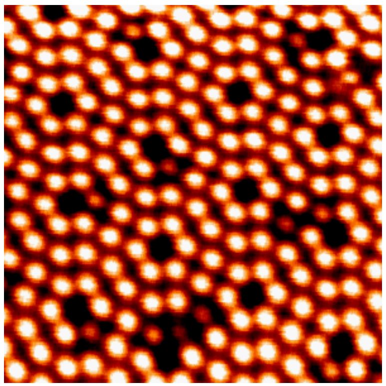
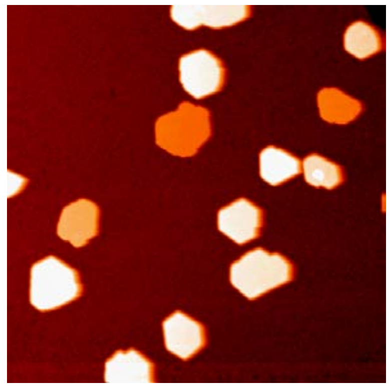
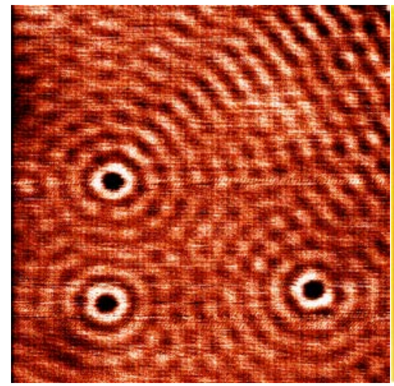
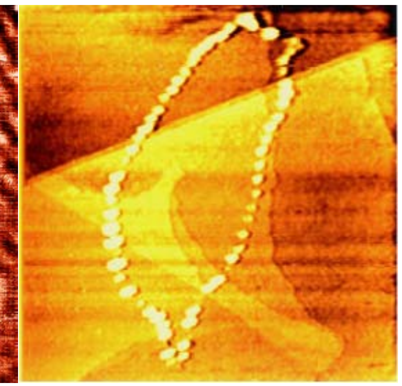
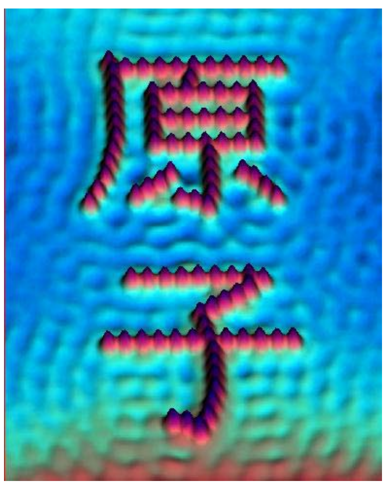
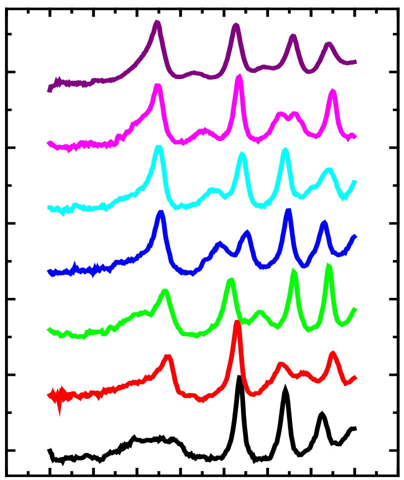
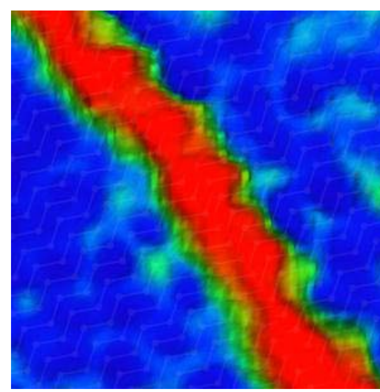
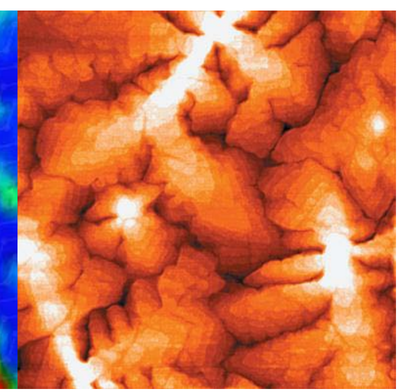
Scanning Tunneling Microscopy

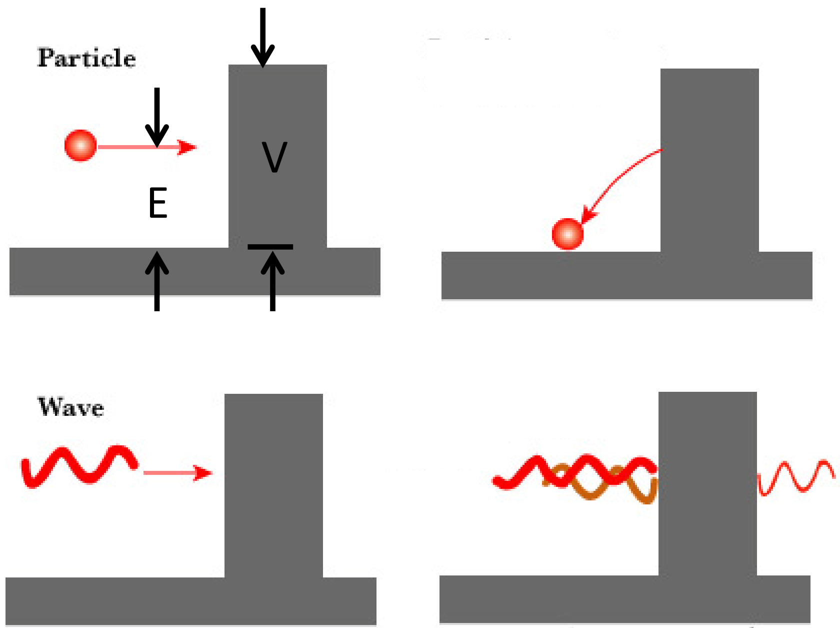
Wei-Bin Su, Institute of Physics, Academia Sinica

