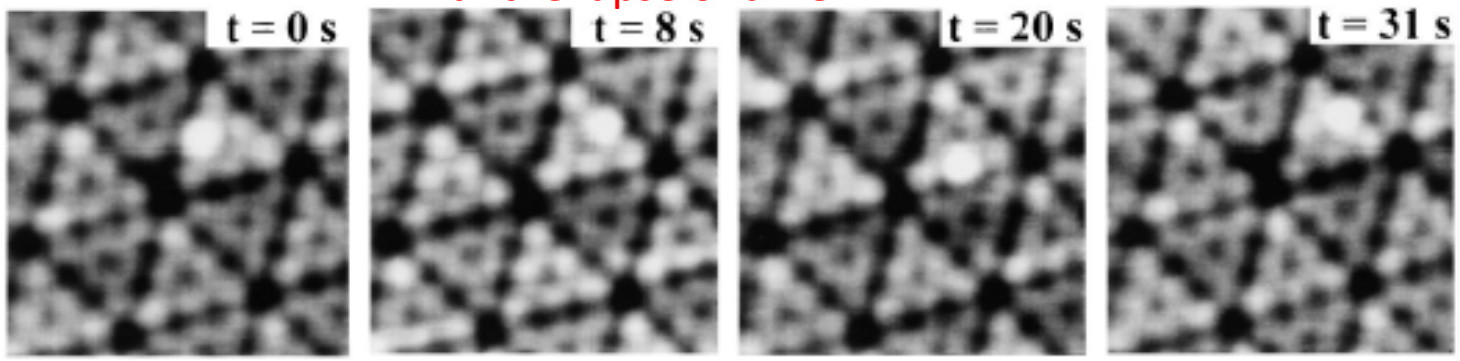
$\ln(\langle x2\rangle/2\alpha\gamma)=\ln(D_0)-E_d/kT$

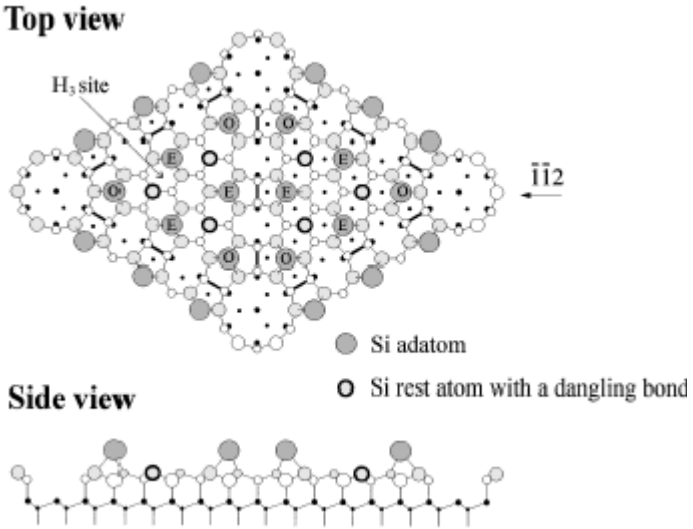


Site Hopping of Single Chemisorbed O_2 Molecule on Si(111)7×7

with the lapse of time ⟶

350^{0}C





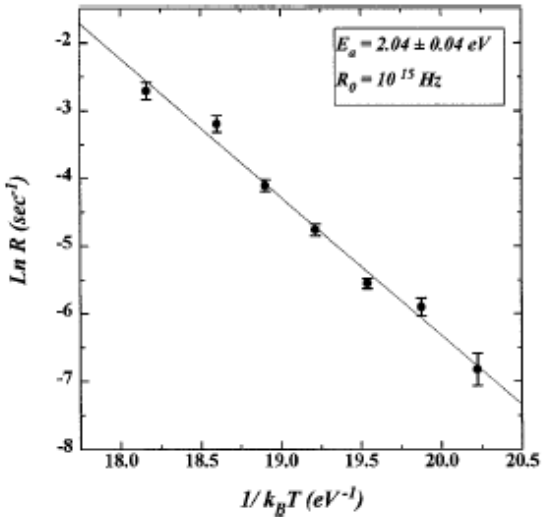
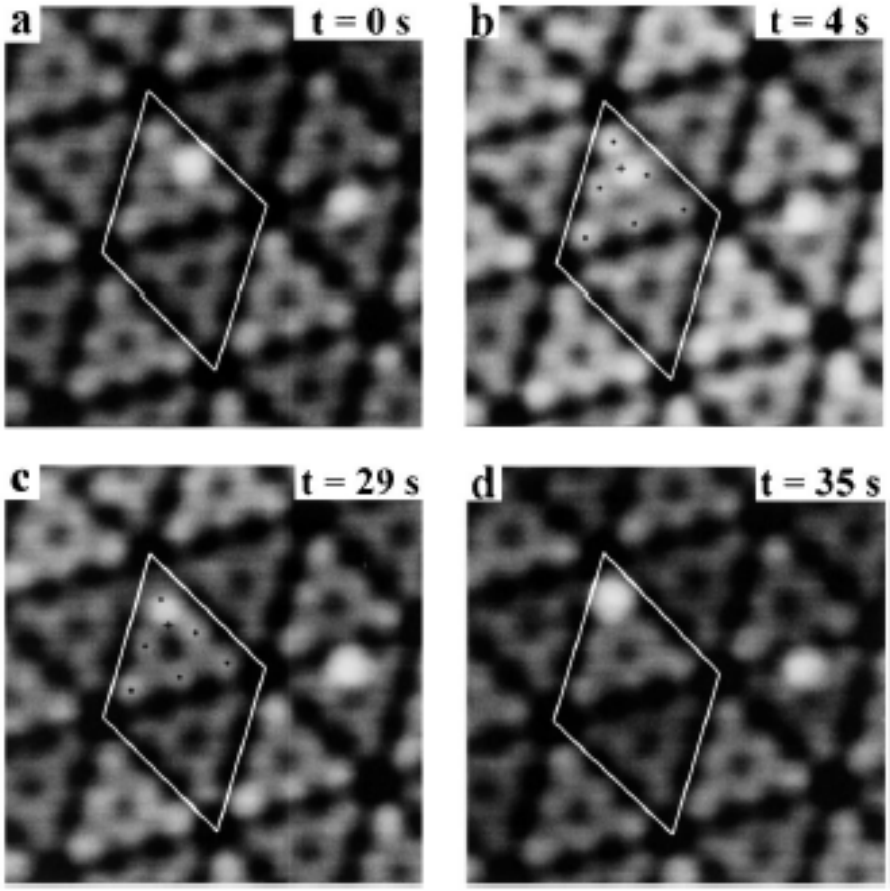


TABLE I. Parameters for site hopping of O_2 on Si(111)-(7 × 7).

Hopping	Activation energy	Frequency factors
FE to FE	2.04 ± 0.04 eV	$10^{15.0}$ s^{-1}
FE to FO	2.29 ± 0.06 eV	$10^{16.2}$ s^{-1}
FO to FE	2.13 ± 0.11 eV	$10^{15.6}$ s^{-1}
UE to UE	2.16 ± 0.04 eV	$10^{15.9}$ s^{-1}
UE to UO	2.01 ± 0.10 eV	$10^{14.6}$ s^{-1}
UO to UE	1.96 ± 0.13 eV	$10^{14.1}$ s^{-1}

Phys. Rev. Lett. 78, 4797 (1997)

300^{0}C



Phys. Rev. Lett. 78, 4797 (1997)

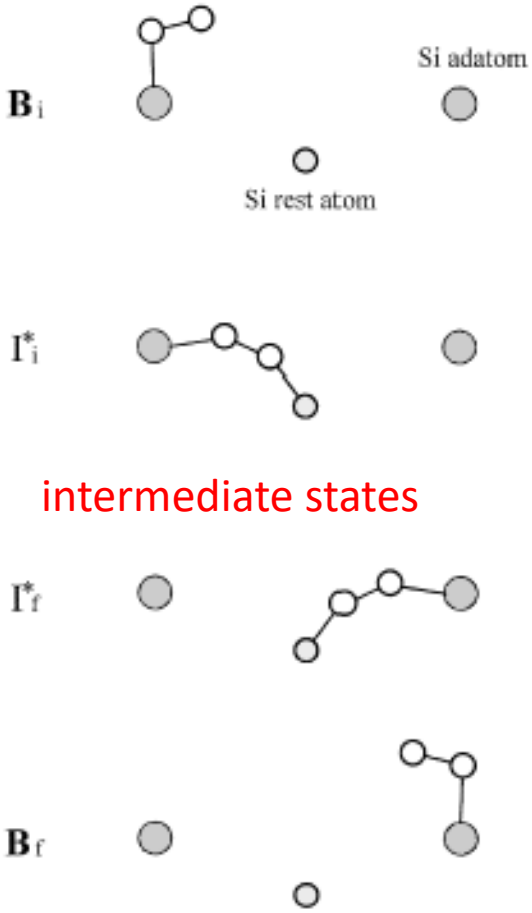
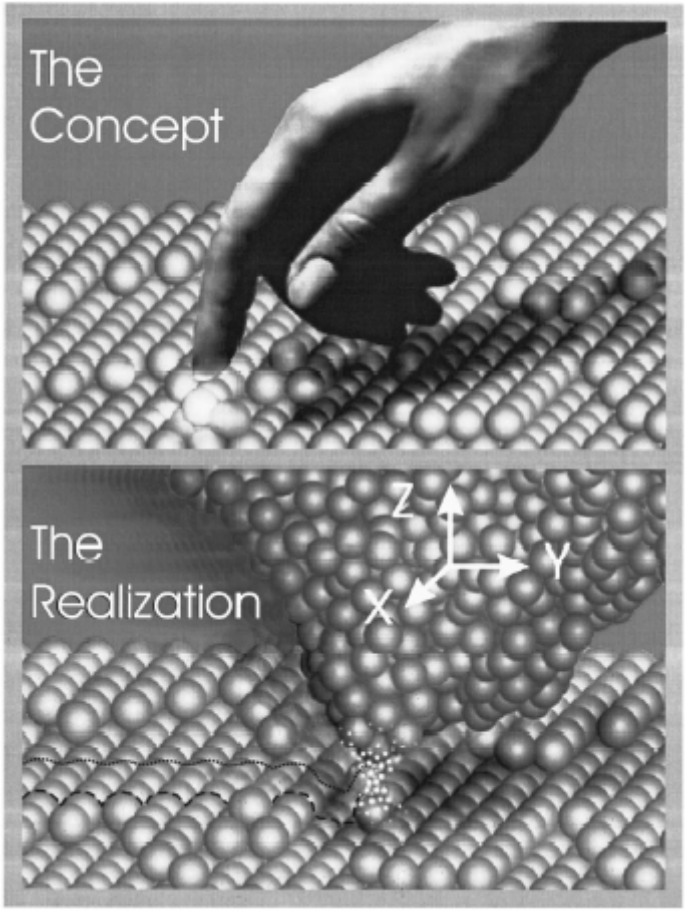
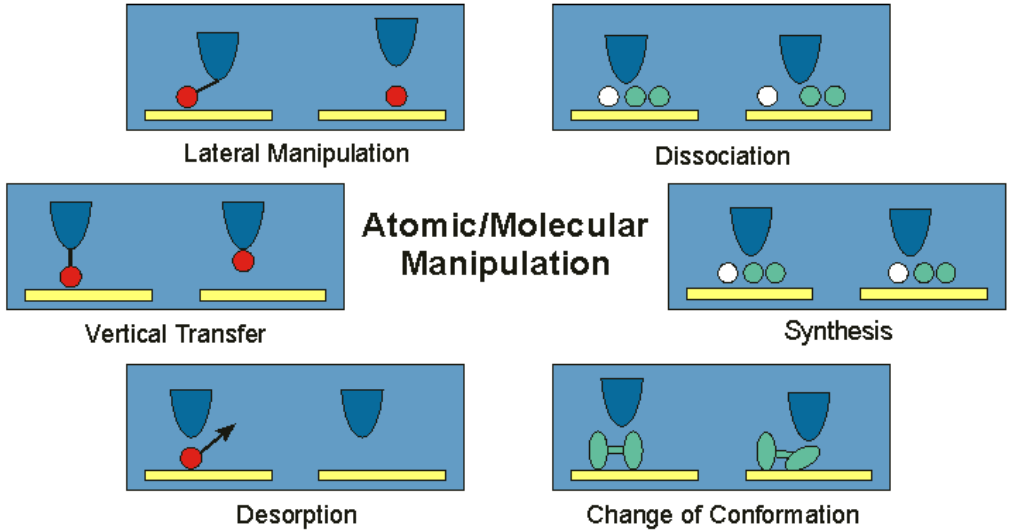


FIG. 5. The model for the site hopping.

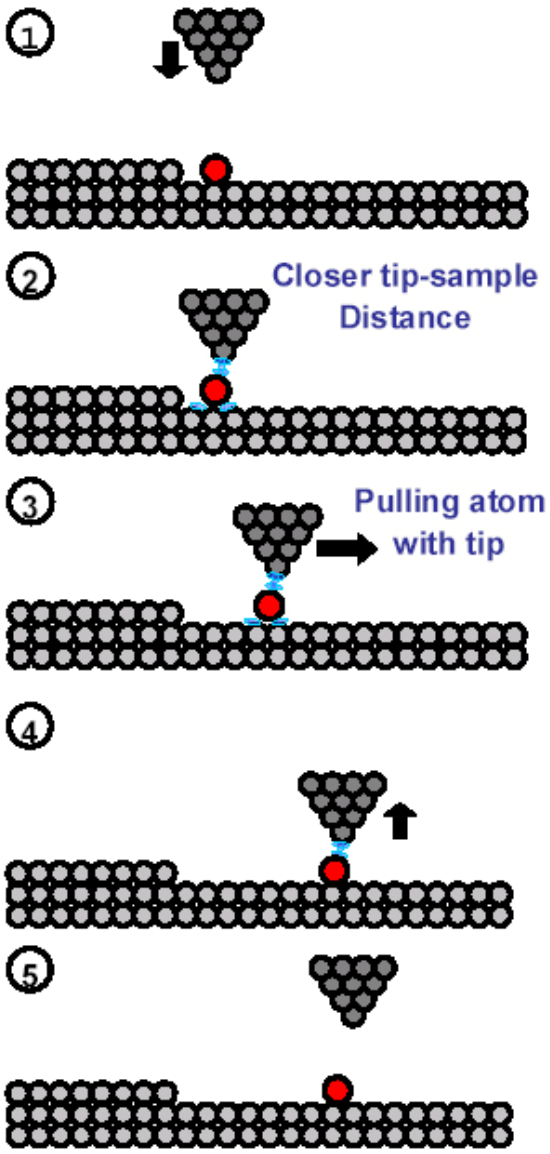
Atom Manipulation and Nanolithography By STM

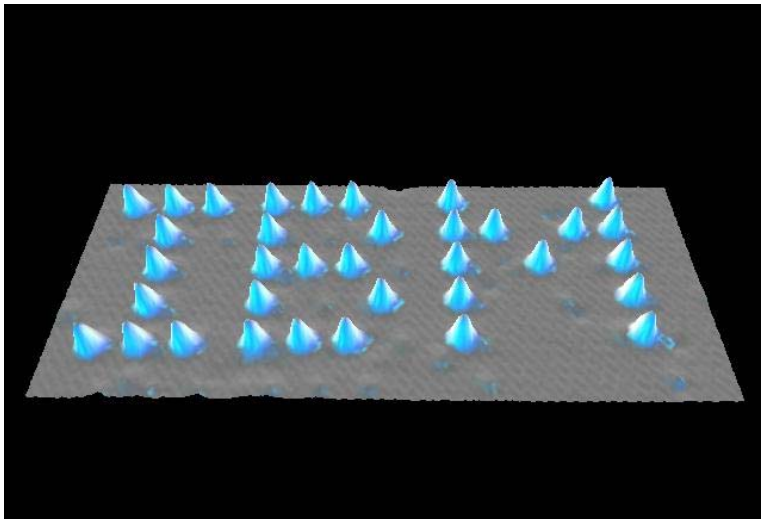




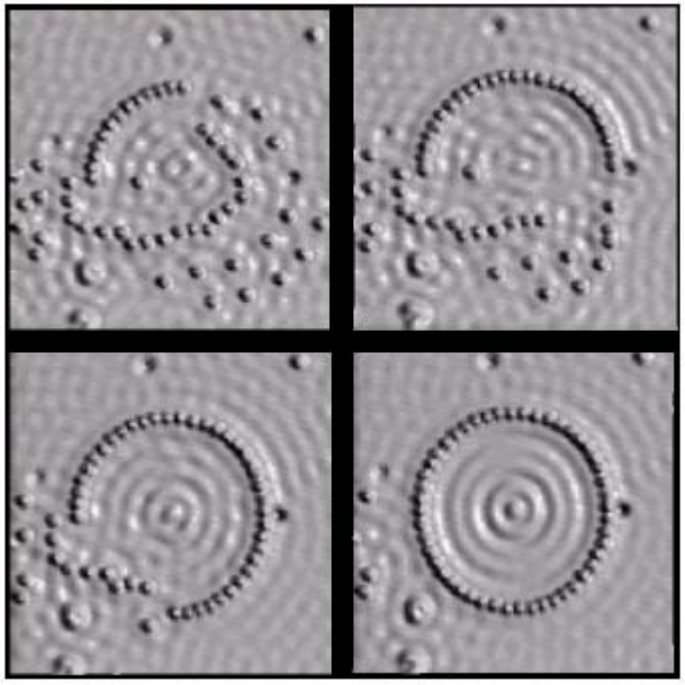
Overview of manipulation processes.