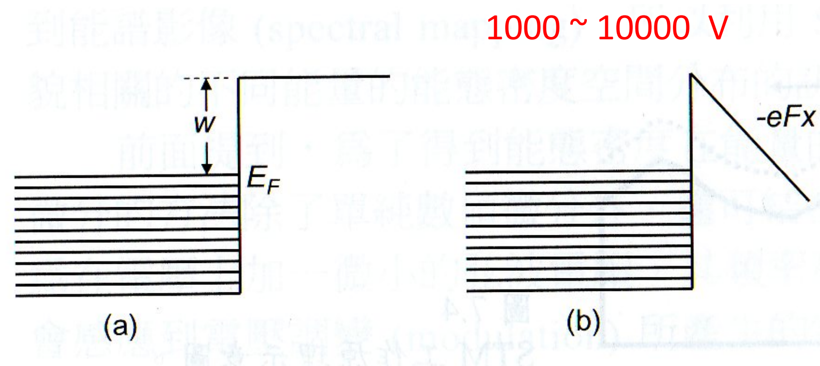
Tunneling effect

Classical physics

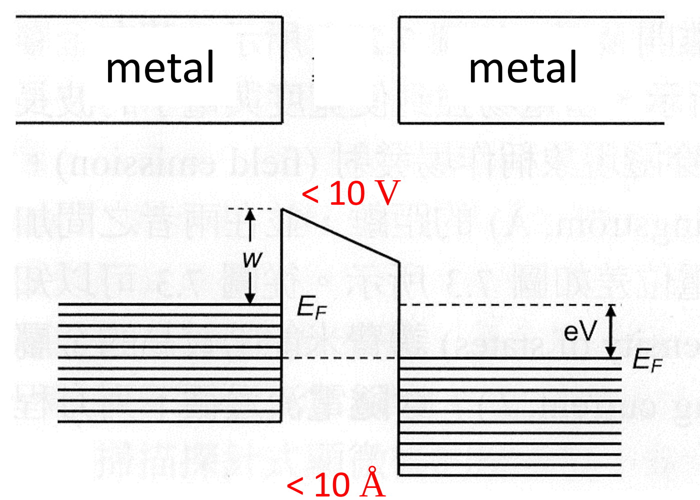


Quantum physics

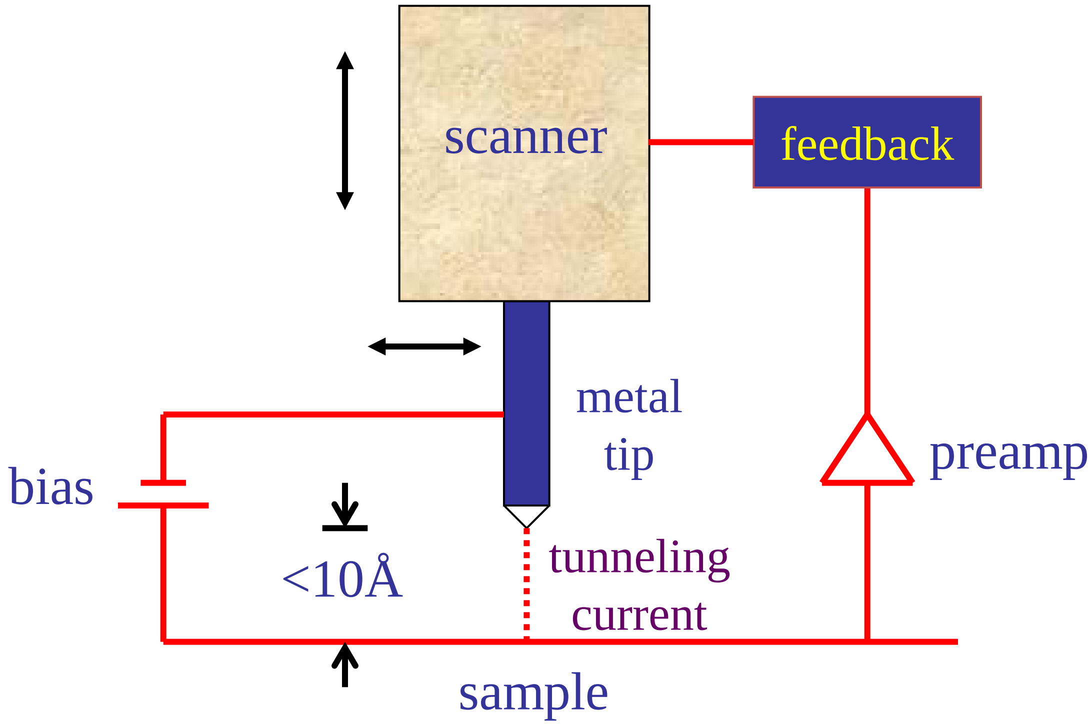
Field emission



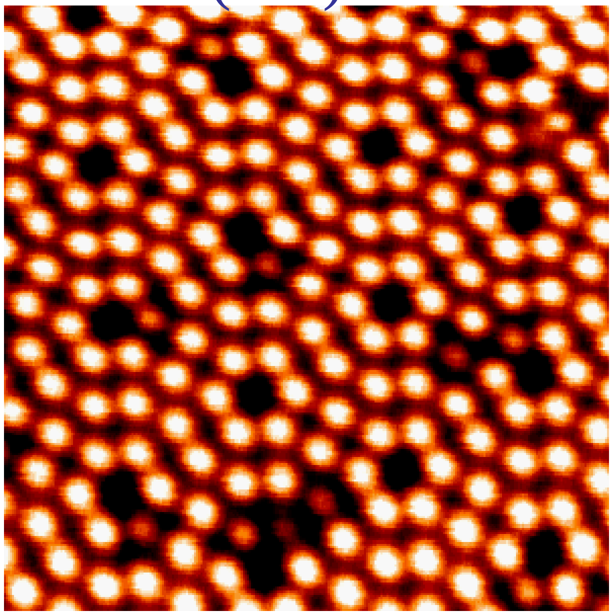
metal-vacuum-metal tunneling

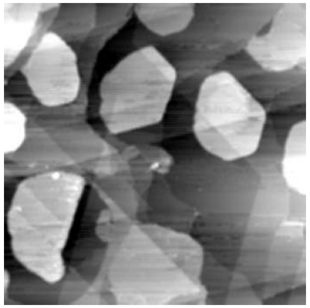


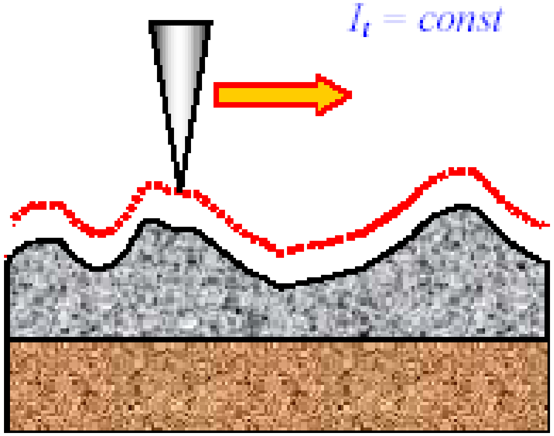
Scanning Tunneling Microscopy (STM)



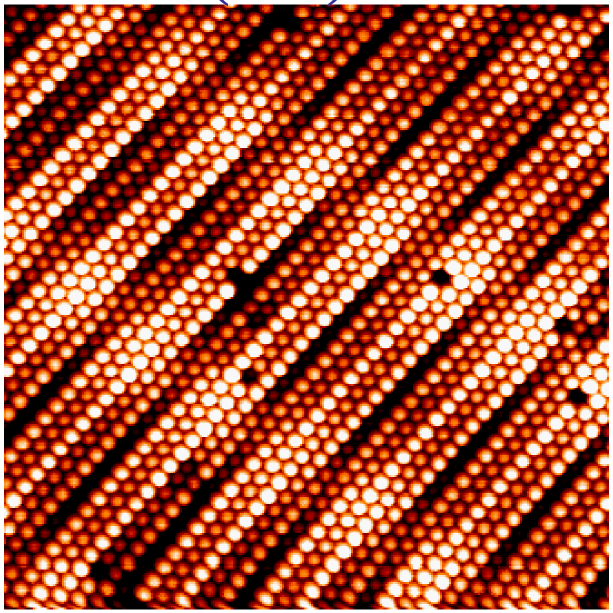
Si(111)7×7



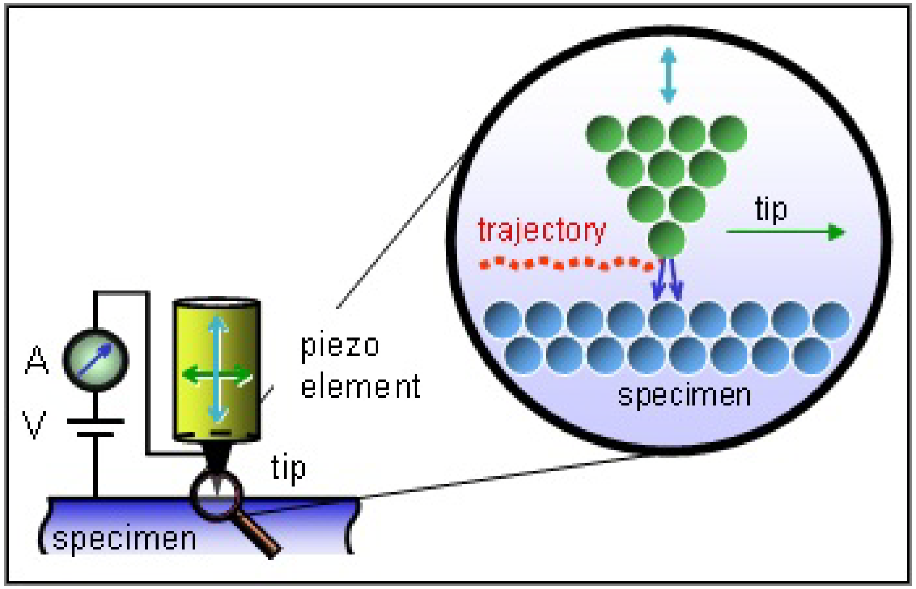


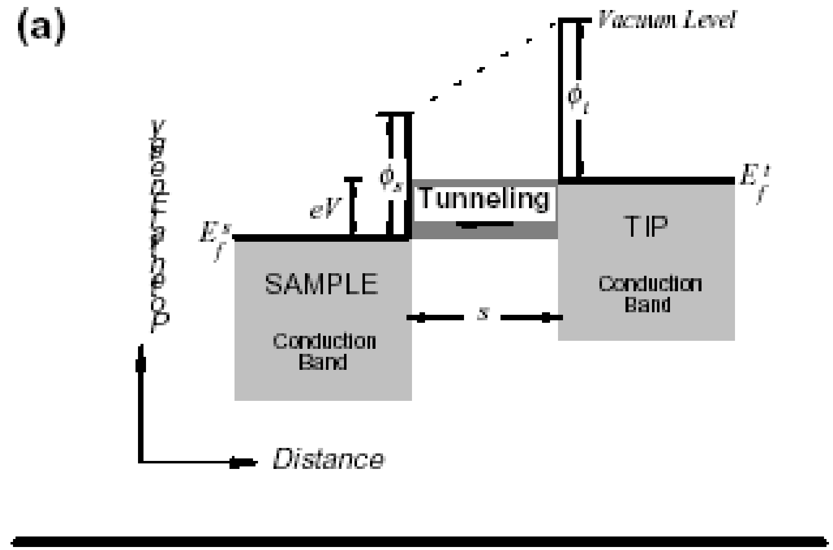


Pt(100)-R0.7^0



Principle of scanning tunneling microscopy





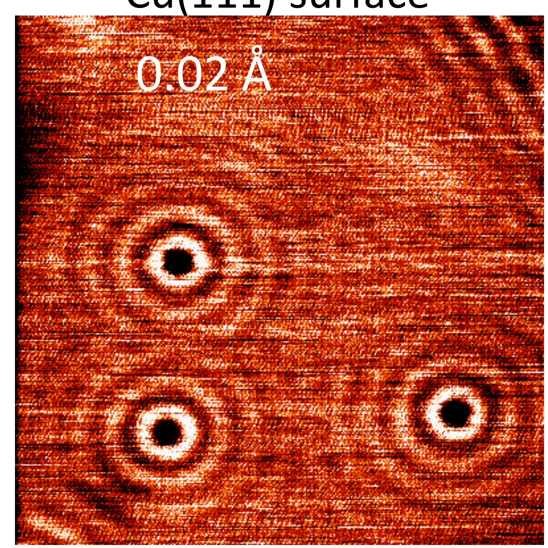
$T(s) \sim \exp(-2\kappa s)$; $\kappa = (2m\phi/\hbar^2)^{1/2}$; $\phi = (\phi_t + \phi_s)/2$