Lateral Manipulation



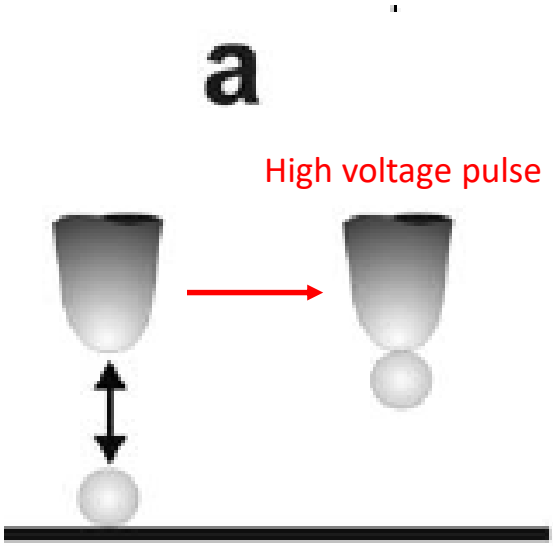


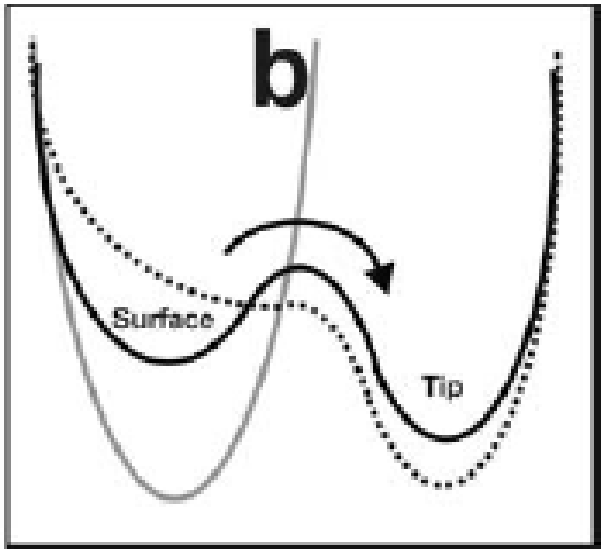
By Eigler et al. Nature 344, 524 (1990)

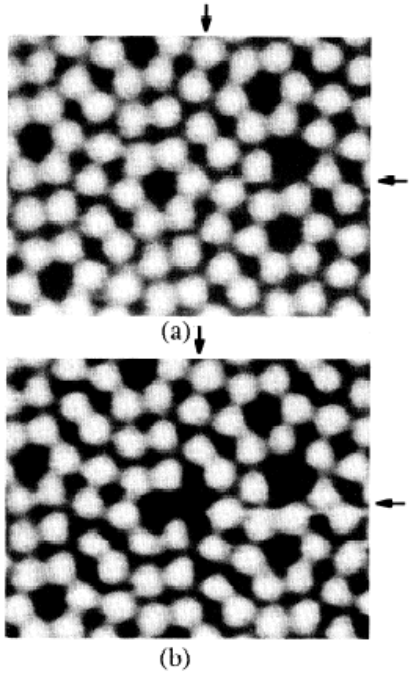


Science 262, 218 (1993)

Vertical Manipulation

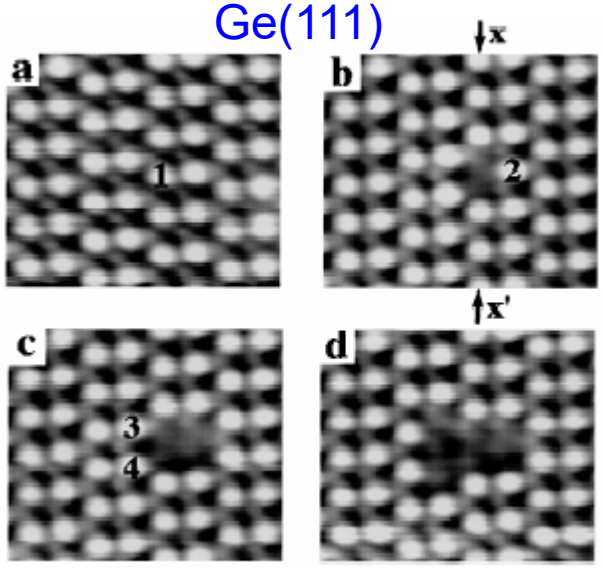






Phys. Rev. Lett. 70, 2040 (1993)

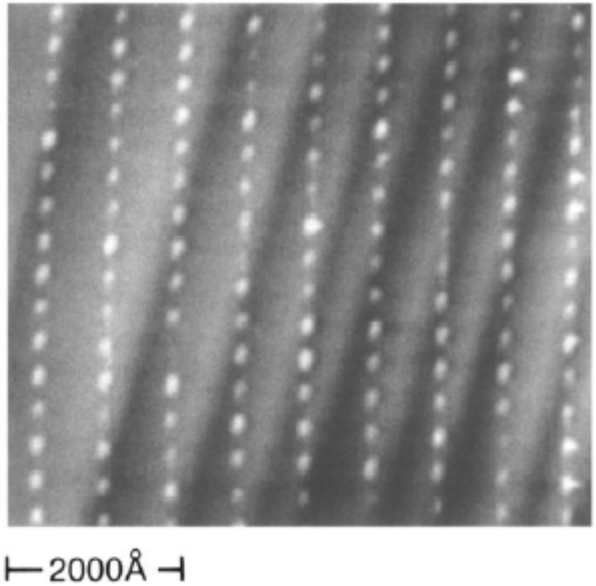
Ge(111)

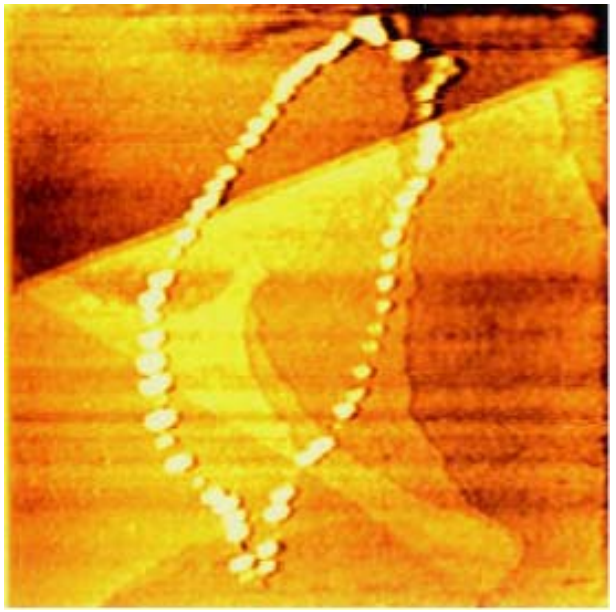


Phys. Rev. Lett. 80, 3085 (1998)

Nanolithography

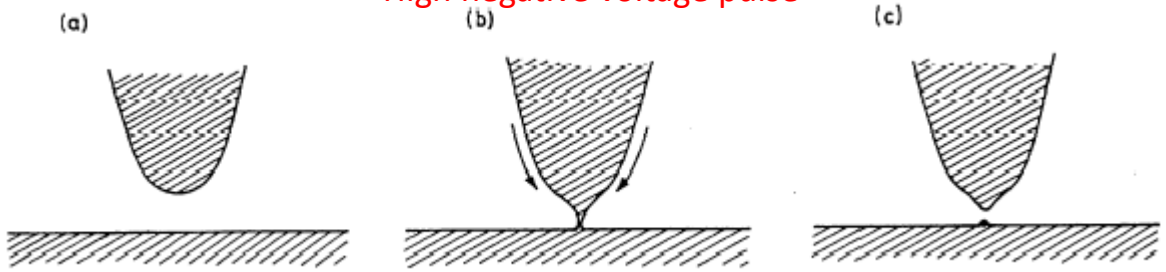
Nano Au cluster created by Au STM tip/Au (in air)





Phys. Rev. Lett. 65, 2418 (1990)

High negative voltage pulse



Melt-then-contact Mechanism

Nucleation and Epitaxial Growth

Fe/Fe(100)

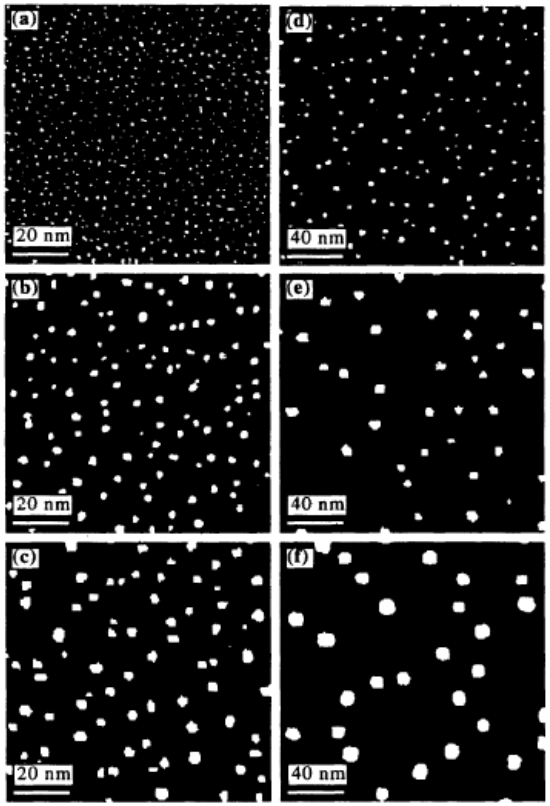


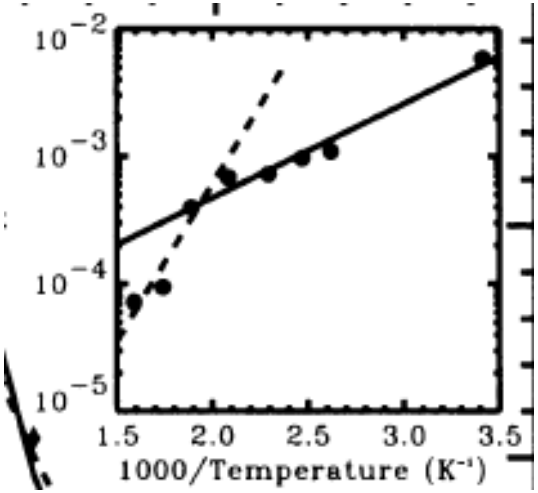
FIG. 1. STM images, 100×100 nm^2, of single-layer Fe islands (white) on the Fe(001) surface (black). Sample temperatures during growth are (a) 20 °C, (b) 108 °C, (c) 163 °C, (d) 256 °C, (e) 301 °C, and (f) 356 °C. Fe was deposited for a fixed time for all measurements with a flux of $1.4\pm0.3\times10^{13}$ atoms cm^{-2} s^{-1}, yielding a coverage of 0.07 ± 0.016 ML (1 ML$=1.214\times10^{15}$ atoms cm^{-2}).

Phys. Rev. B 49, 8522 (1994)

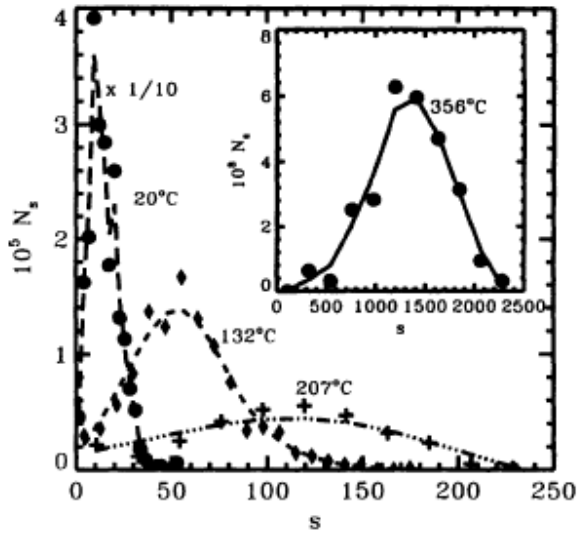
$$N\sim\eta(\Theta)(r/\nu)^{\chi}\exp[\chi(E_d+E_i/i)/k_BT]\ ,$$

E_d : activation energy

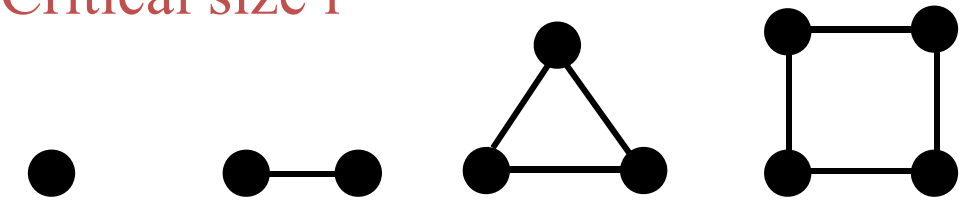
E_i : binding energy of critical size i



i ➡ number of atoms to form stable nucleation



Critical size i



i=0 monomer i=1 dimer i=2 trimer i=3 tetramer

Scaling theory

$$Ns = \theta S^{-2} f_i(s/S)$$

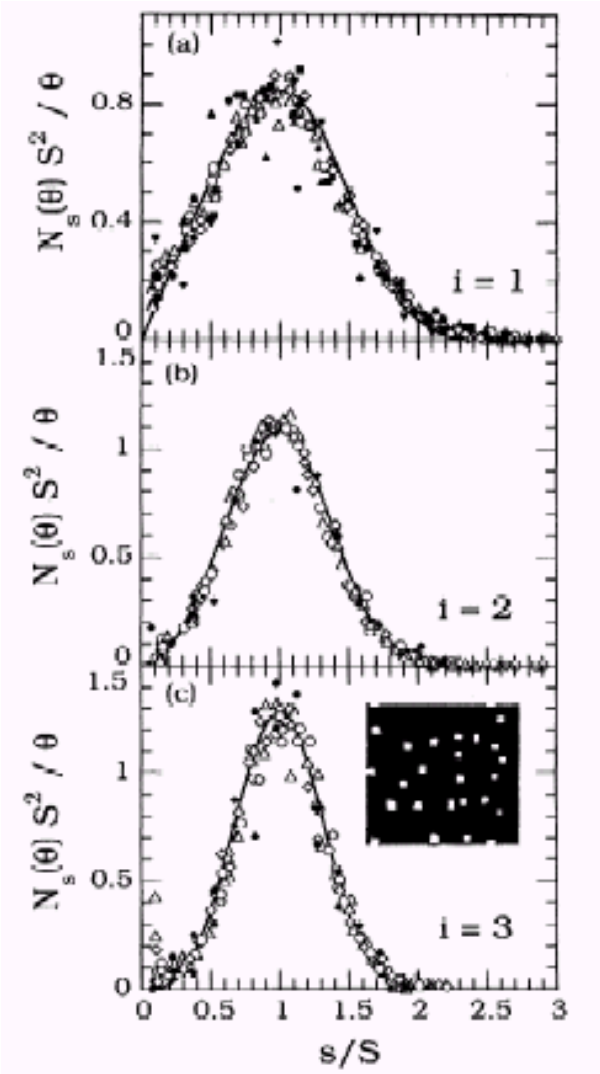
Ns : island density at size s

θ : coverage

S : average island size

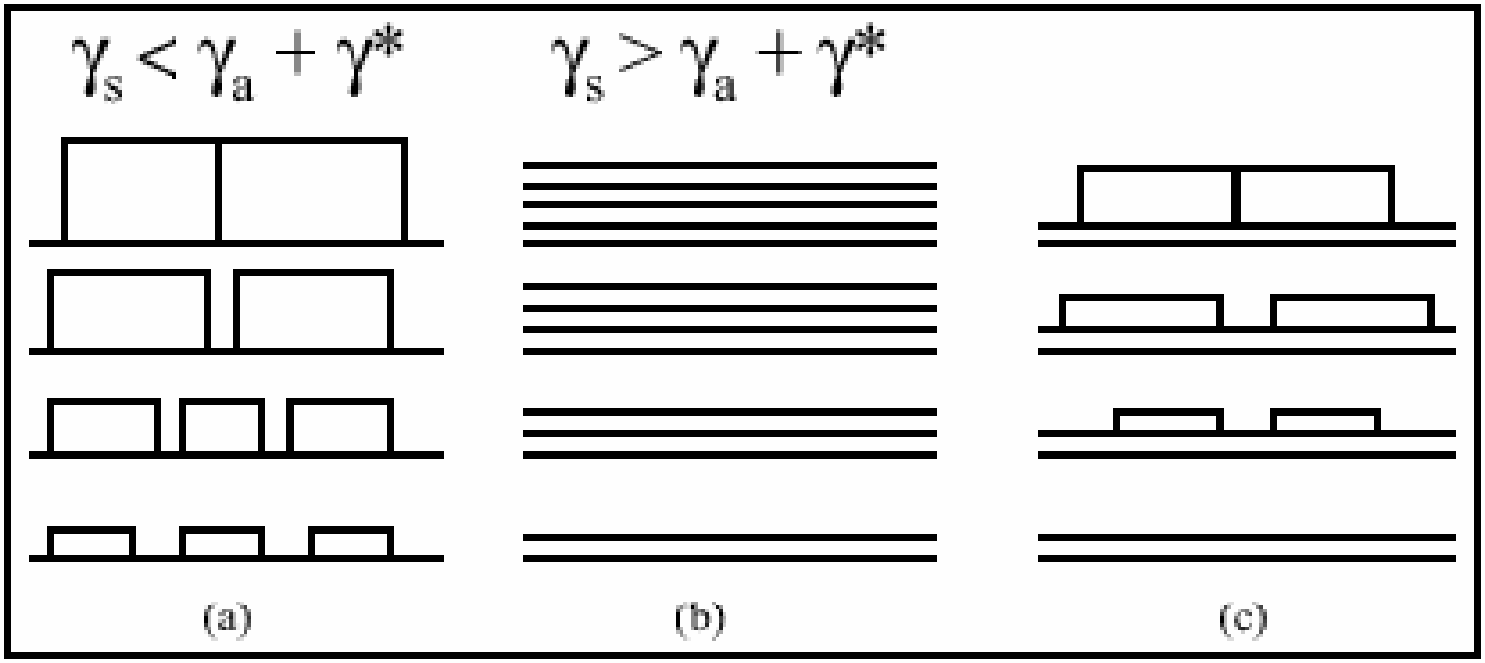
$$Ns\, S^2/\, \theta = f_i(s/S)$$

$f_i(s/S)$ is an universal Scaling function at critical size i



J. G. Amar and F. Family
Phys. Rev. Lett. **74**, 2066 (1995)

Epitaxial Growth Mode



Volmer-Weber (VW)

Frank-van-der-Merwe (FM)

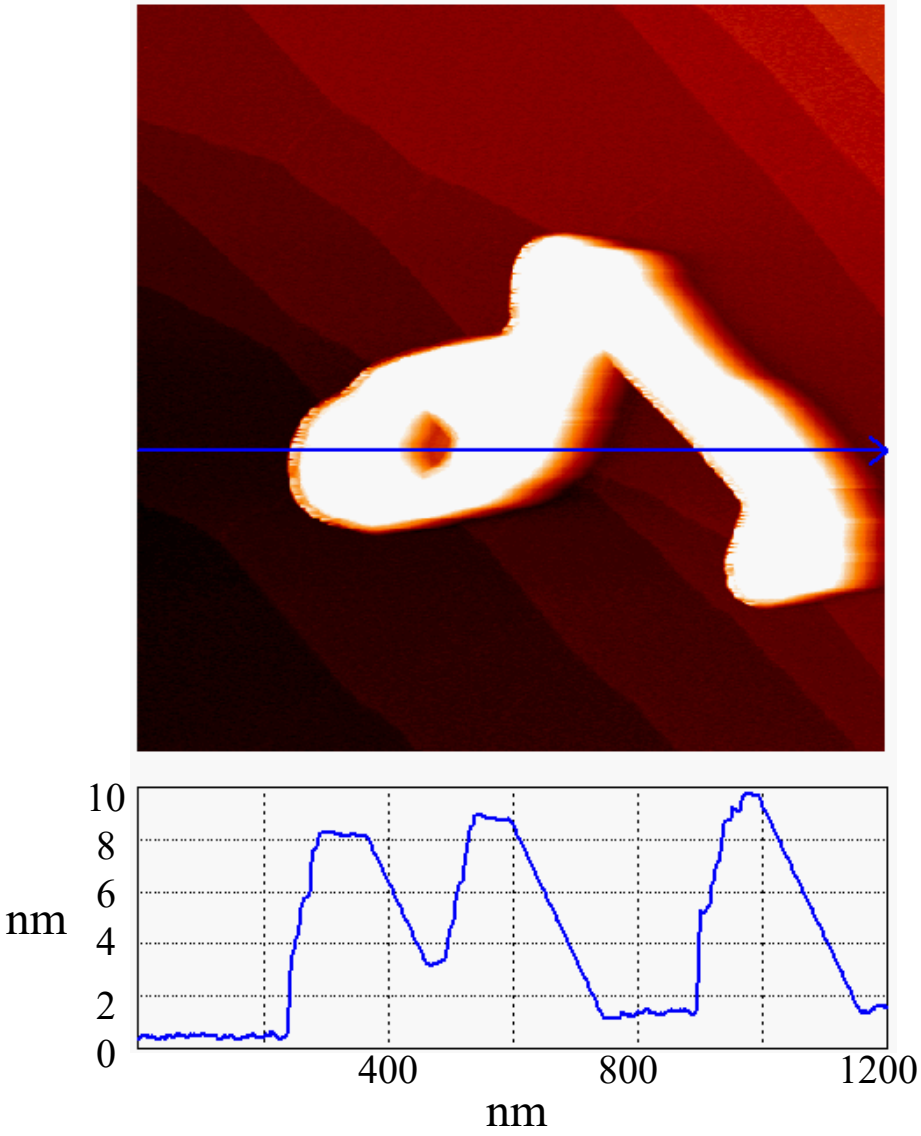
Stranski-Krastonov (SK)

γ_s : surface free energy of substrate

γ_a : surface free energy of adsorbate

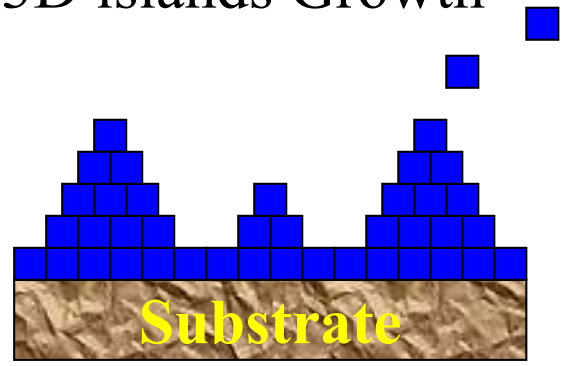
γ^* : interfacial free energy

Pb/Si(111) at RT



Stranski-Krastanov growth mode

3D islands Growth

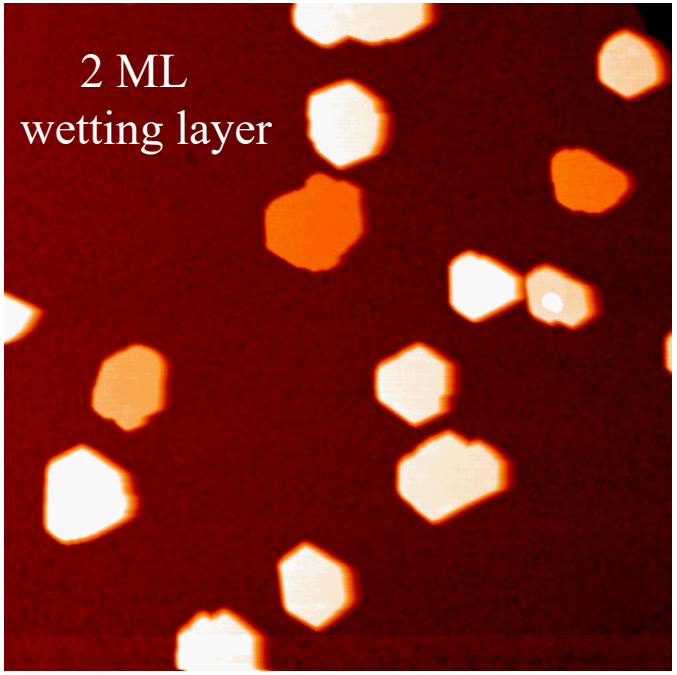


Layer + Island (SK) Growth

The Growth of 2D Pb islands on Si(111)7×7 surfaces at Low Temperature

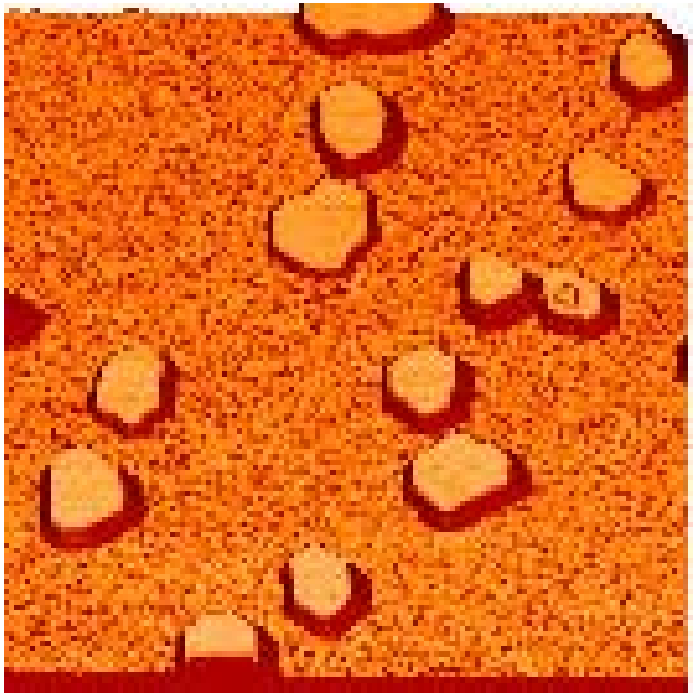
T=208K, θ = 3.2 ML Pb

Topography

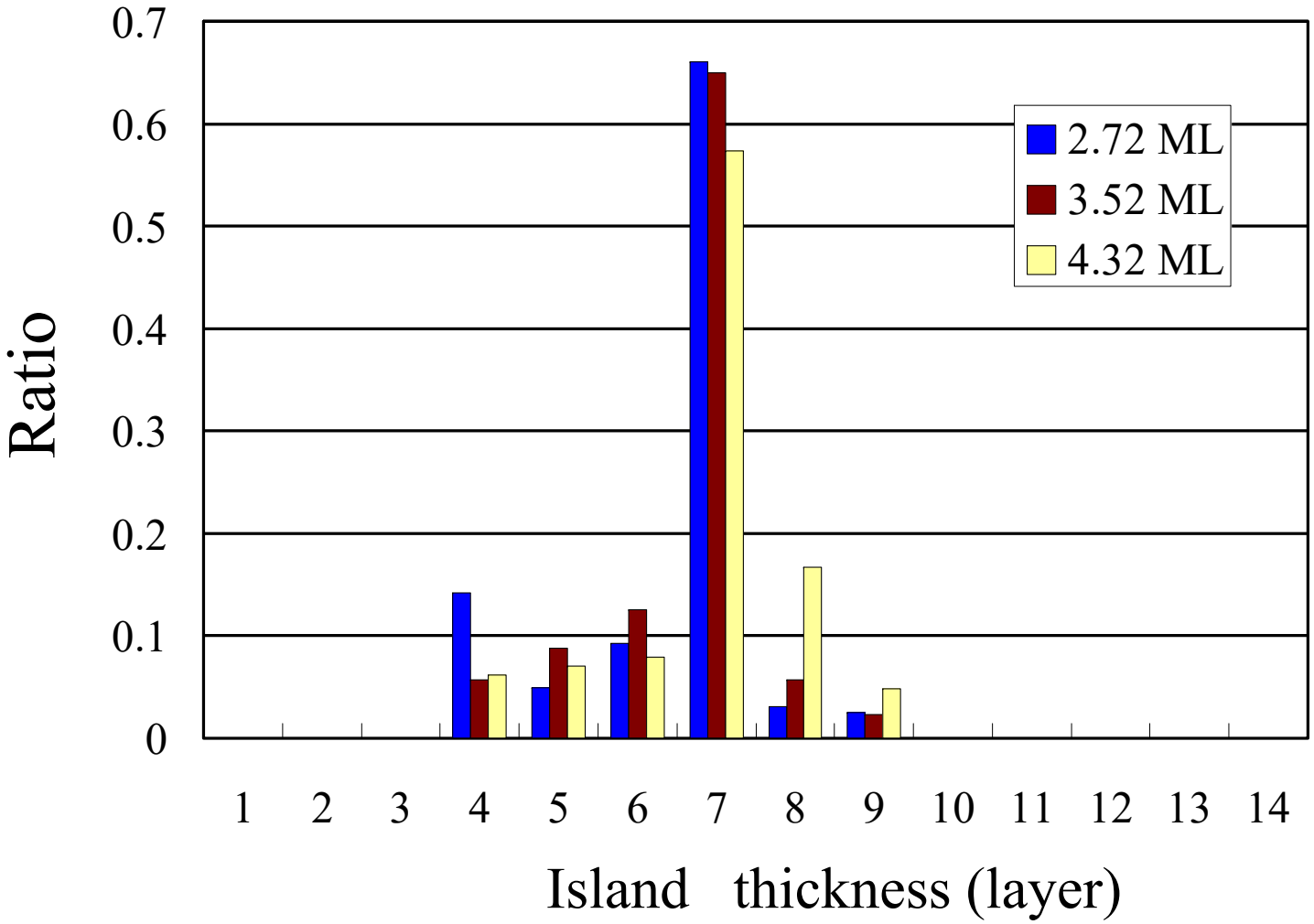


100 nm

3D image of topography



Phys. Rev. Lett. 86, 5116 (2001)

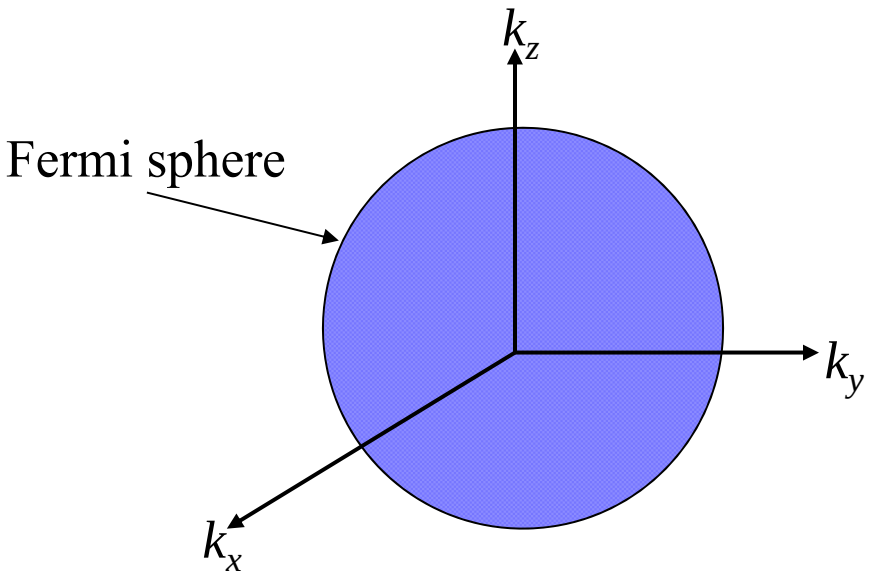

0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
Ratio
2.72 ML
3.52 ML
4.32 ML
1
2
3
4
5
6
7
8
9
10
11
12
13
14
Island thickness (layer)