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

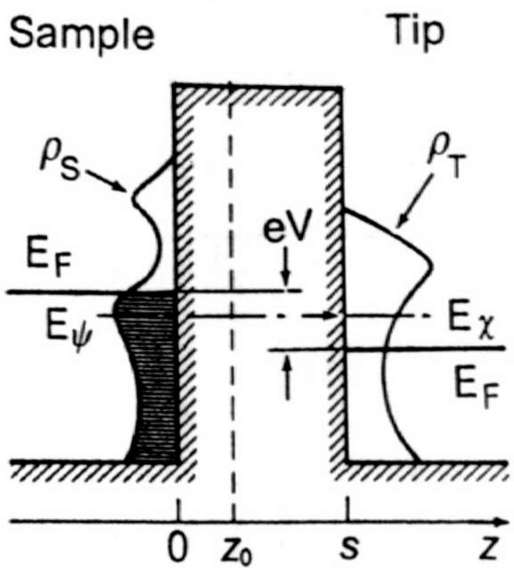
$$I \propto \int_0^{eV} \rho_s(E_F - eV + \varepsilon)\, \rho_T(E_F + \varepsilon)\, d\varepsilon$$

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

(b) Cu(111) surface

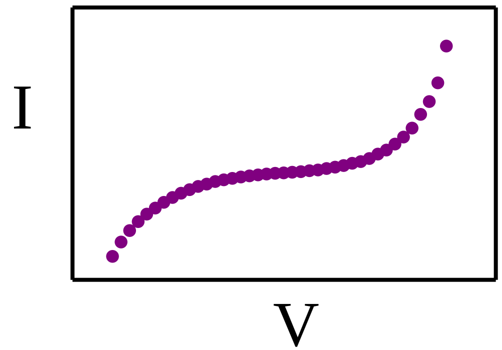


Scanning Tunneling Spectroscopy (STS)



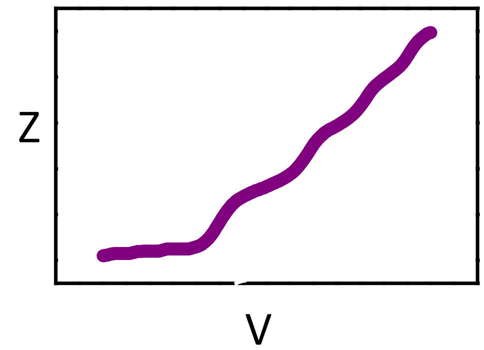
(feedback off)

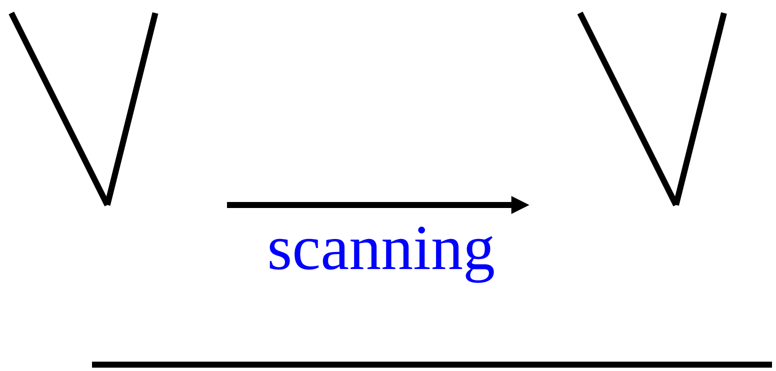
I-V spectroscopy



(feedback on)

Z-V spectroscopy



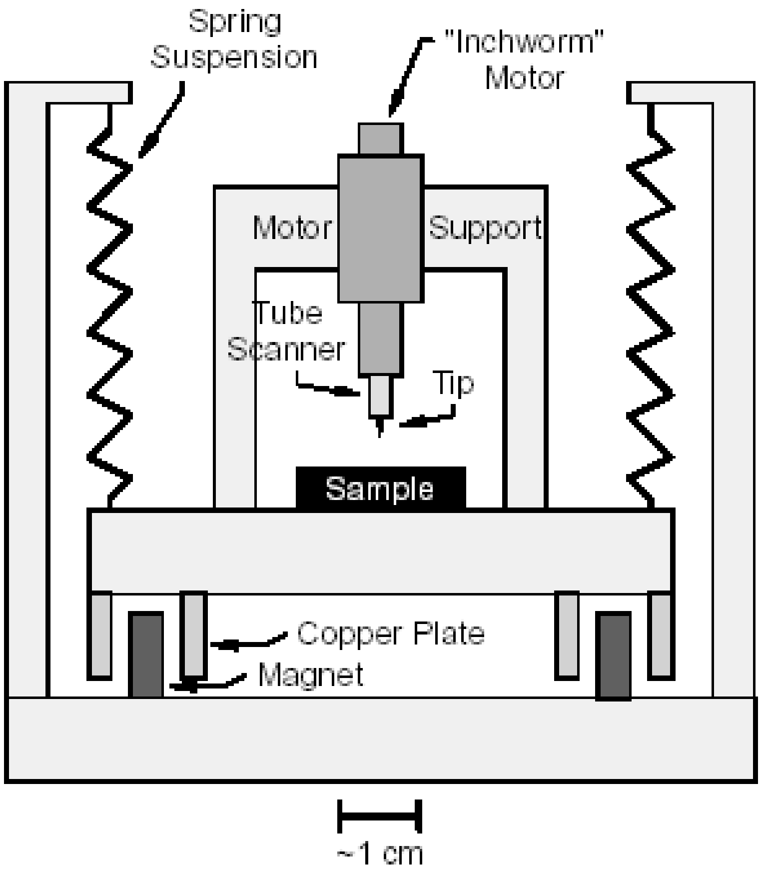


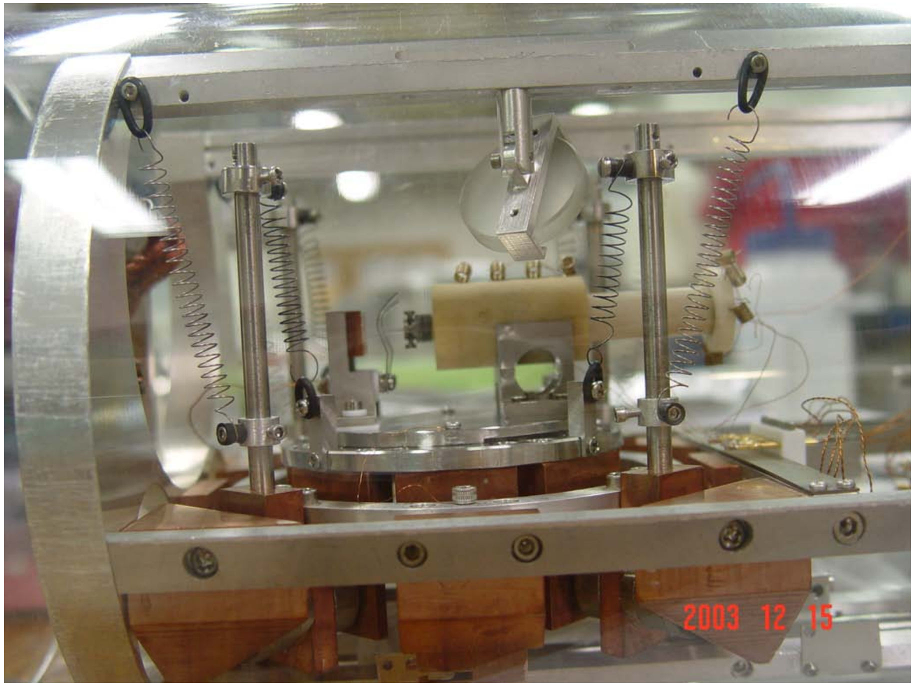
sample

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

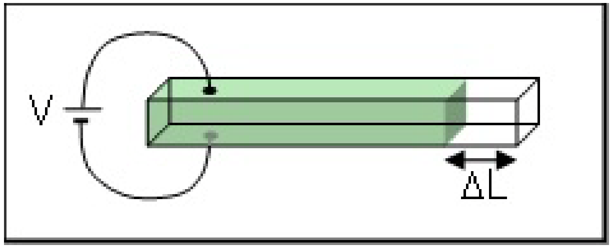
ρ_T is constant $\Rightarrow dI/dV \propto \rho_s(E_F - eV)$

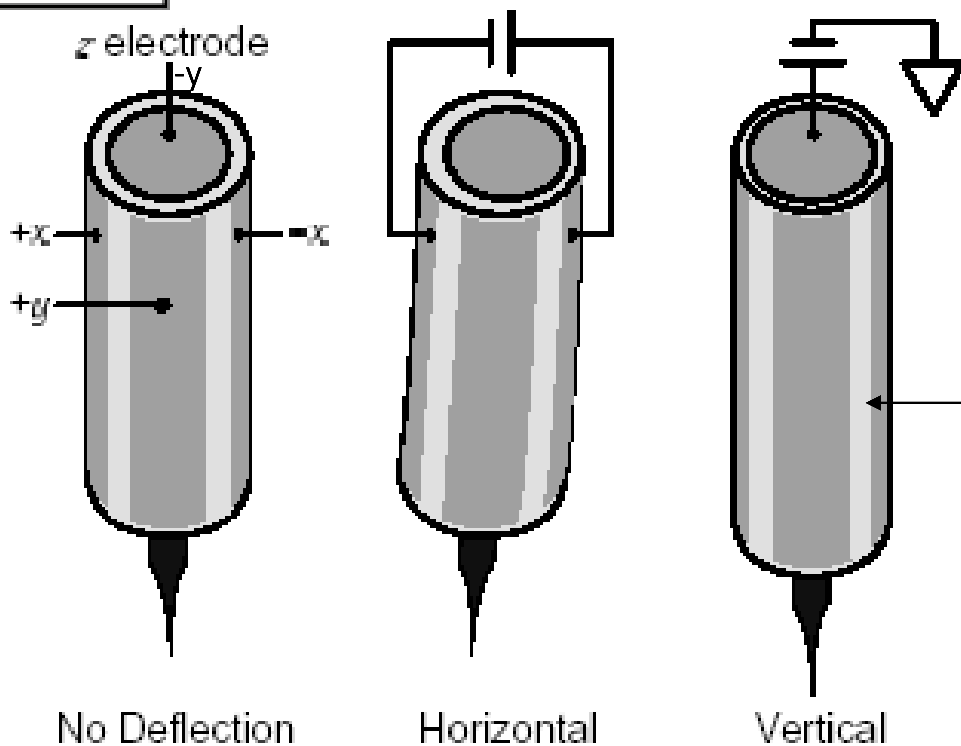
Structure of STM





Tube Scanner



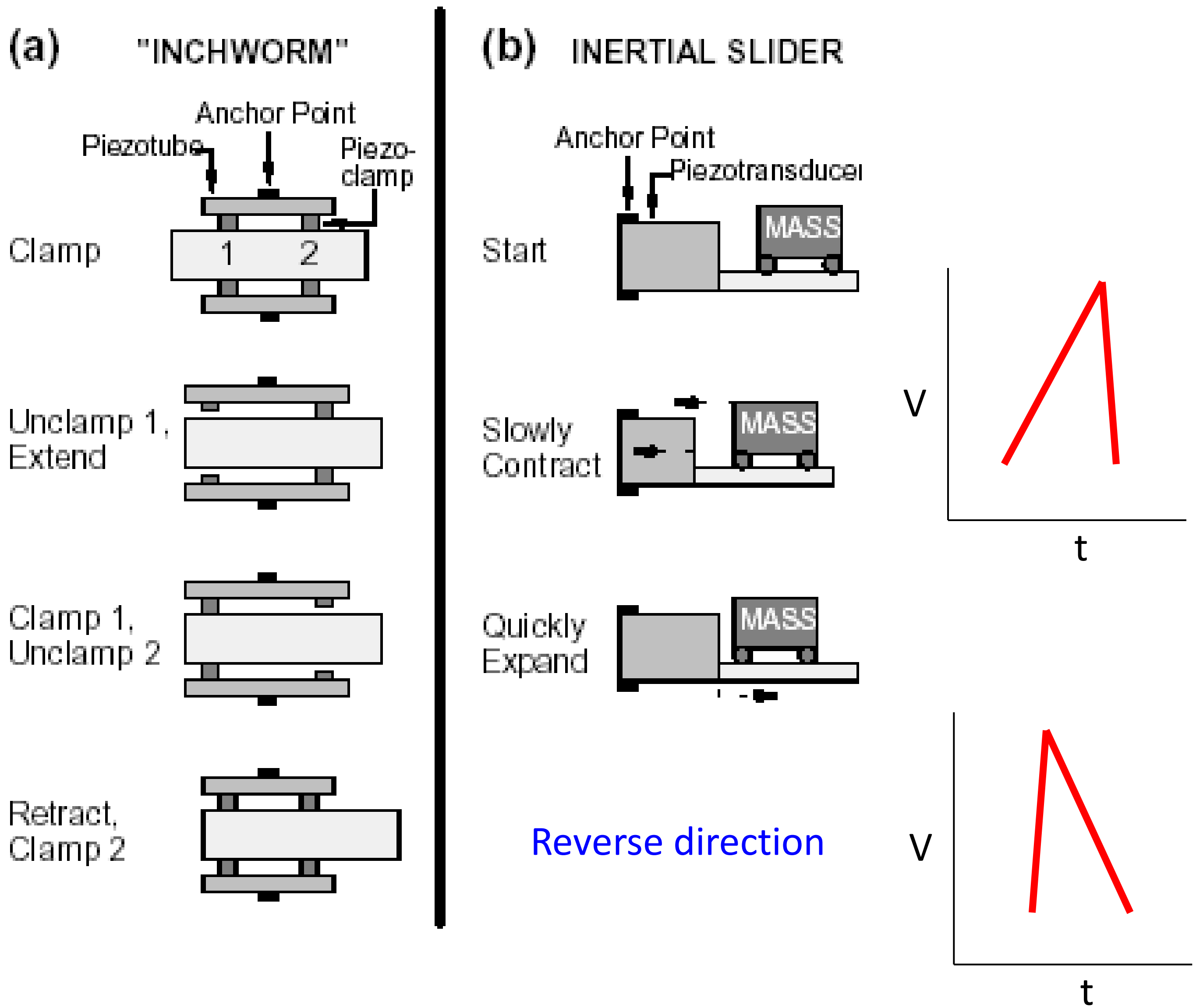


Metal free area

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

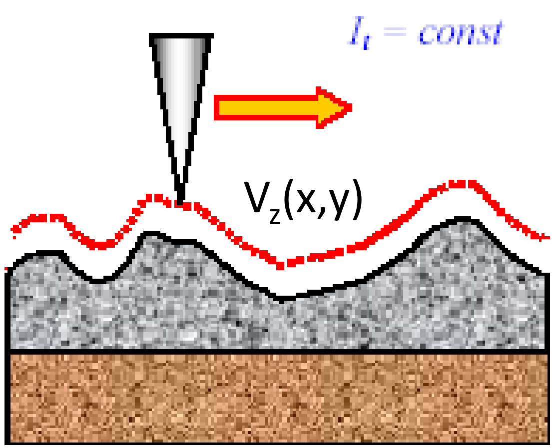
(piezo)

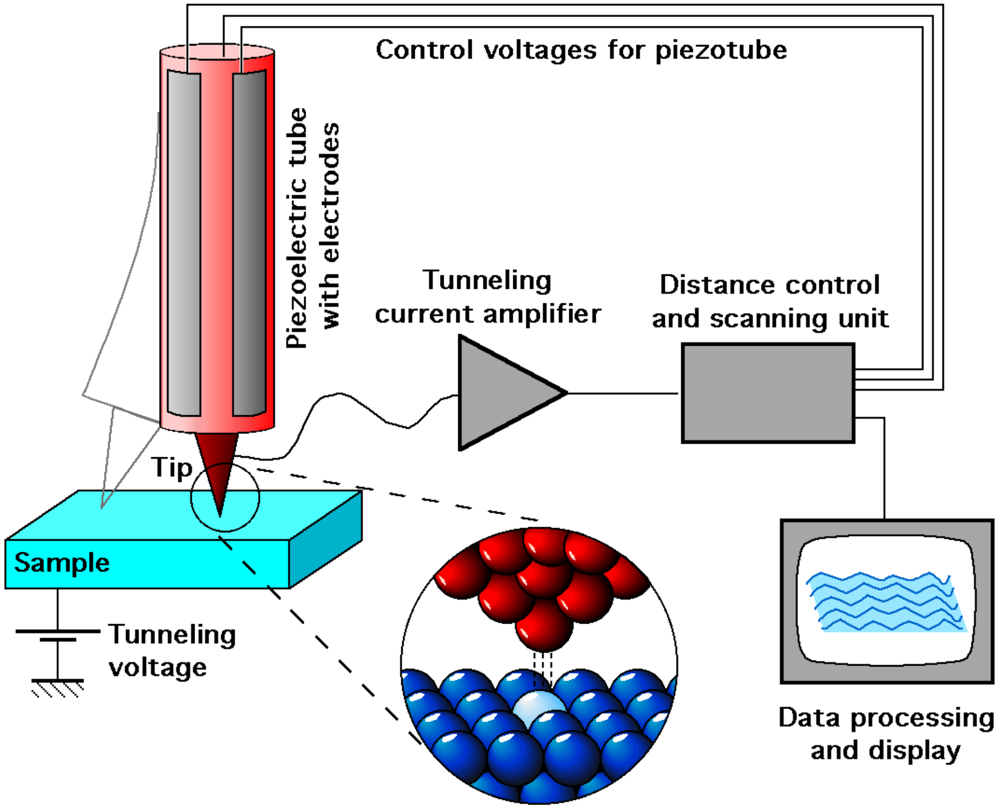
Motor for coarse approach



Electronic Control

1. Auto approach
2. Data acquisition





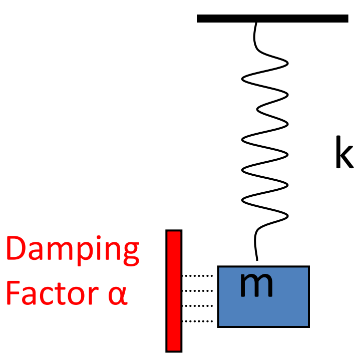
The contrast of STM image is the variation of voltage applied to z-electrode of tube scanner.

Vibration Isolation

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.