Quantum Size Effect-Driven Epitaxial Growth

λ = de Broglie wavelength of electron

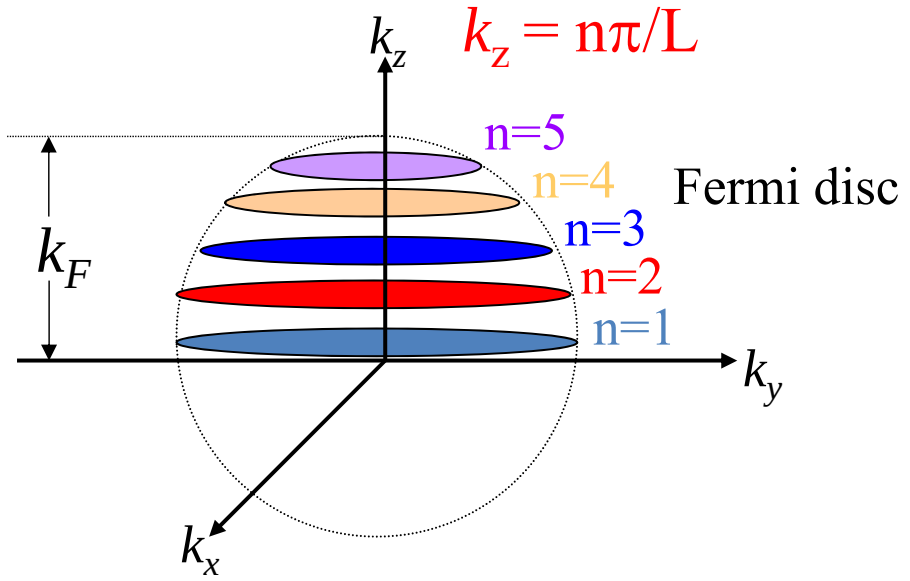
L>> λ

Substrate

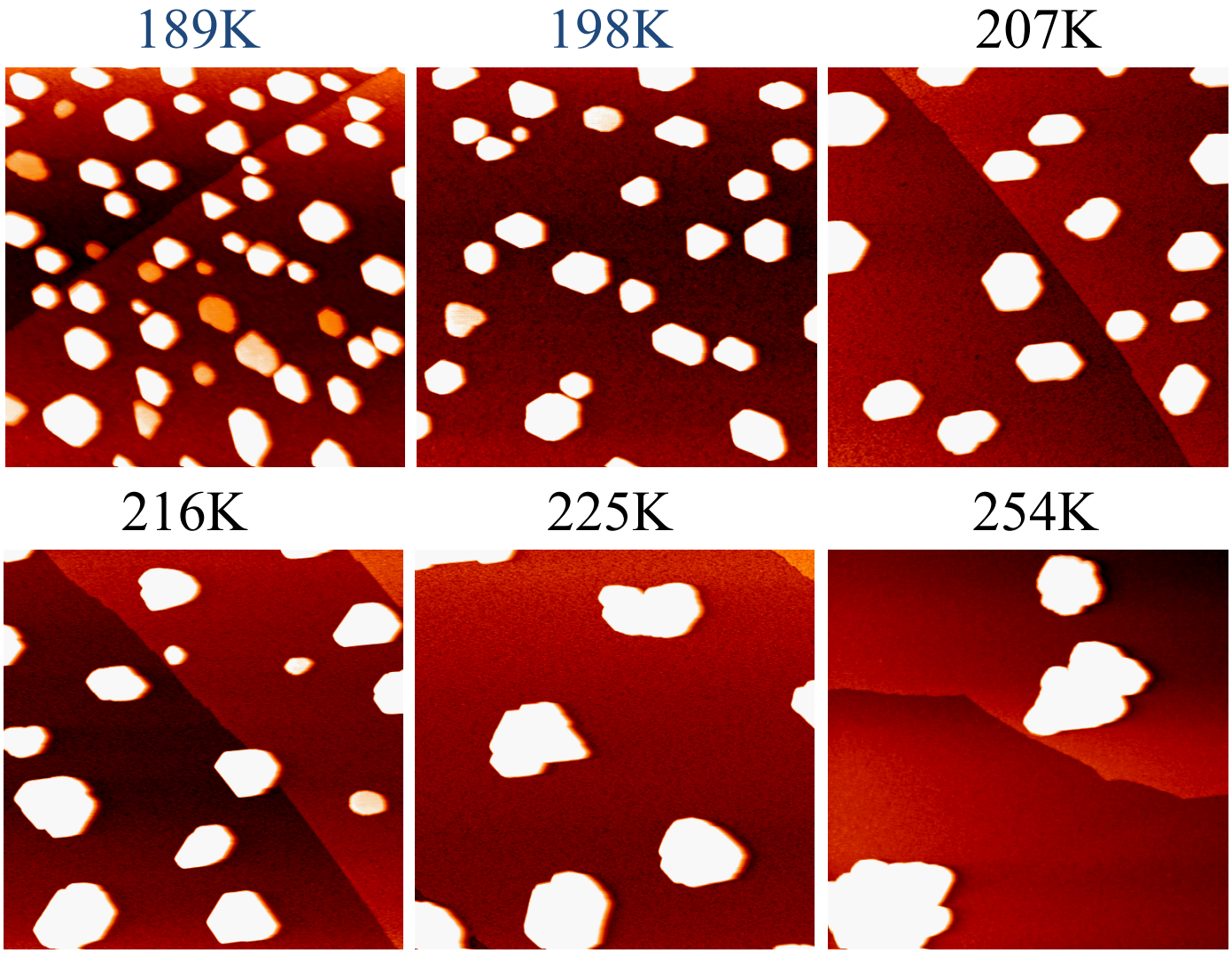


L≅ λ

Substrate



Phys. Rev. Lett. 80, 5381 (1998)



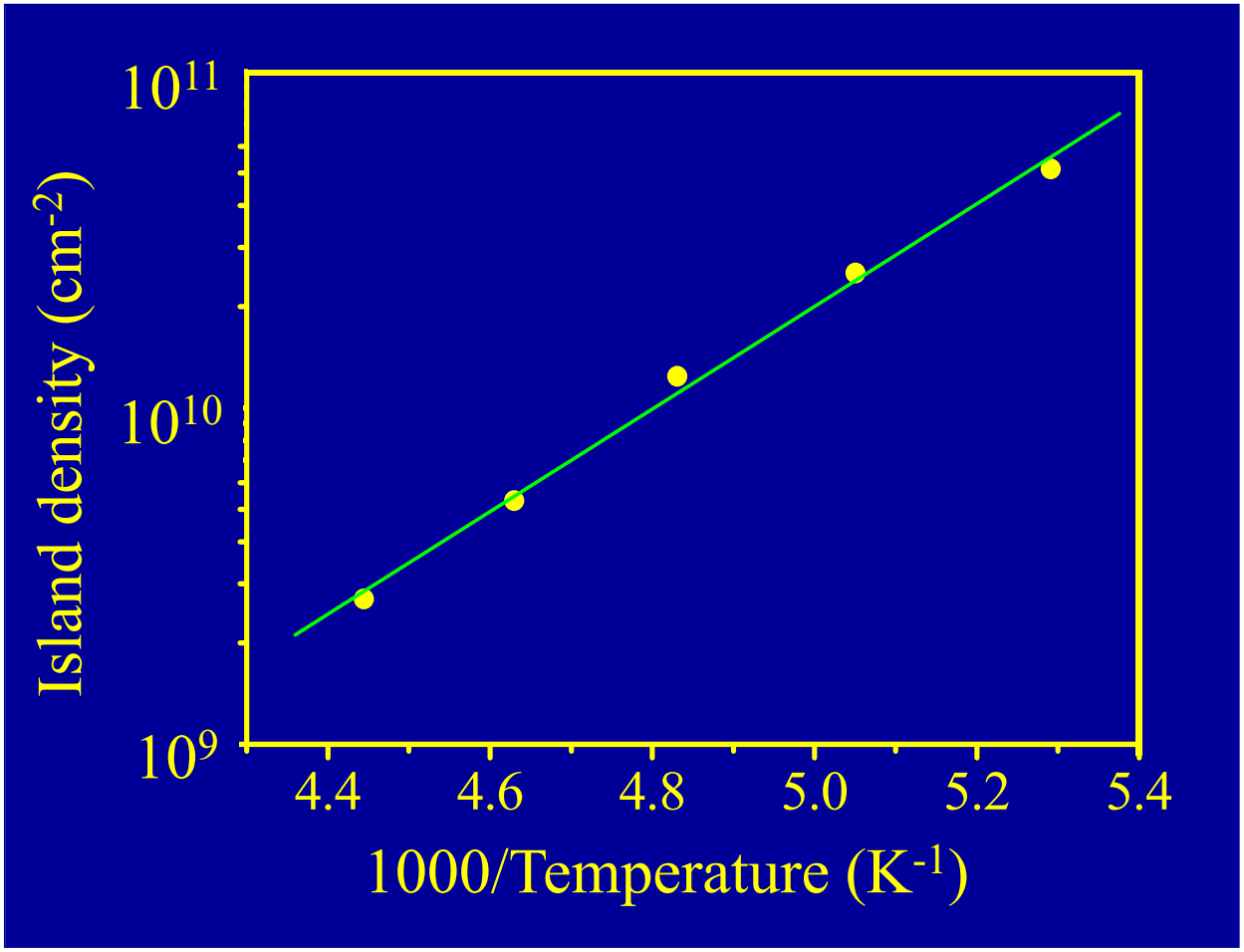
$N \sim \exp[(iE_d+E_i)/(i+2)k_BT]$

E_d : the activation for diffusion

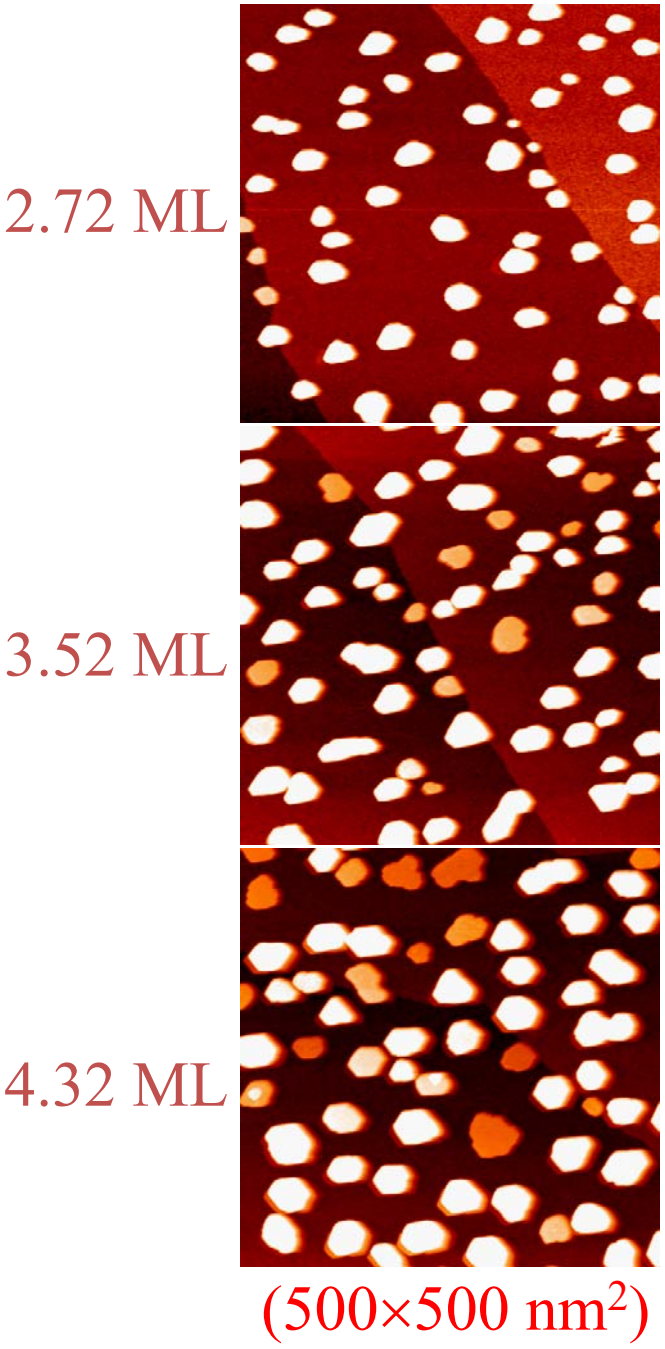
E_i : the binding energy for the critical size i

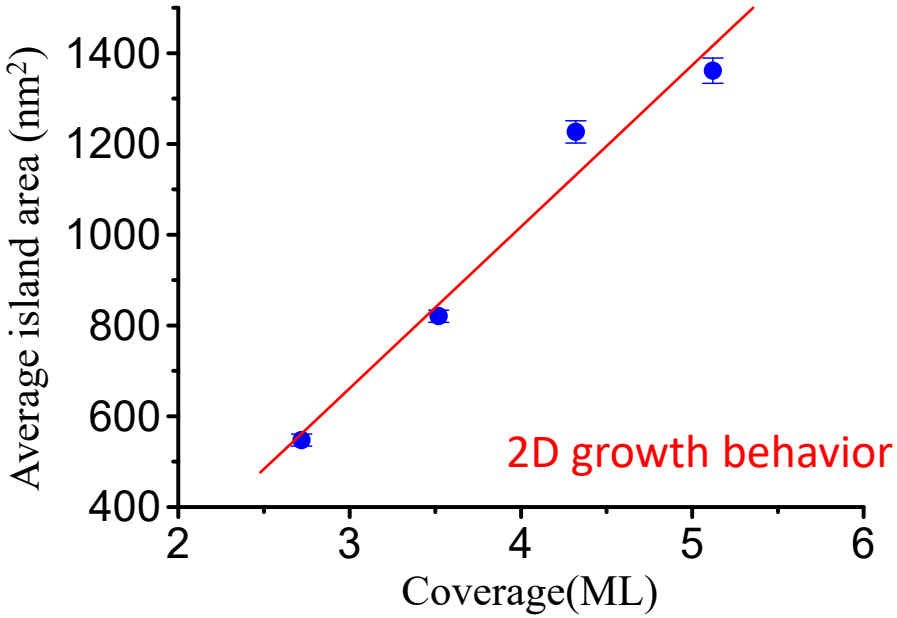
Phys. Rev. B 65, 245401 (2002)

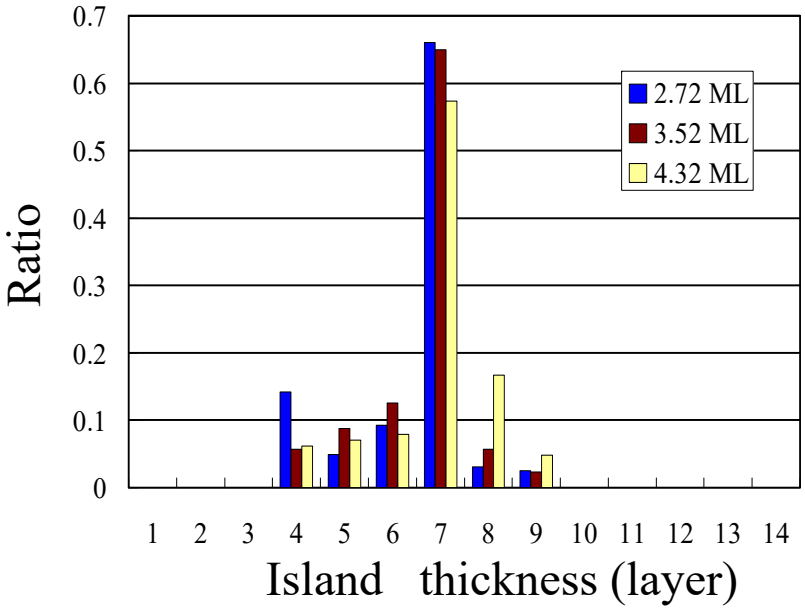
Arrhenius Plot : Island density vs. 1/Temperature



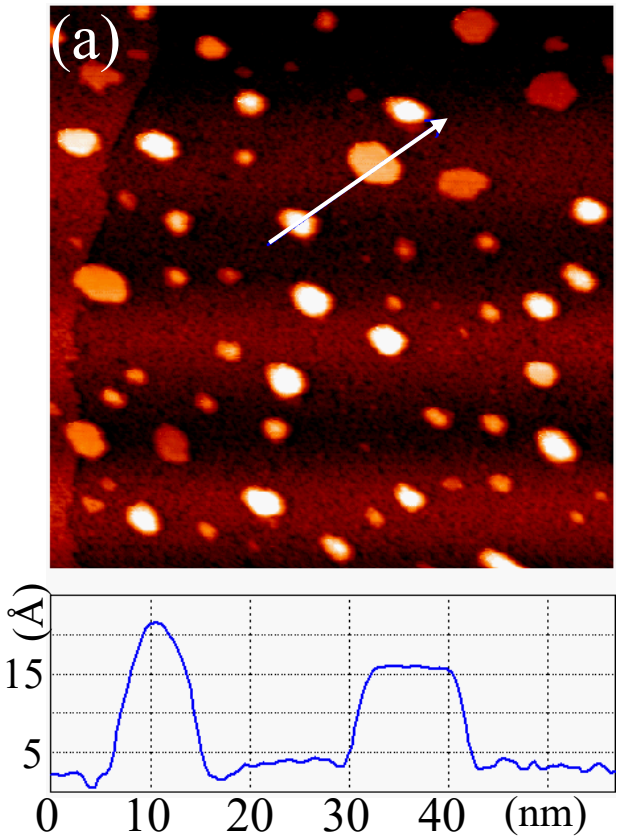
- The nucleation and the quantum size effect are two independent factors in the formation of an island, the former results in the creation of an island and the latter determines the thickness of the created island.