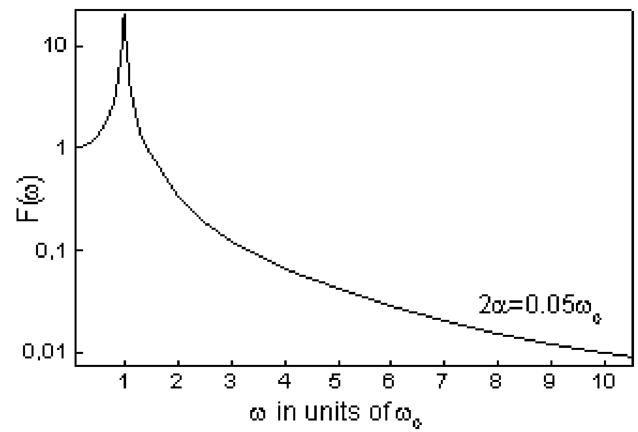
Environmental vibrations are caused by:

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



$\omega_0 = \sqrt{k/m}$

$Q = \omega_0/2\alpha$



Vibration damping can be done by

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

magnets and copper plates

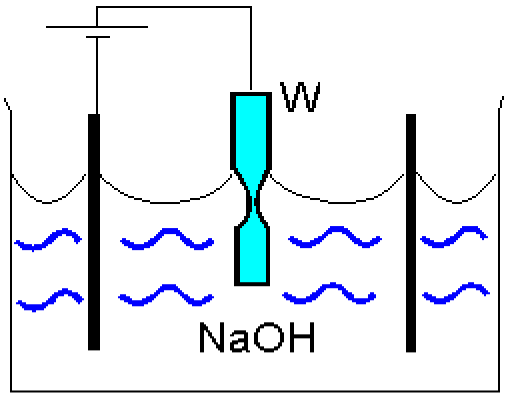
Pneumatic systems

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, platinum or a Pt-Ir wire.

A sharp tip can be produced by:

- Cutting and grinding
- Electrochemical etching



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.

It is also possible to do tip-sharpening during tunneling.

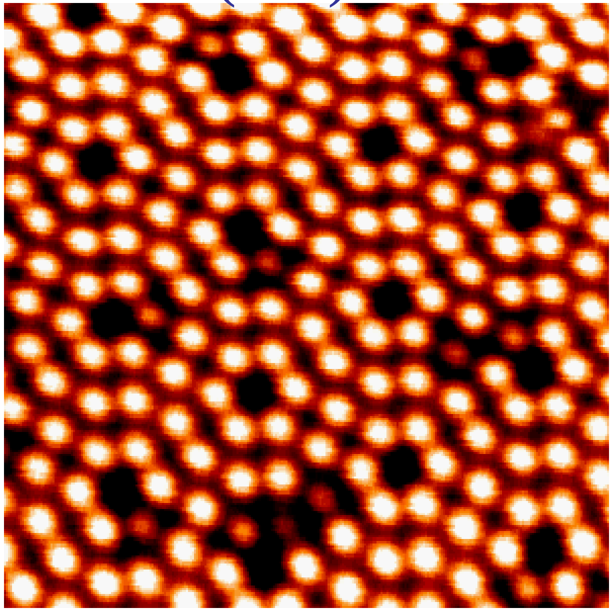
- Sudden rise of the bias voltage to about -7V (at the sample) for 2-4 scan lines.
  By this treatment some W atoms may walk to the tip apex due to the nonuniform electric field and form a nanotip.
- Controlled collision on Si surface.
  The tip may pick up a Si-cluster which forms a monoatomic apex with a p_z like dangling bond.

Environment for STM : Air, Liquid, Ultra high vacuum (UHV)

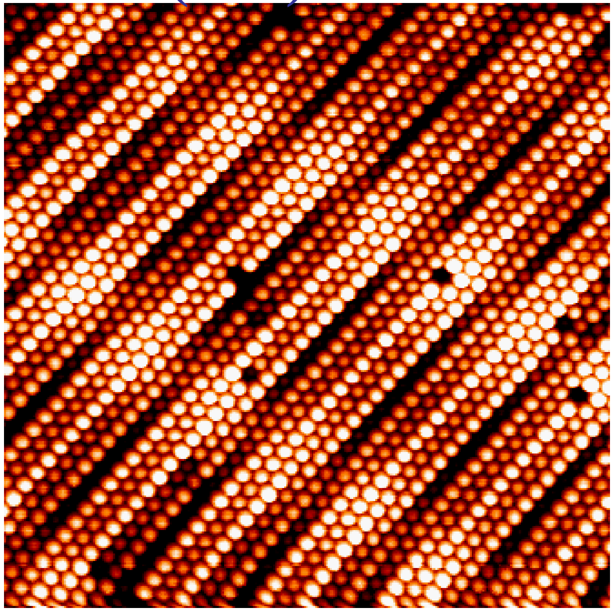
Working temperature of STM : RT, HT (high to 1200 K), LT (low to 0.3 K)

Atomic scale resolution

Si(111)7×7

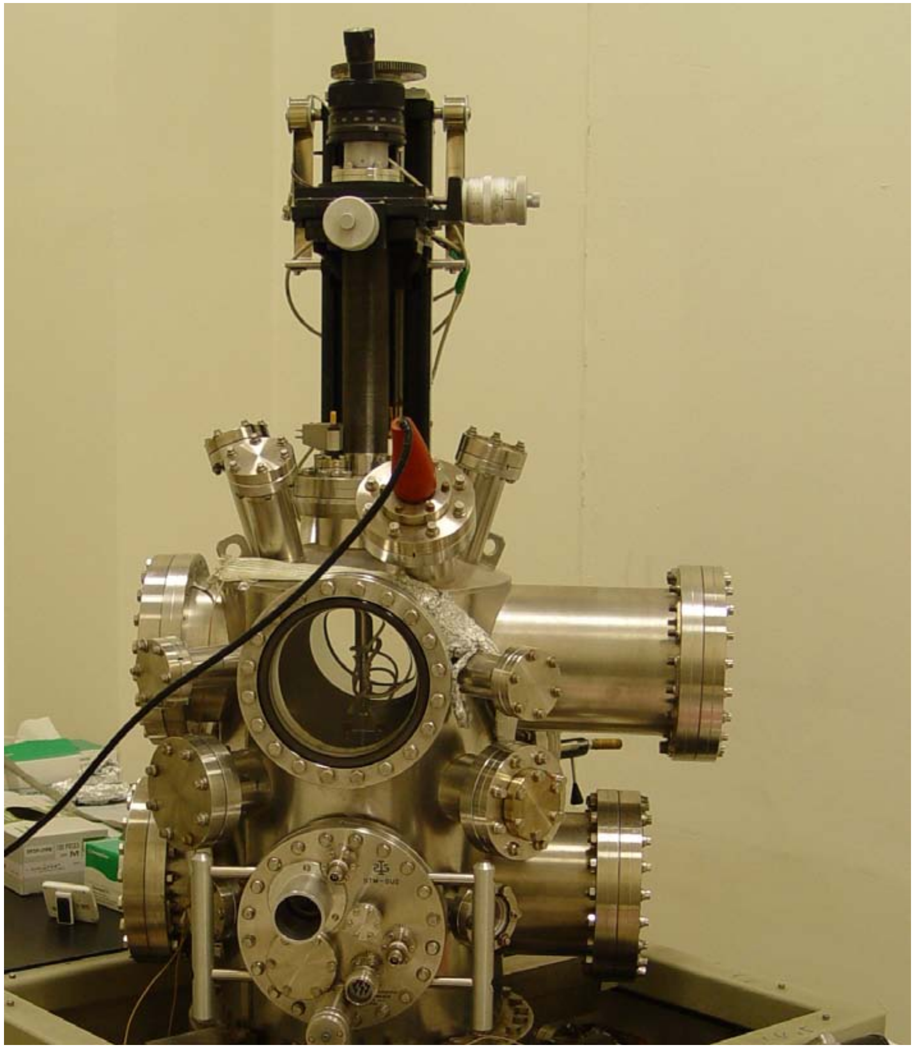


Pt(100)-R0.7^0

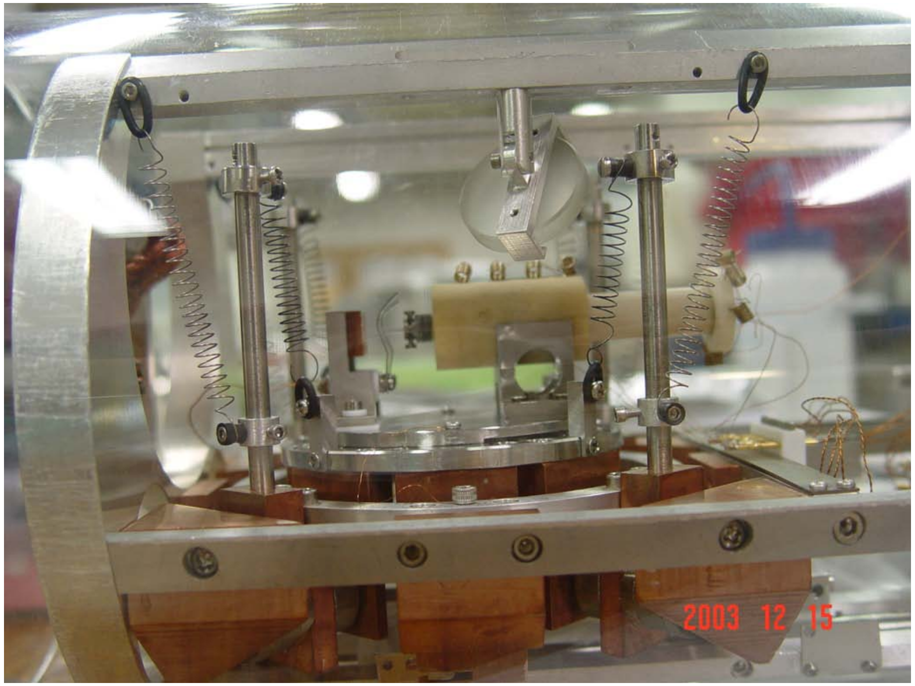


For obtaining order arrangement of atom, UHV is necessary.