2.72 ML
3.52 ML
4.32 ML
(500×500 nm²)

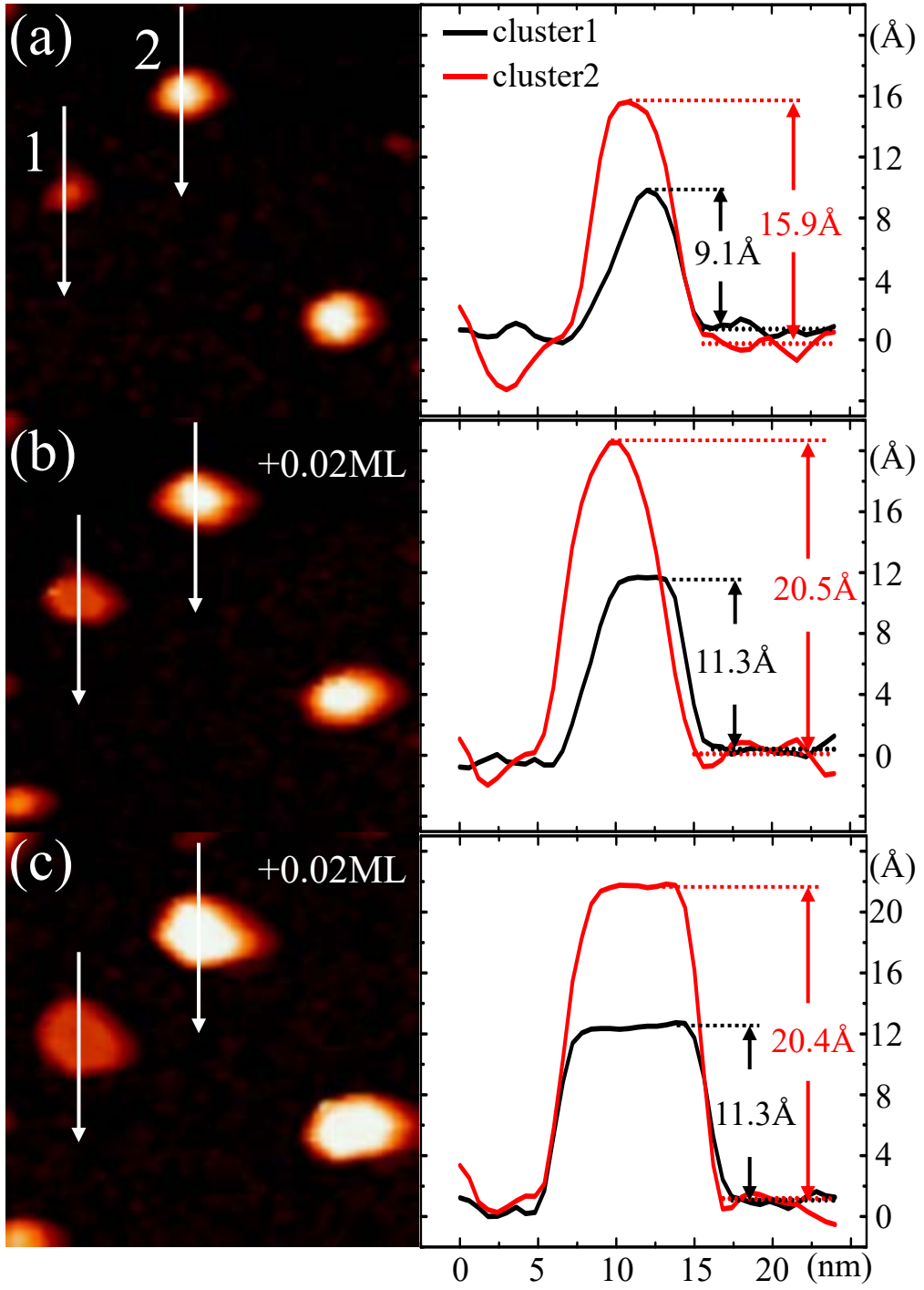

Average island area (nm²)
1400
1200
1000
800
600
400
2
3
4
5
6
Coverage(ML)
2D growth behavior

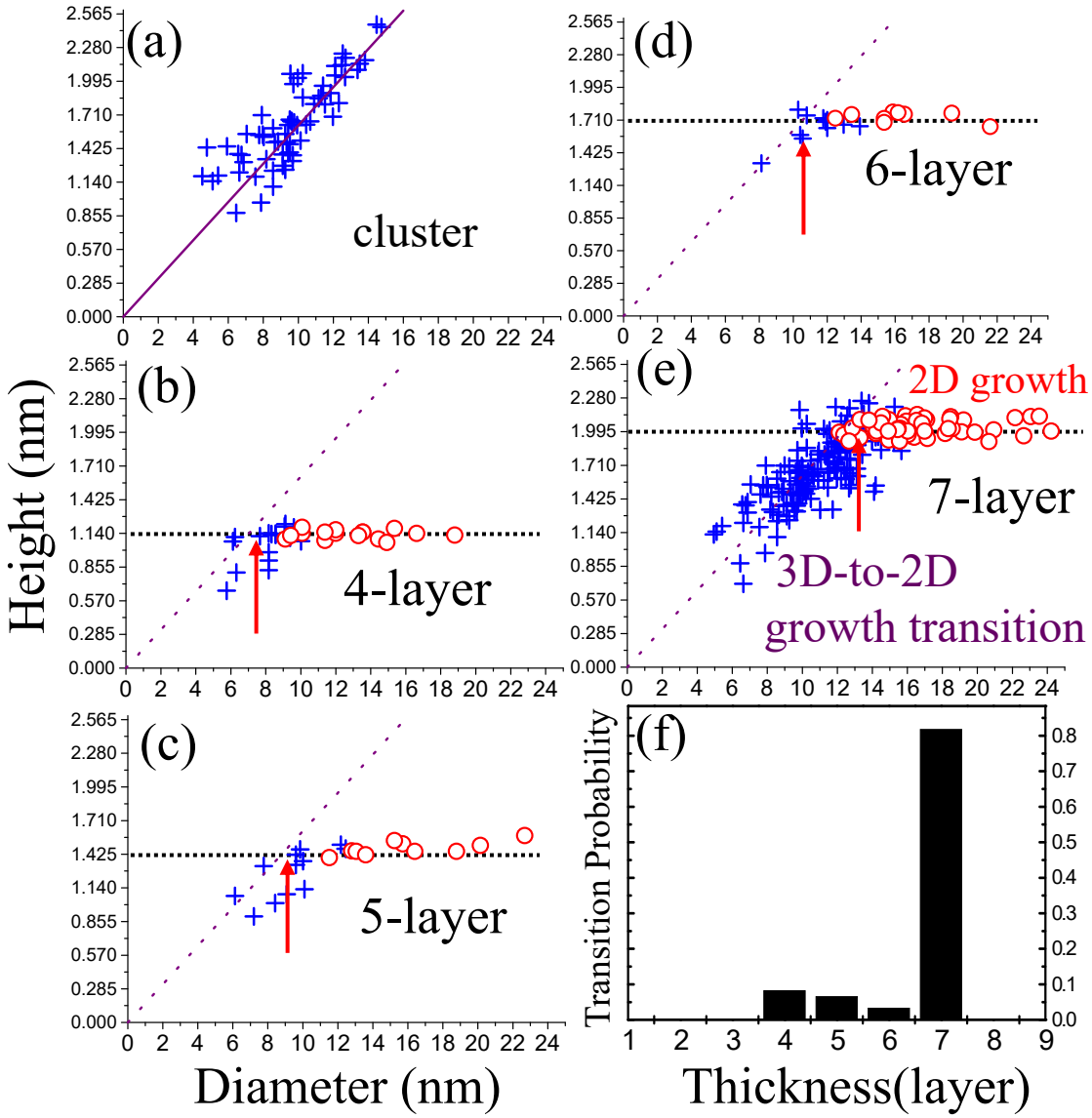

Ratio
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
1 2 3 4 5 6 7 8 9 10 11 12 13 14
Island thickness (layer)
2.72 ML
3.52 ML
4.32 ML

2.3 ML, 170 K



Phys. Rev. B 68, 033405 (2003)



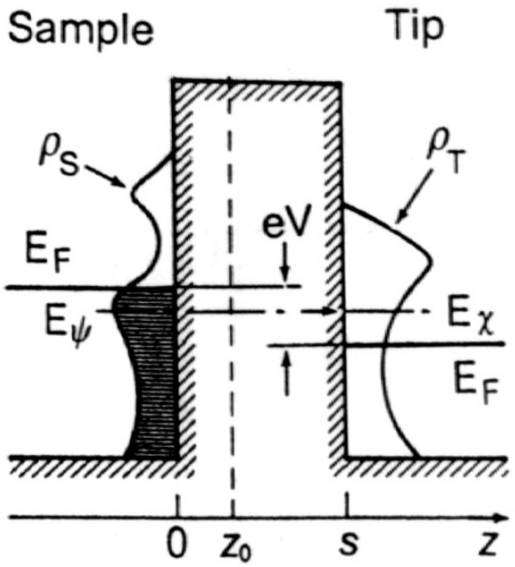


- Growth transition induced by the quantum size effect
- Independent transition pathway:

  N-layer thickness island is transformed from N-layer height cluster
- Identical cluster can be of different electronic structure (quantum size effect).

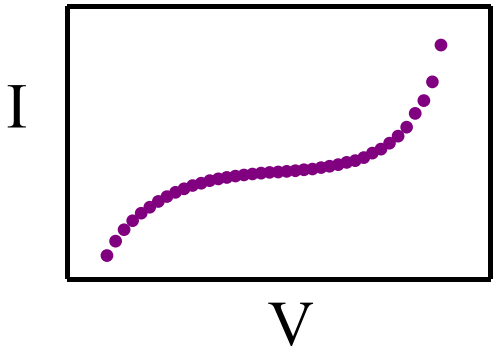
Phys. Rev. B 71, 073304 (2005)

Scanning Tunneling Spectroscopy (STS)



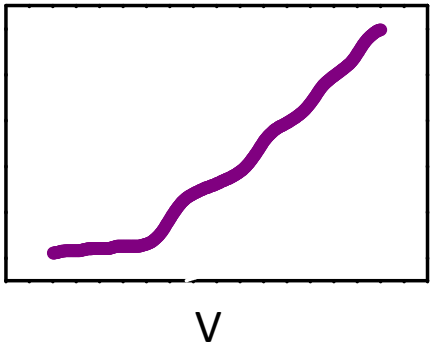
(feedback off)

I-V spectroscopy



(feedback on)

Z-V spectroscopy



$$I \propto \int_0^{eV} \rho_s(E_F\text{-}eV+\varepsilon)\, \rho_T(E_F+\varepsilon) d\,\varepsilon$$

ρ_T is constant

$\Rightarrow dI/dV \propto \rho_s(E_F\text{-}eV)$

Numerical differentiation

Lock-in technique

Lock-in technique

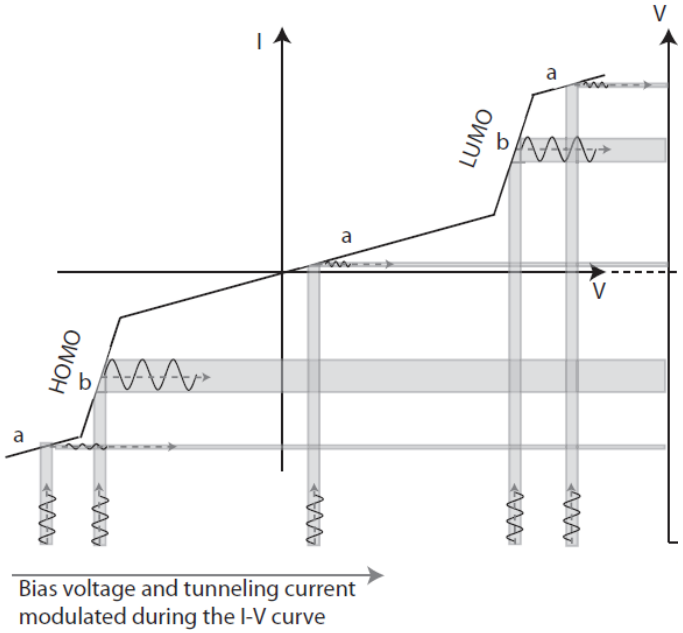
$V_{bias}+V_{mod}\sin(\omega t)$ ω: 500-5000 Hz

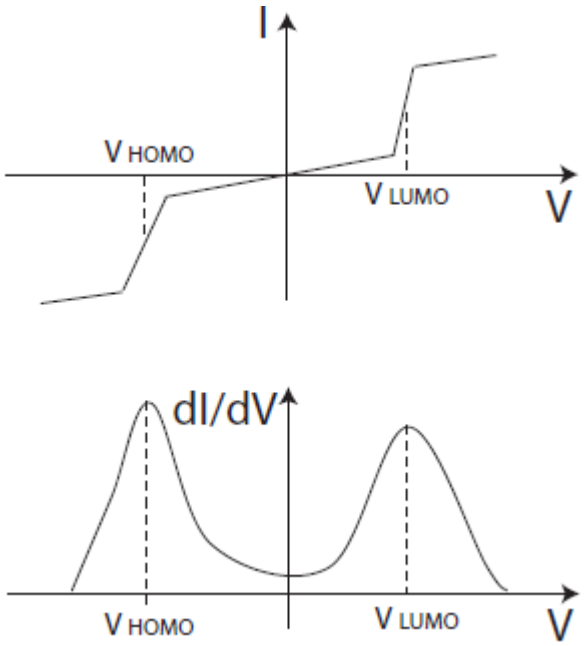
$$I(V_{bias}+V_{mod}sin(\omega t)) \sim I(V_{bias})+\frac{dI(V_{bias})}{dV}\cdot V_{mod}sin(\omega t)$$