UHV chamber



UHV RT STM



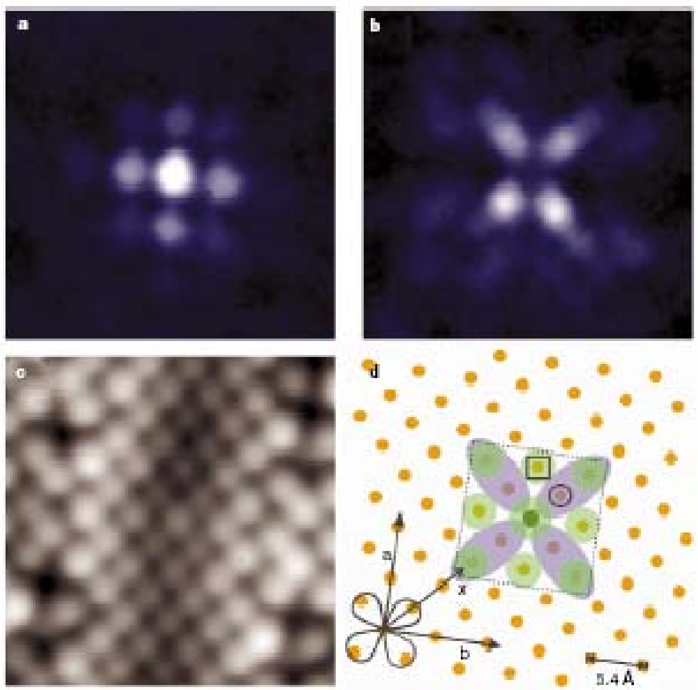
Defects of UHV RT STM:

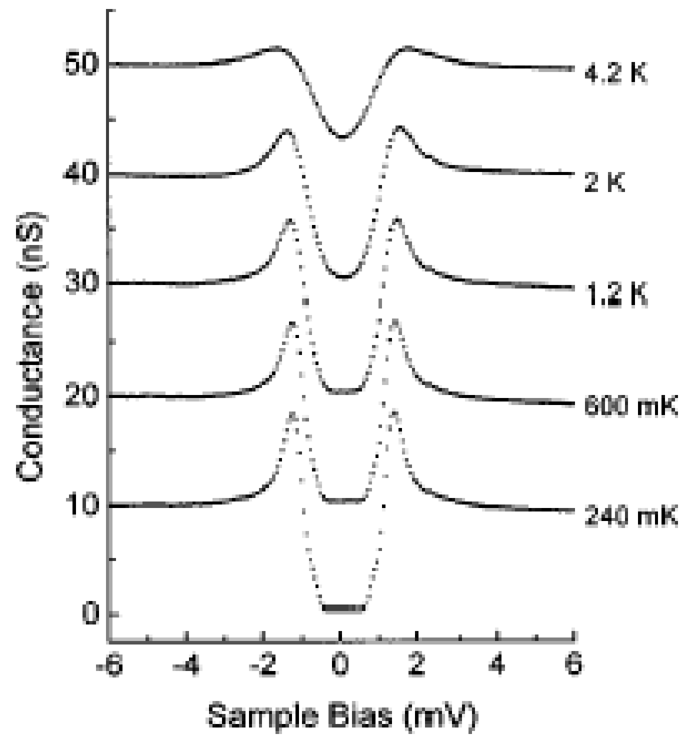
- Thermal effect reduces the energy resolution in scanning tunneling spectroscopy
- Physical phenomena appearing at low temperature cannot be observed.
- Thermal drift (relative movement of tip and sample)

↓

Development of LT-STM

Improvement of Energy resolution by reducing temperature

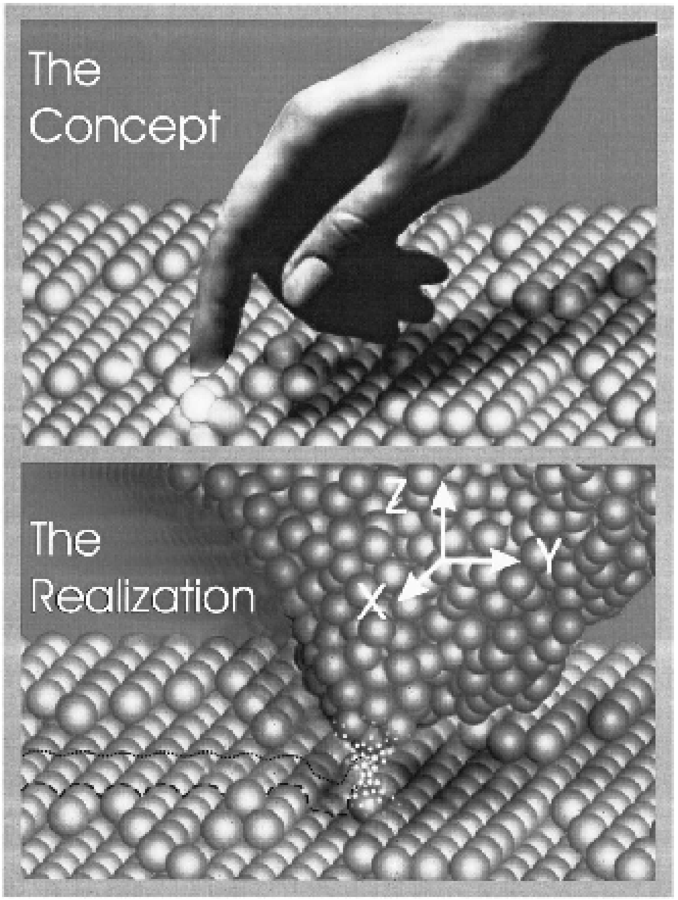


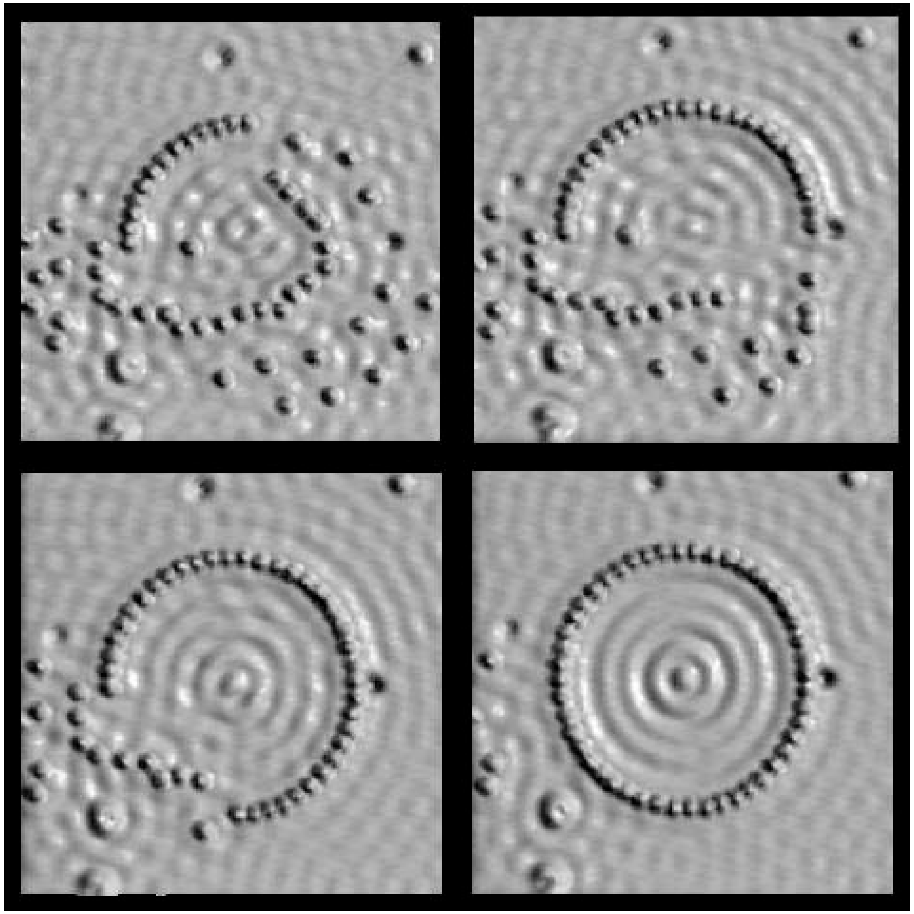


S.H. Pan *et al*., Nature **411**, 920 (2001).