modulation of current

detected by

lock in amplifier

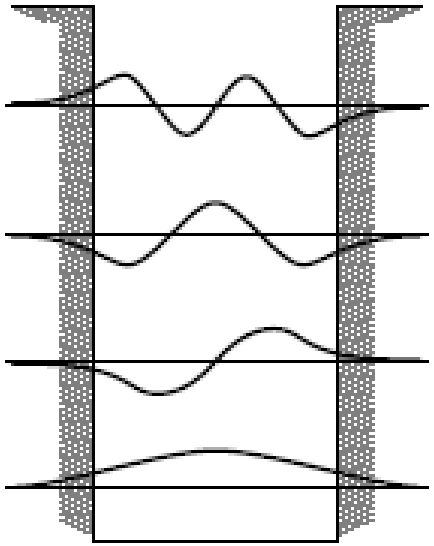




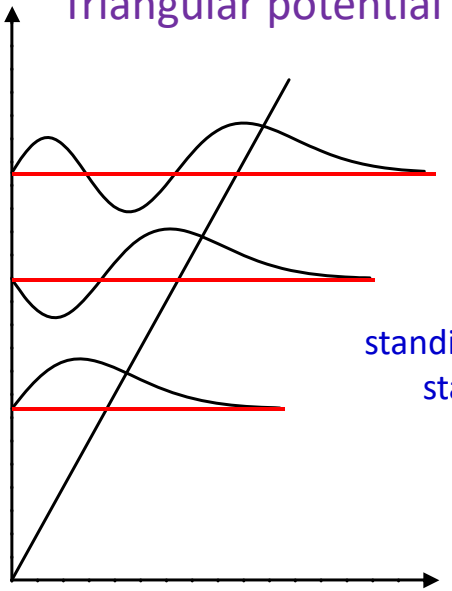
Quantum Confinement Effect

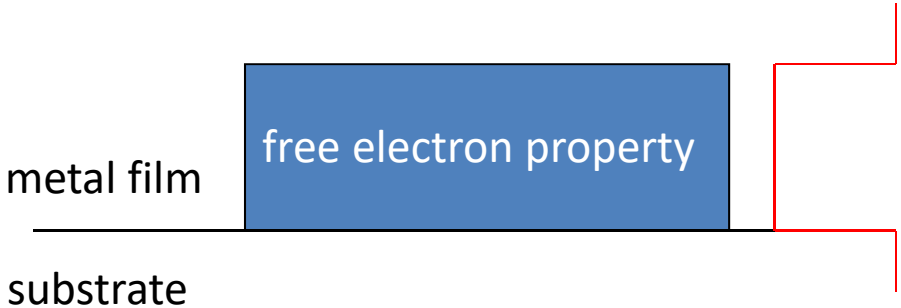
Square potential

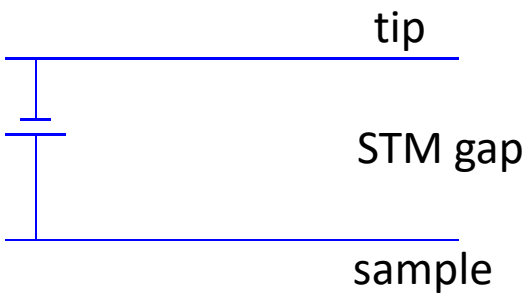
quantum-well states



Triangular potential

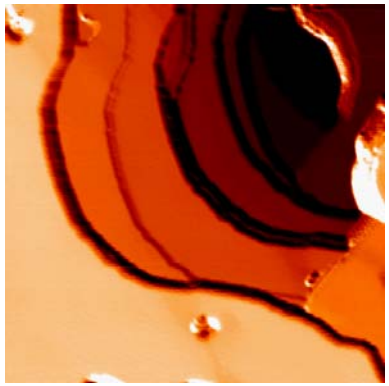


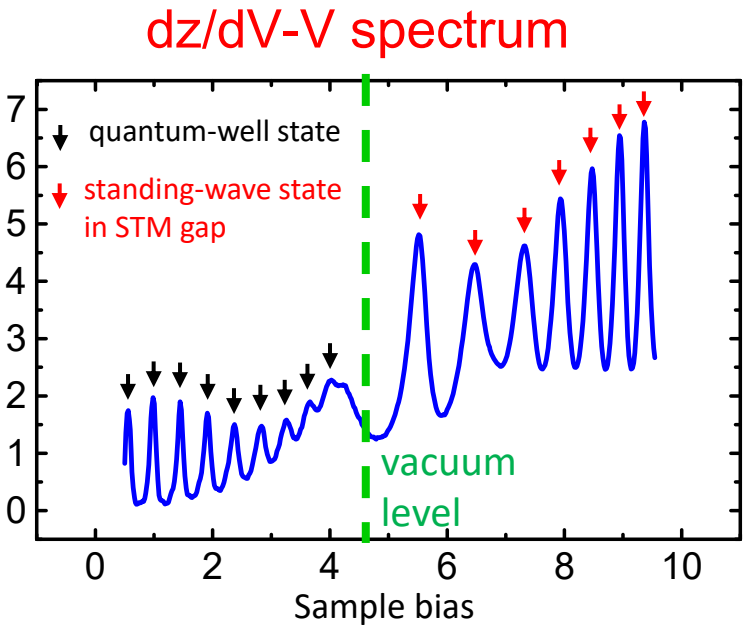


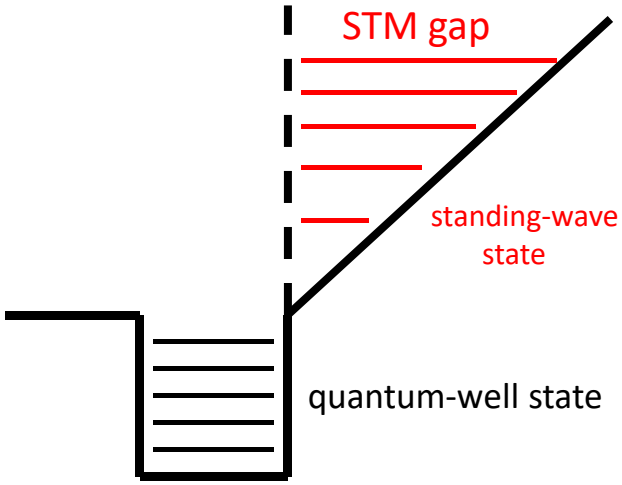


Visualization of quantum confinement effect by STS

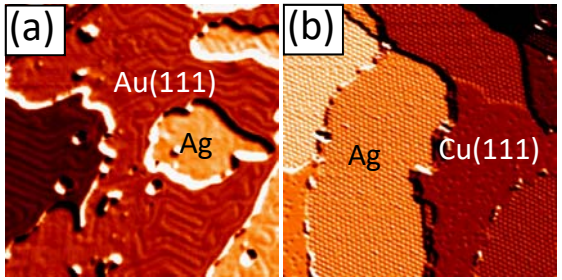
Pb/Cu(111)

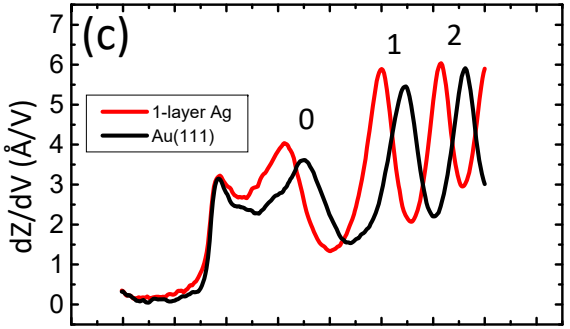


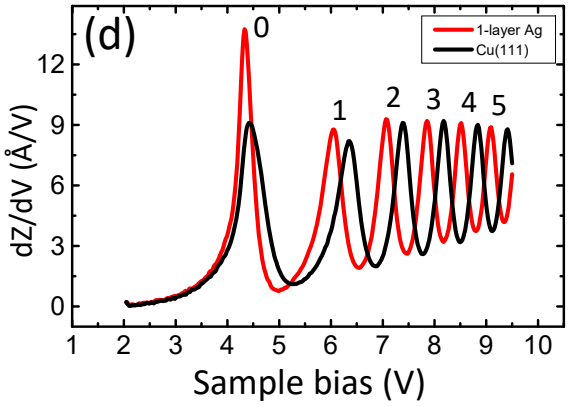


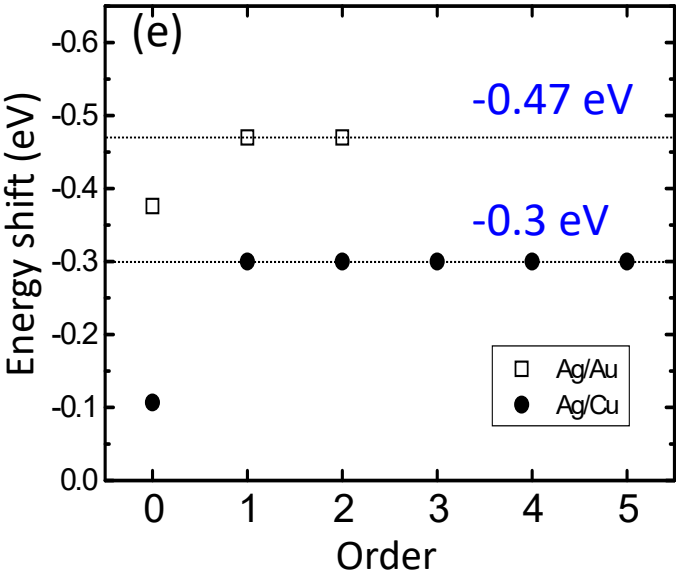


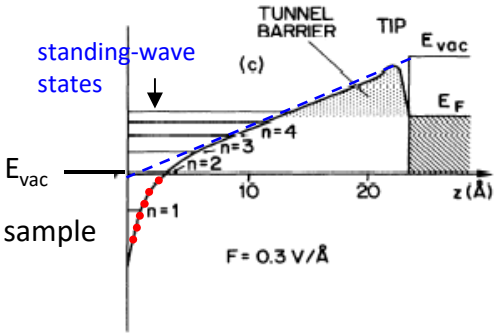
Application of standing-wave state in STM gap on work function measurement of thin metallic film



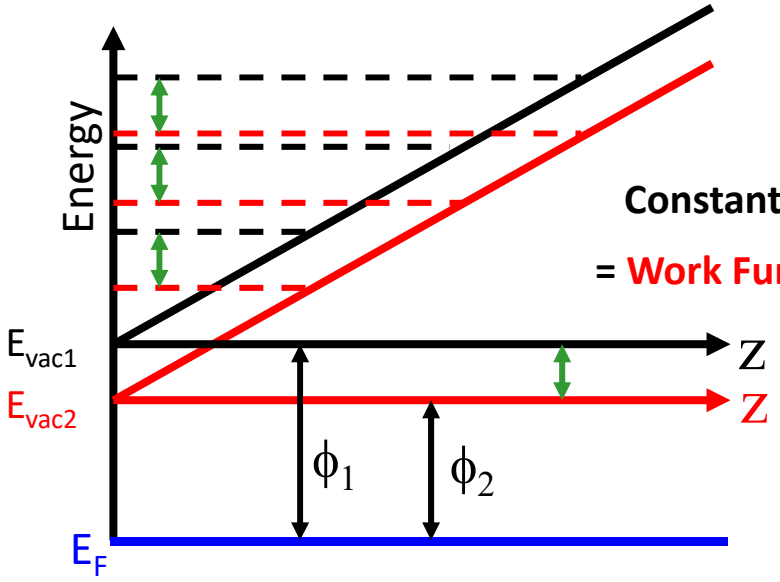








Superposition of image potential and applied potential

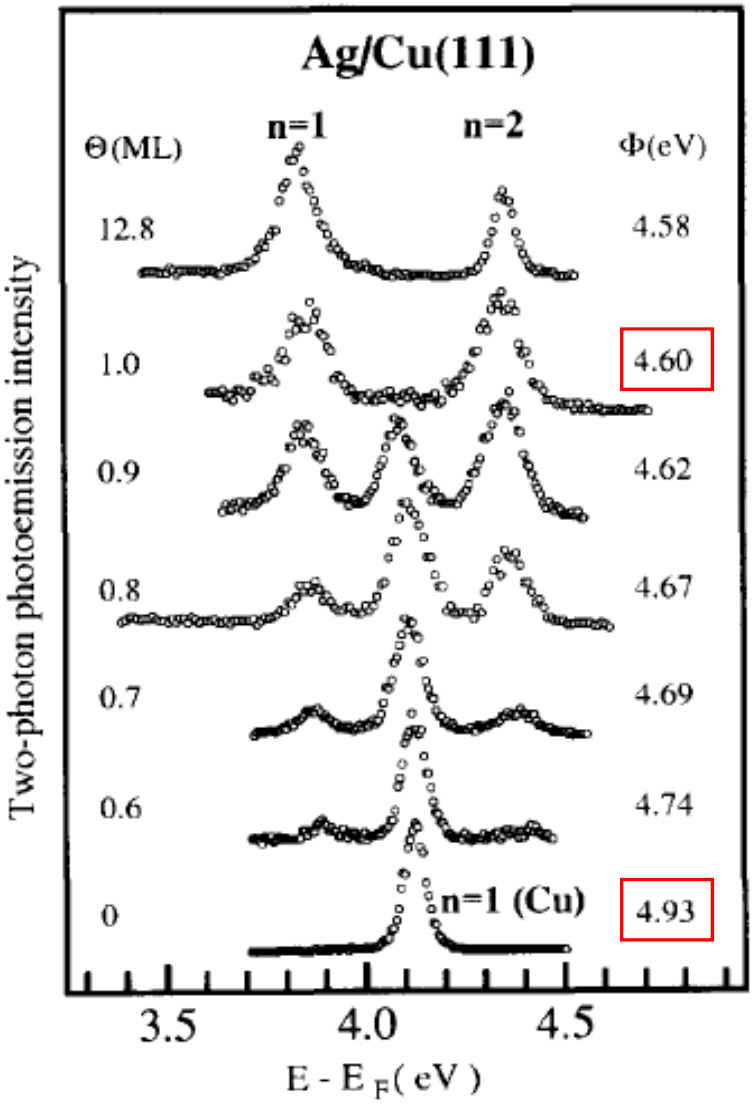


Constant Energy Shift

= Work Function Difference

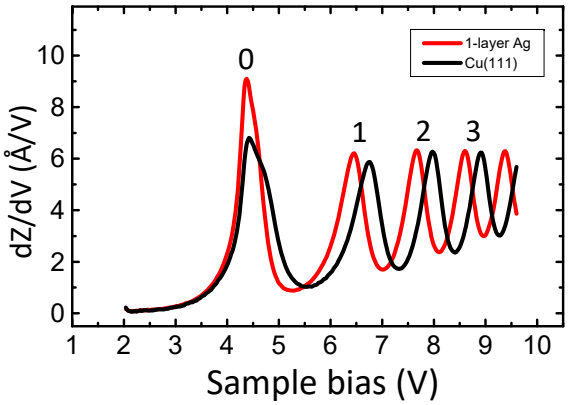
Phys. Rev. Lett. 99, 216103 (2007)

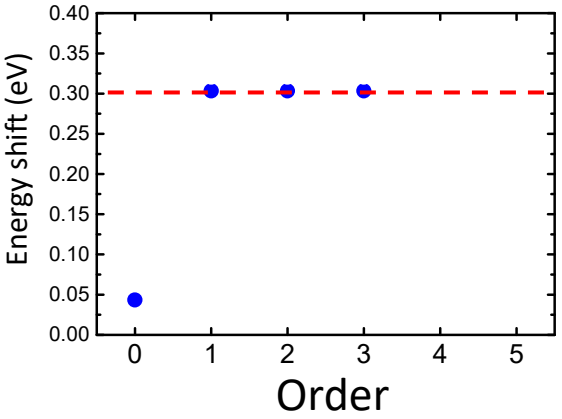
Photoemission (-0.33 eV)



Wallauer et al., Surf. Sci 331, 731 (1995)

Standing-wave states (-0.3 eV)

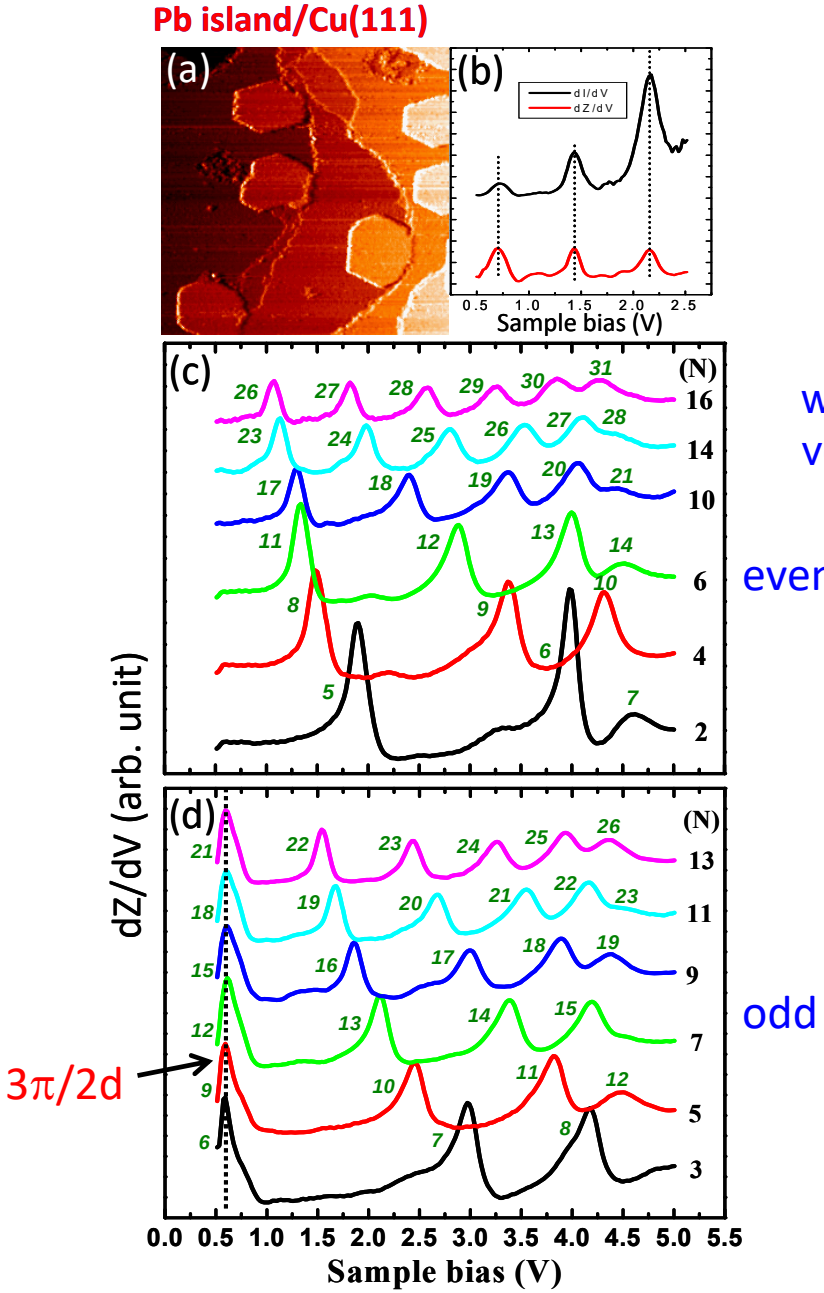




Both techniques are consistent.

Precision can be better than 20 meV.