Superconducting gap

Atomic Manipulation



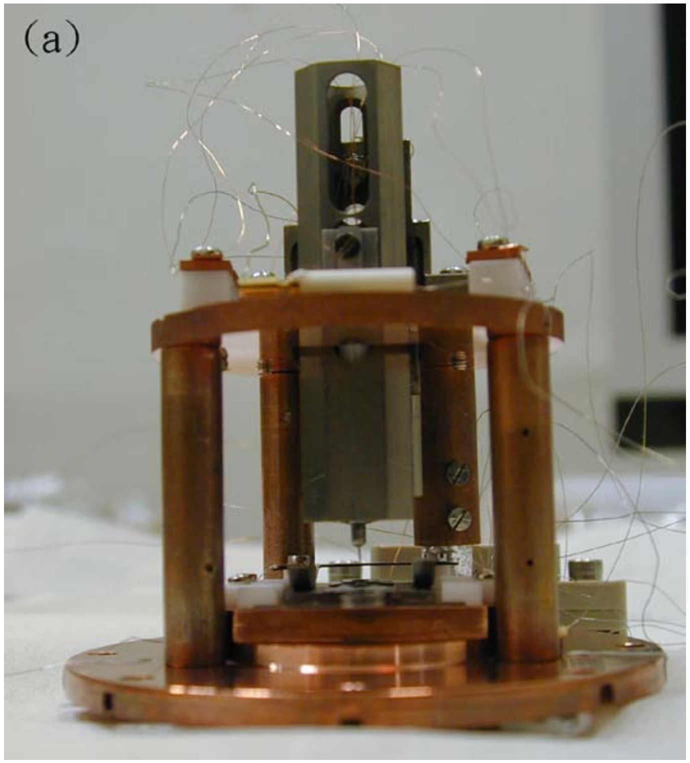


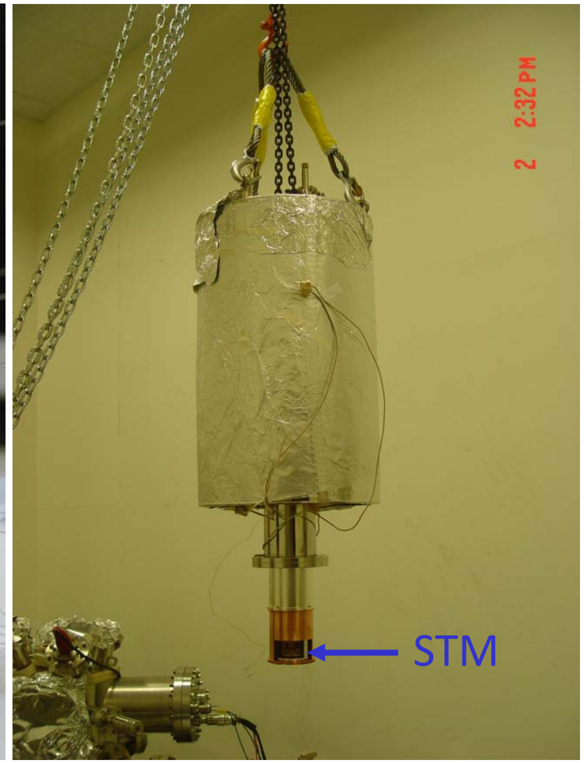
Low temperature can reduce the relative movement between tip and sample, facilitating atomic manipulation.

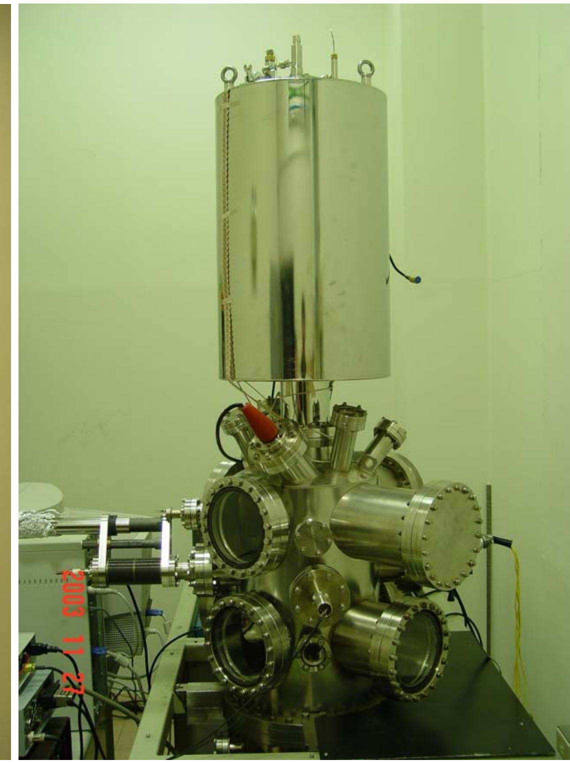
Home made LT UHV STM

Homemade STM

UHV-compatible
LHe Cryostat





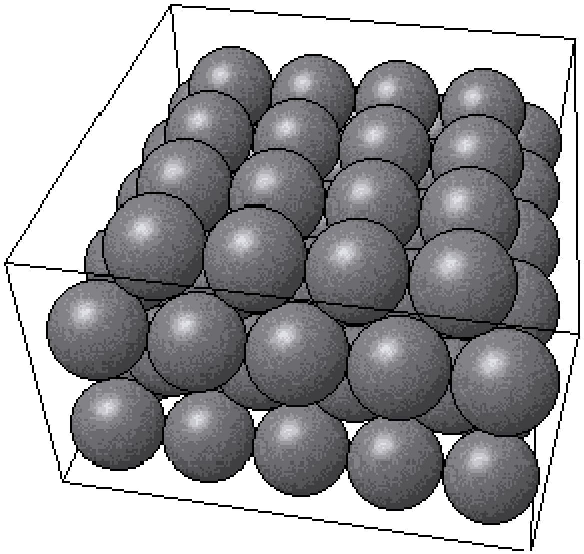


Lowest temperature ~ 5 K

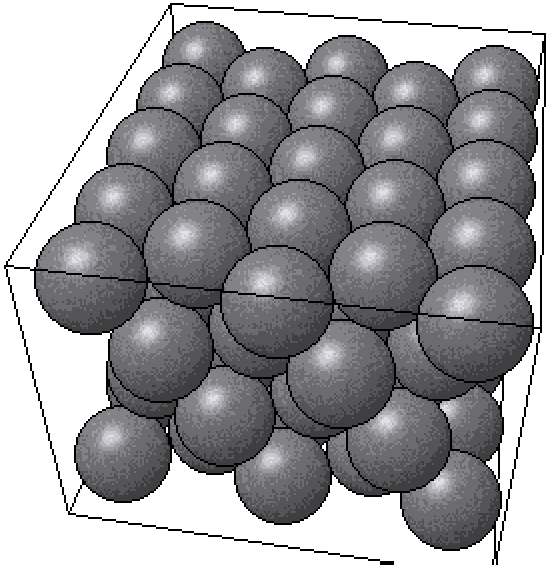
Applications of scanning tunneling microscopy

Surface reconstruction

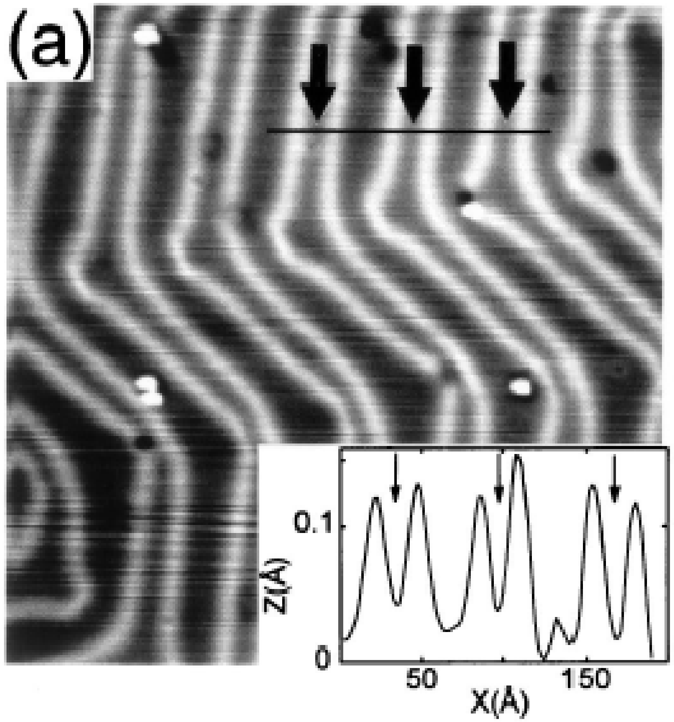
FCC(100)