Phase contribution of image potential on empty quantum well States



even

odd

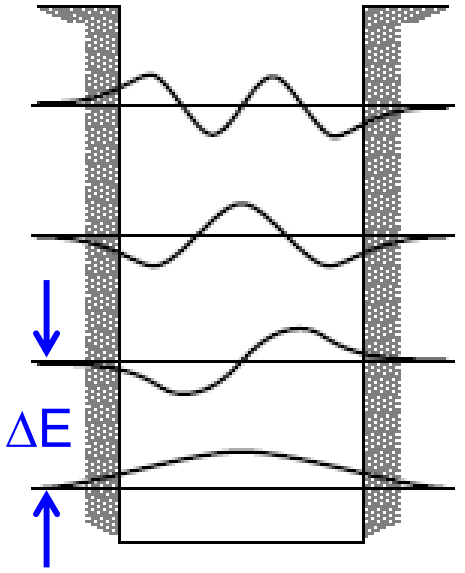
thickness

quantum number

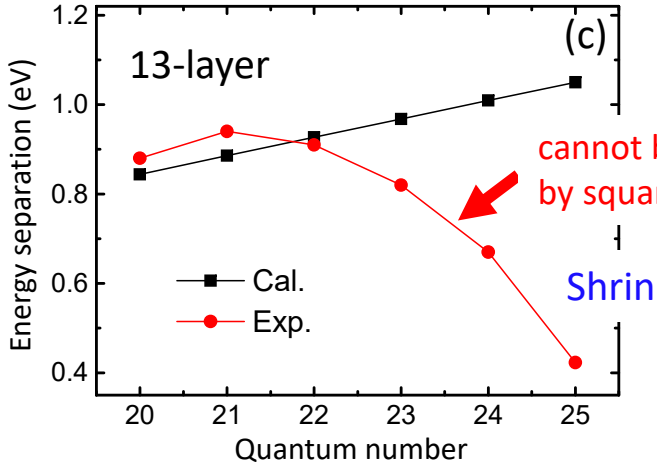
$2k(N+1)d=2n\pi$

wave vector

Interlayer spacing



$$\Delta E = \hbar^2(2n+1)\pi^2/2m^*(N+1)^2d^2$$

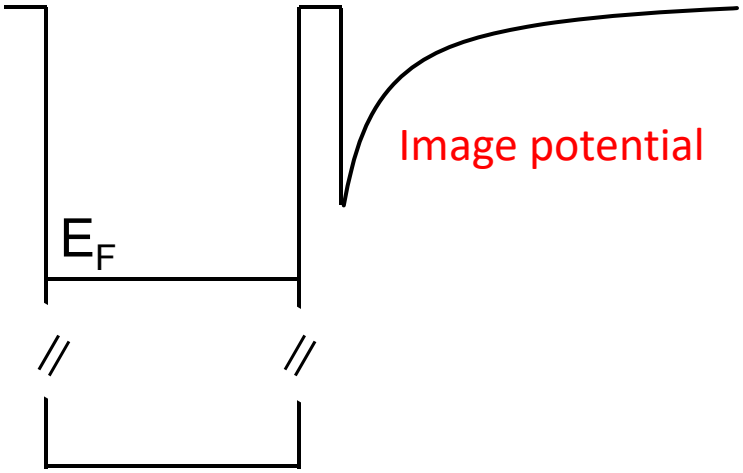


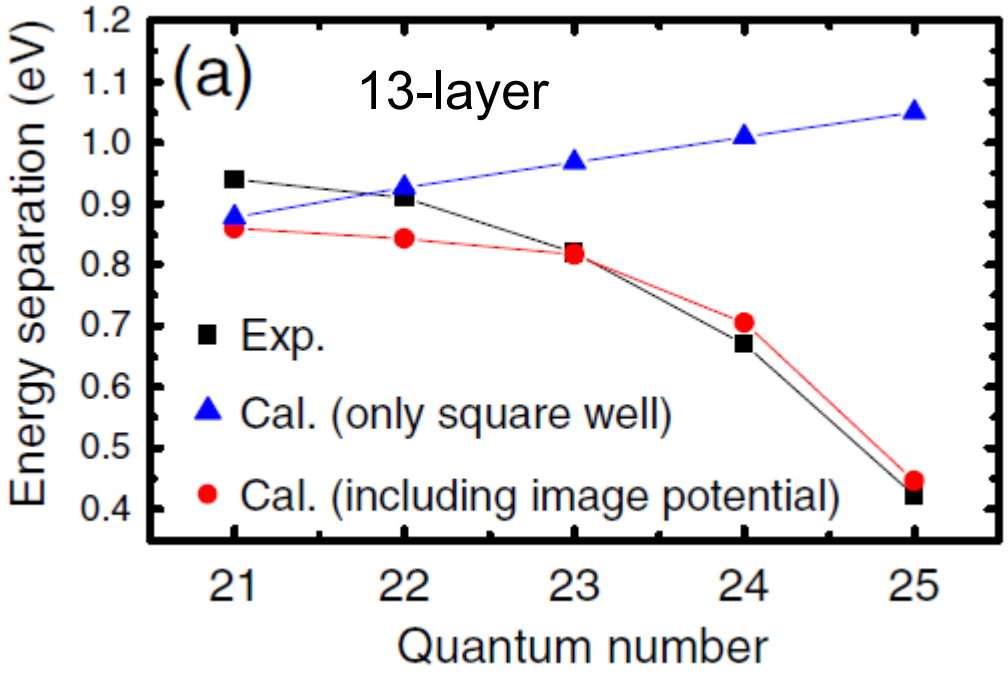
cannot be explained by square potential

Shrinking behavior

Phys. Rev. Lett. 102, 196102 (2009)

Phase contribution of image potential on empty quantum well States





For simple square well:

$$2k(N+1)d=2n\pi$$

Including phase ϕ_B contributed from image potential

$$2k(N+1)d+\phi_B=2n\pi$$

$$\phi_B/\pi=[3.4\ eV/(E_V-E)]^{1/2}-1$$

Echenique et al.
J. Phys. C 11, 2065 (1978).

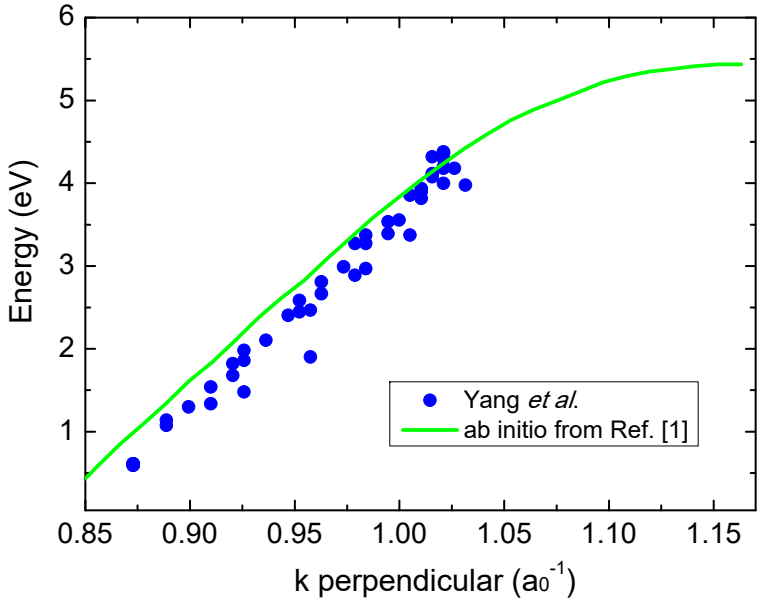
E: energy of quantum well state

E_V: vacuum level

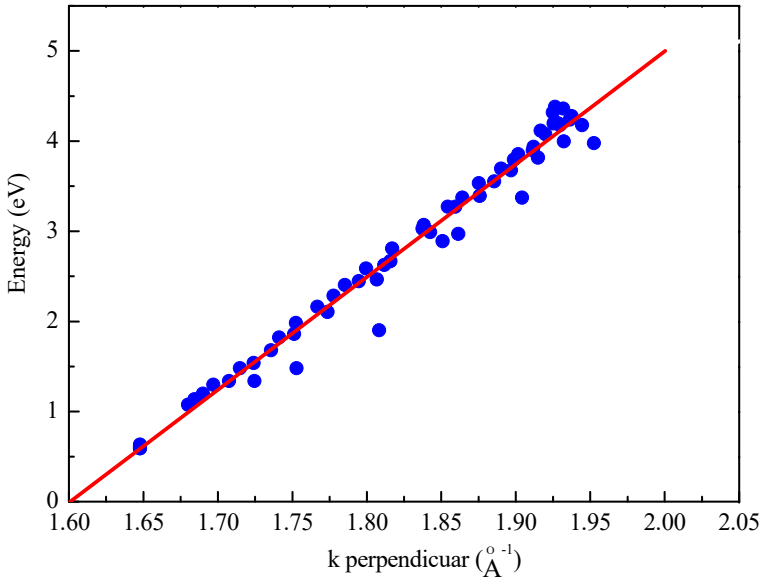
Pb band structure along Γ-L direction: probed with quantum-well states

$$2k(N+1)d+\phi_B=2n\pi$$

$$\phi_B/\pi=[3.4\ eV/(E_V-E)]^{1/2}-1$$



Phys. Rev. Lett. 106, 249602 (2011)

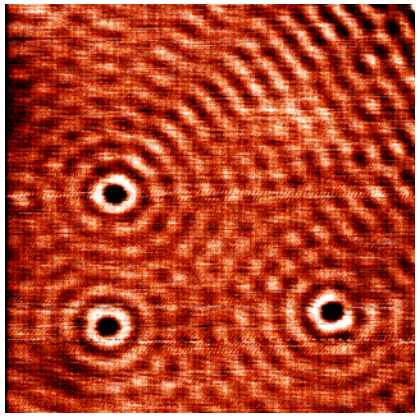


$k_F=1.6\ \AA^{-1}$

angle-resolved photoemission spectroscopy, $k_F=1.598\ \AA^{-1}$ (bulk)

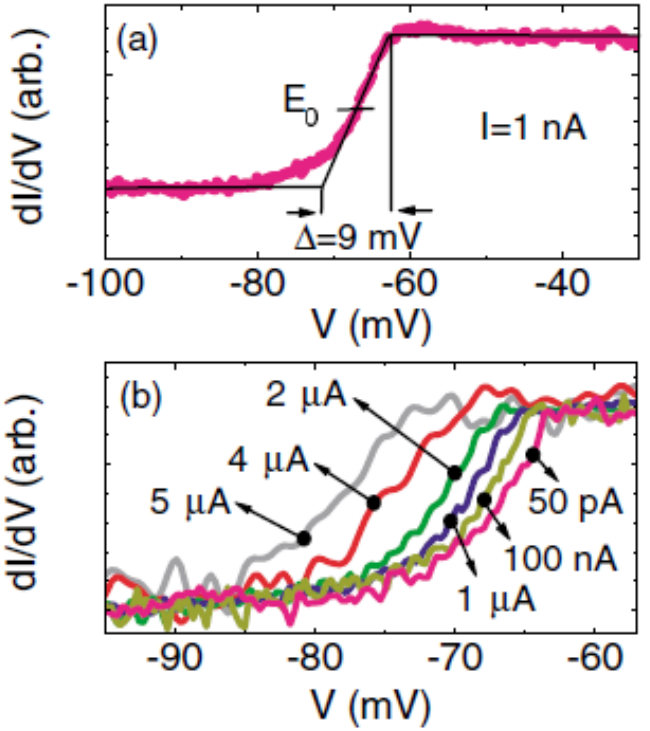
Field effect

surface state on Cu(111)



Electric field in STM junction ~ 0.3 V/Å

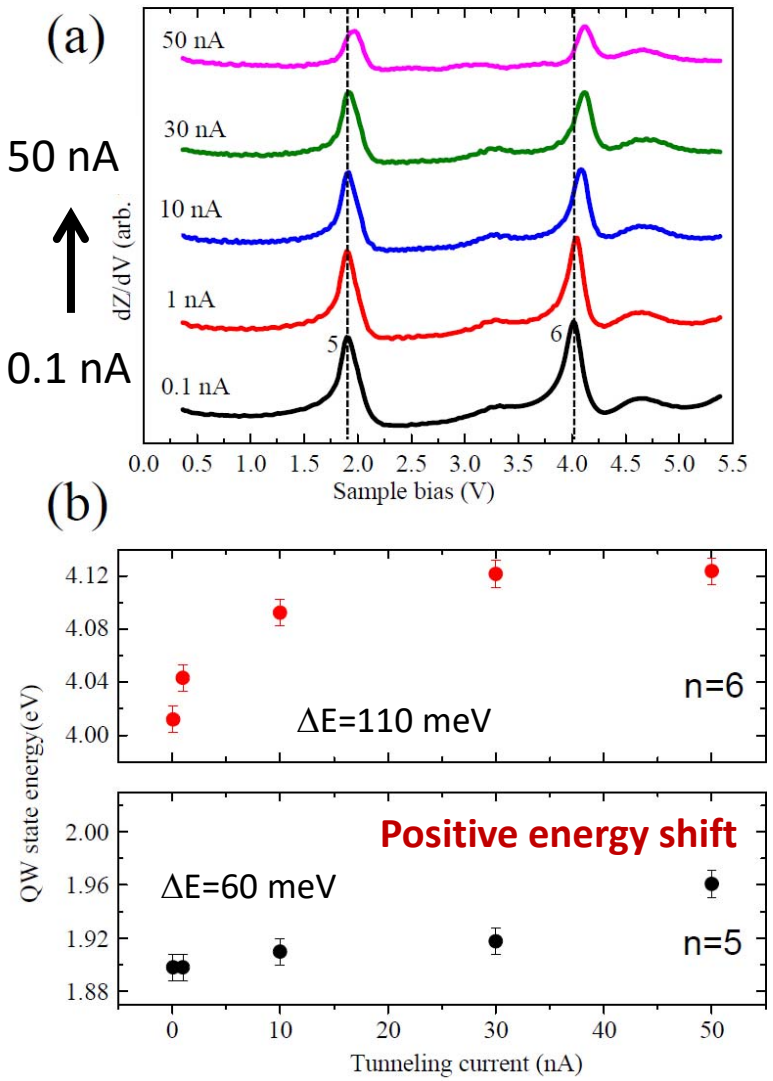
Field-induced energy shift of surface state



Limot et al., Phys. Rev. Lett. 91, 196801 (2003)

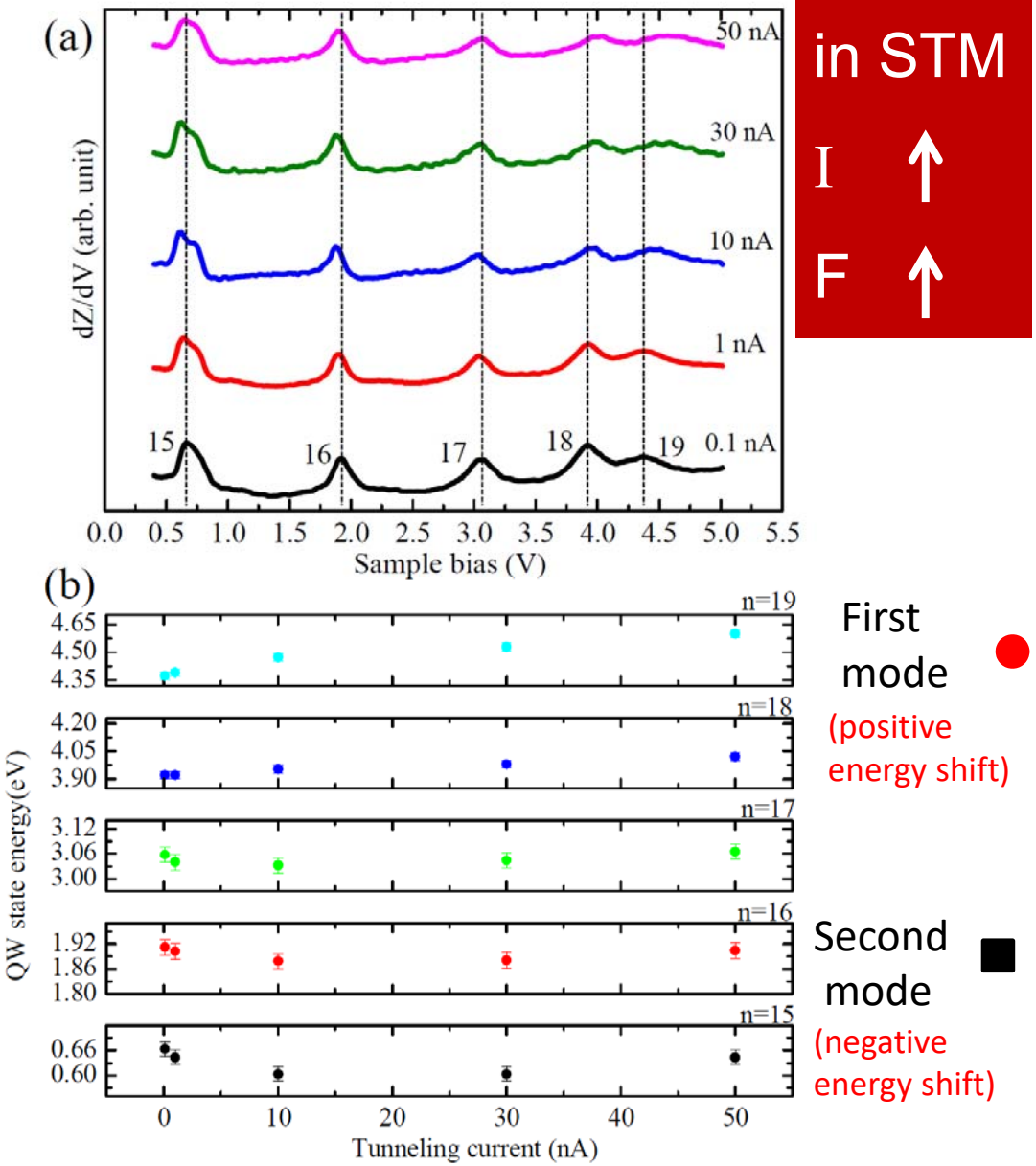
Field-induced energy shift of empty quantum well states in Pb islands on Cu(111)

2-layer



Phys. Rev. Lett. 108, 146102 (2012)

9-layer



in STM

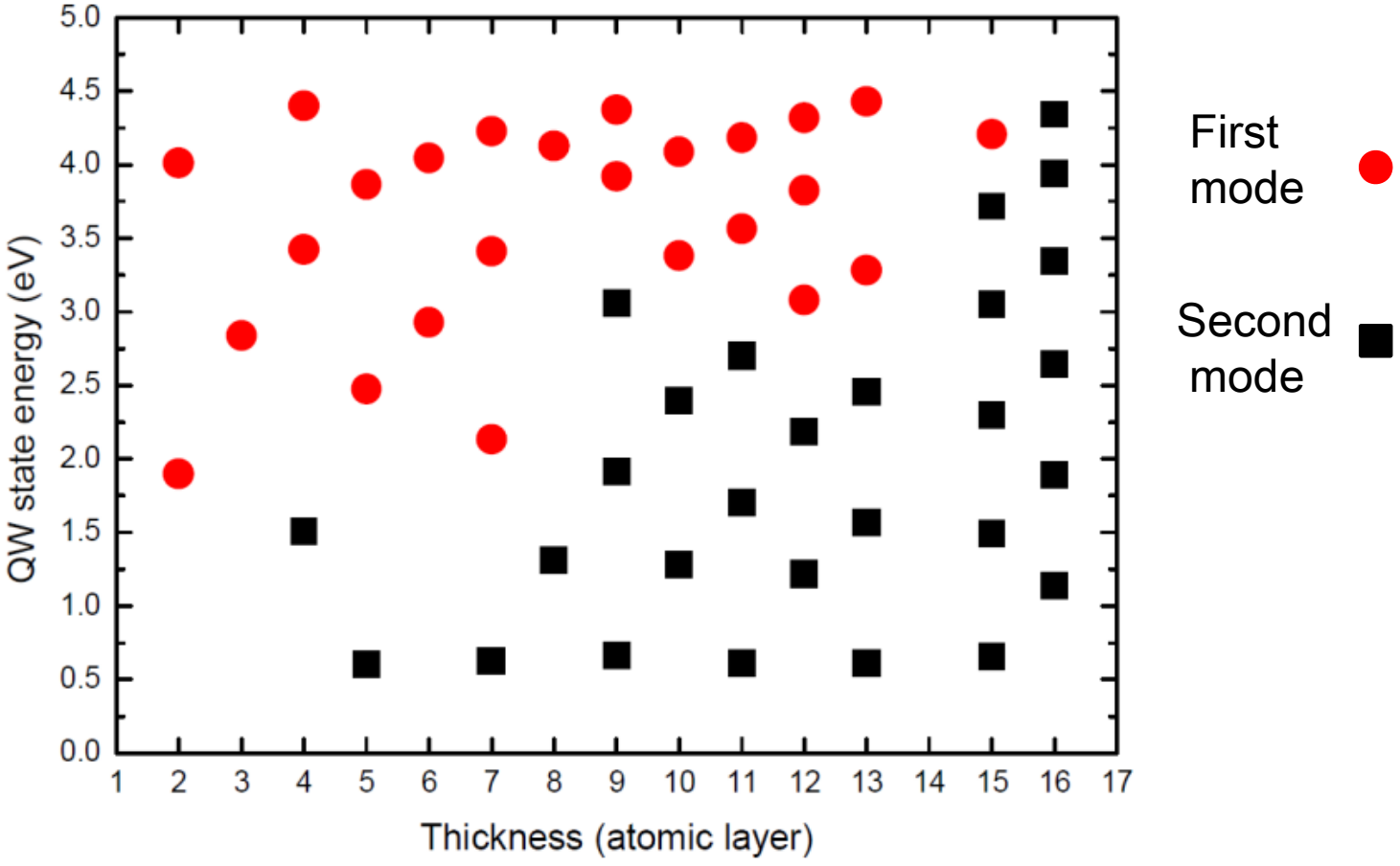
I ↑

F ↑

First mode ●
(positive energy shift)

Second mode ■
(negative energy shift)

Mode distribution with thickness dependence



free space

due to image potential

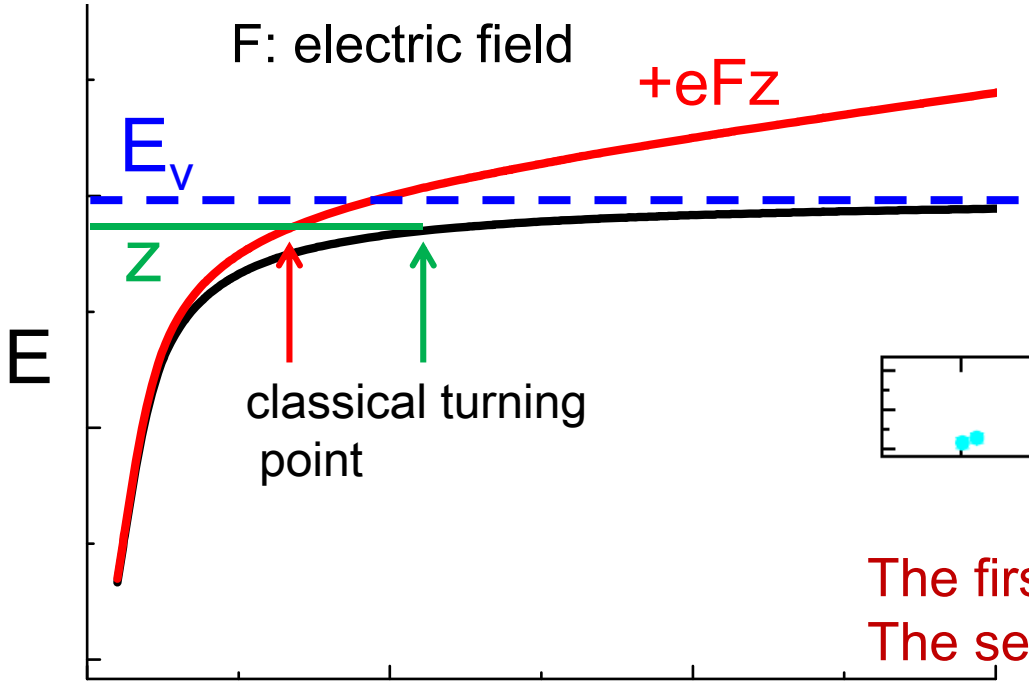
$2k(N+1)d+\phi_B=2n\pi$

$$\phi_B/\pi = [3.4\ \mathrm{eV}/(E_V - E)]^{1/2} - 1,$$

$$E_V - E = e^2/16\pi\epsilon_0 z,$$

Z: distance between surface and classical turning point

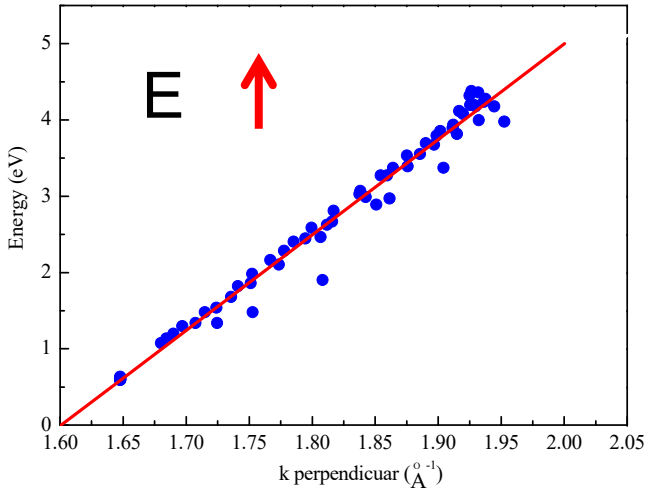
ϕ_B is proportional to $(z)^{1/2}$



under electric field

$2(k+\Delta k)(N+1)d+(\phi_B-\beta)=2n\pi$

$\beta > 0, \Delta k > 0$



F

monotonic positive energy shift

The first mode is the only choice.

The second mode cannot be explained (negative energy shift)

When electric field is applied,

$$2(k+\Delta k)(N+1)d+\phi_B+(\alpha-\beta)=2n\pi$$

$$\alpha > 0$$

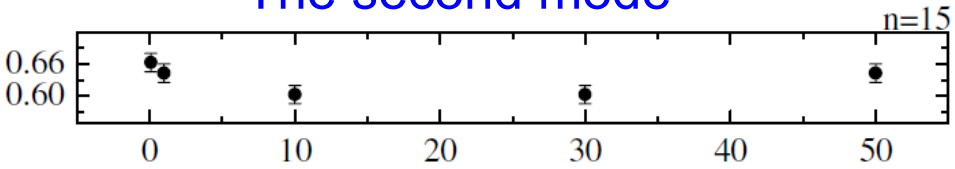
$\alpha-\beta < 0$ positive energy shift ($\Delta k > 0$)

$\alpha-\beta > 0$ negative energy shift ($\Delta k < 0$)

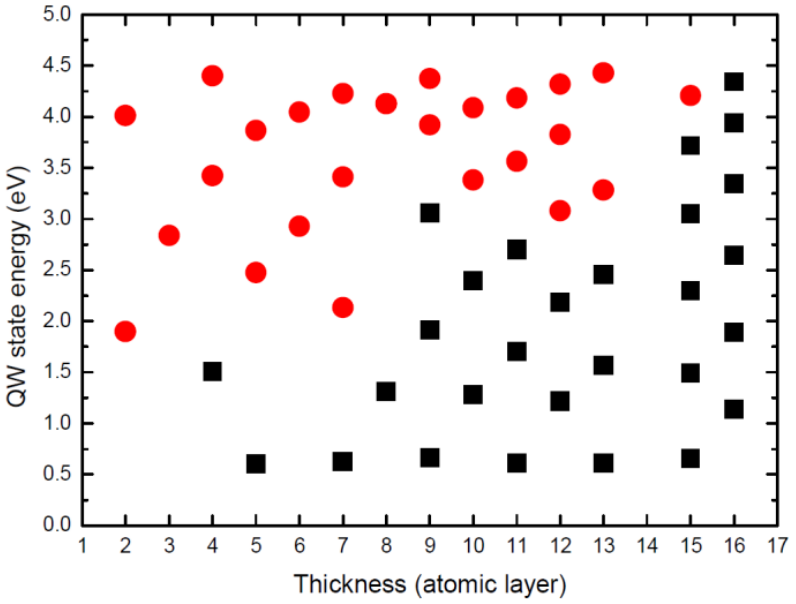
properties of α :

(i) α increases with increasing F

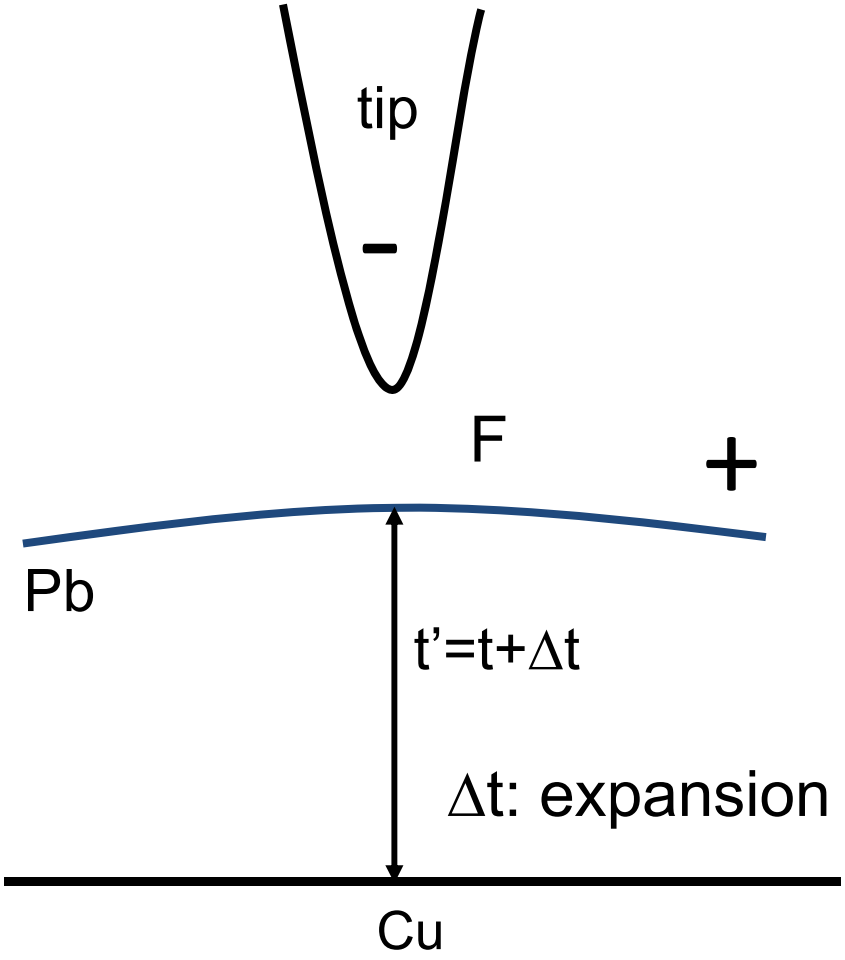
The second mode



(ii) α is proportional to thickness



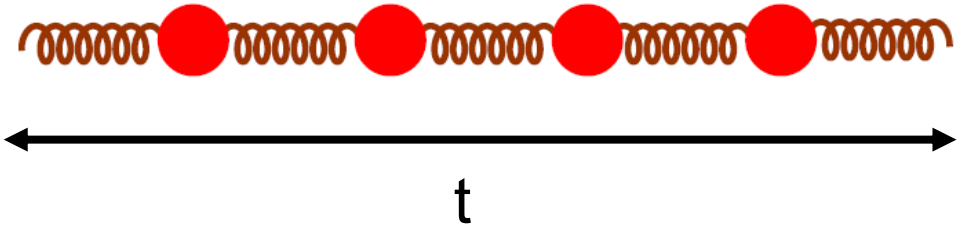
Local expansion deformation due to electrostatic force in STM gap



(i) Δt increases with increasing F

(ii) Δt is proportional to thickness

Solid state physics



under external force, Δt is proportional to N

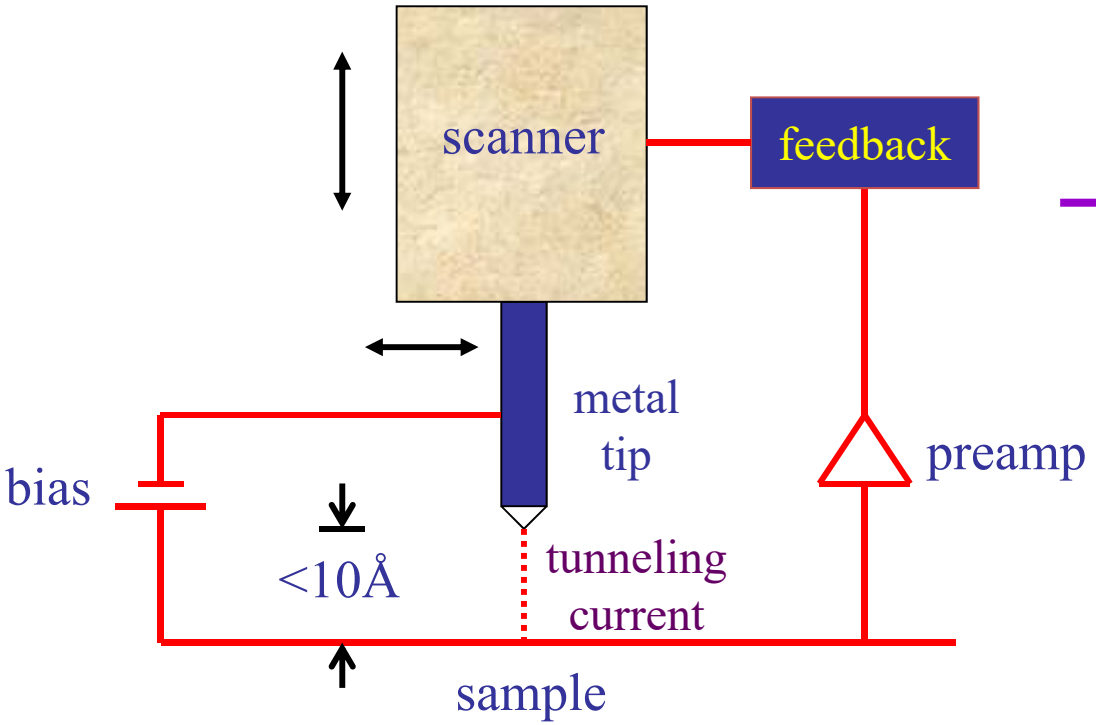
assume $\Delta t = N\Delta d \longrightarrow \alpha = kN\Delta d$

Δd: expansion of interlayer spacing

Scanning Probe Microscopy

Scanning Tunneling Microscopy (STM)

Gerd Binnig, Heinrich Rohrer
1986 Nobel Prize in Physics



Detecting the interaction between probe and sample:

- Atomic force (AFM)
- Magnetic force (MFM)
- Electrostatic force (EFM)
- Near field optics (NSOM)
- ⋮