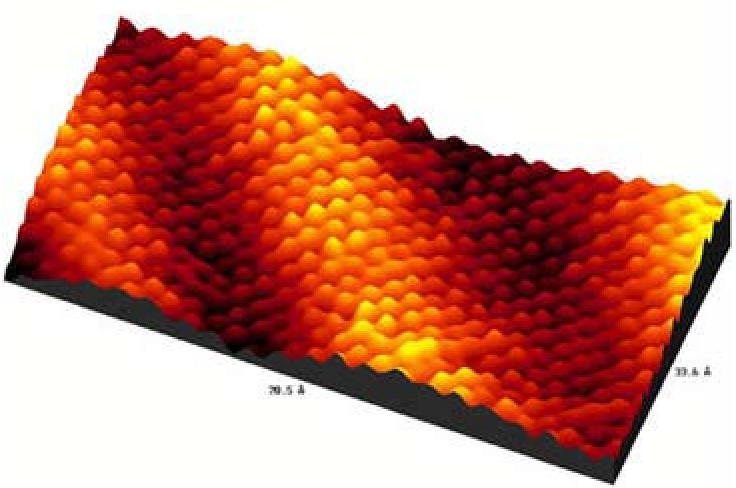


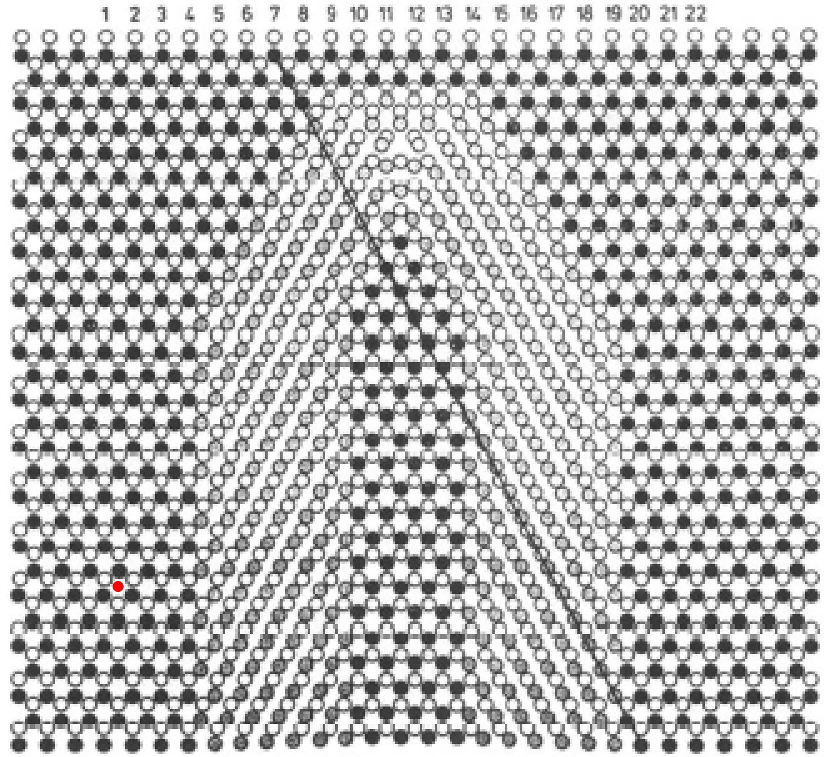
FCC(111)



22×√3 Reconstruction of Au(111) surface

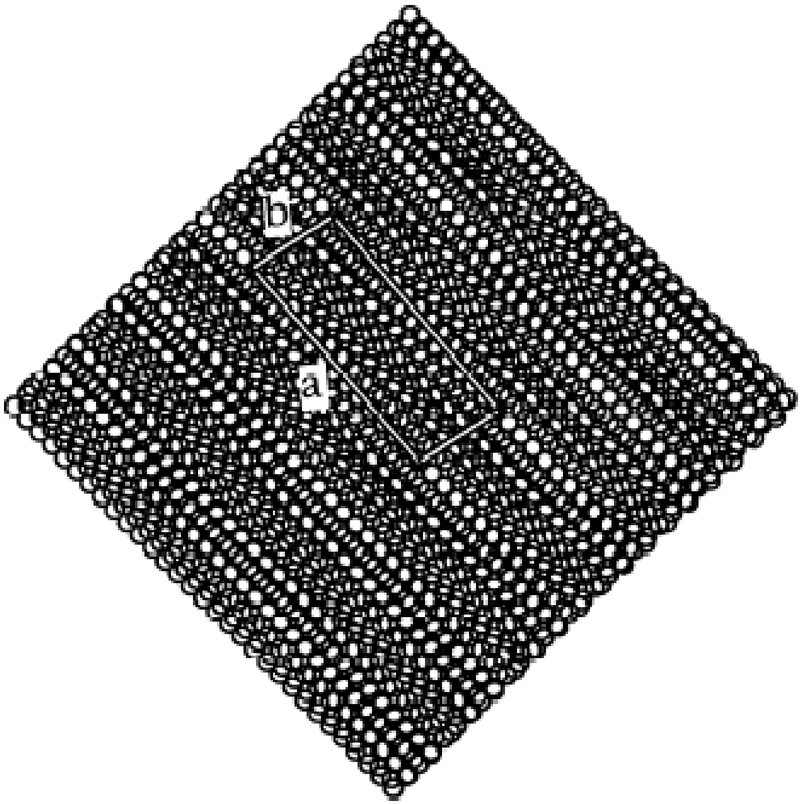




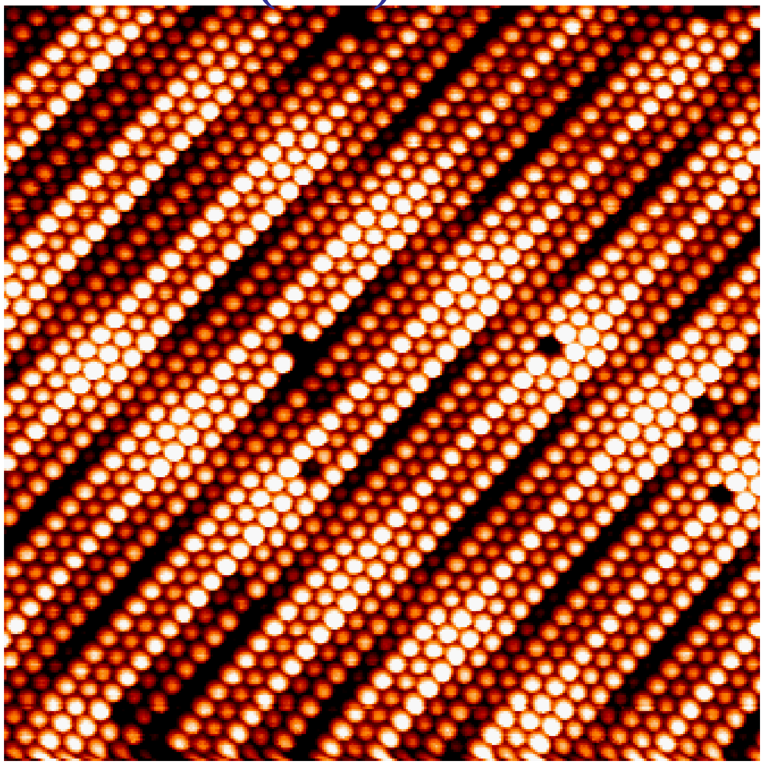


FCC (ABC) HCP (ABA) FCC

Reconstruction on Pt(100)



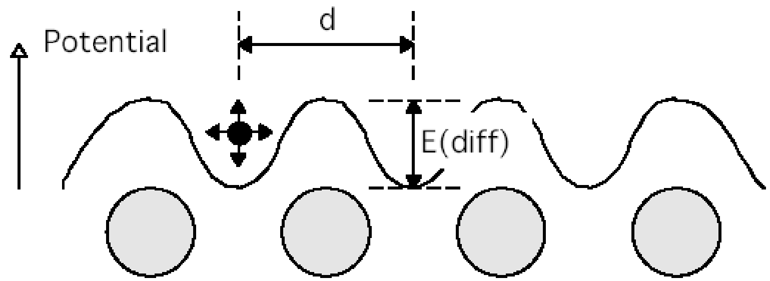
Pt(100)-R0.7^0



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

Surface Diffusion

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



D: diffusion coefficient,

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

$\alpha=1$ for one dimensional diffusion

$\alpha=2$ 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 $\langle x^2\rangle=Nd^2$

d: mean jump distance

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

$$D=d^2\Gamma/2$$

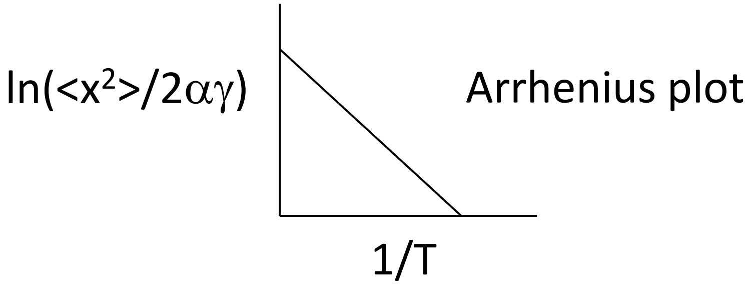
$$\Gamma=\nu_0 \exp(-E_d/kT)$$

ν_0 is vibration frequency,
E_d is activation energy

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

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

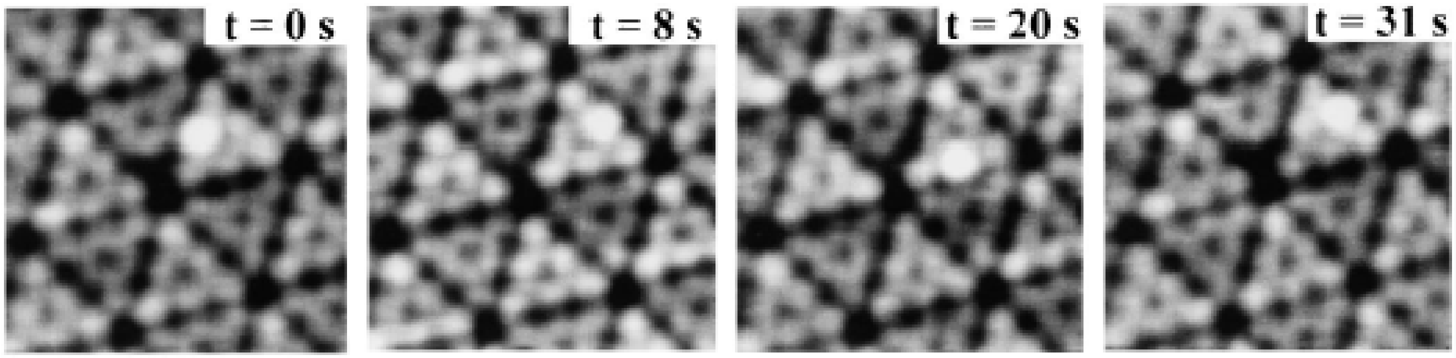
$$\ln(\langle x^2\rangle/2\alpha\gamma)=\ln(D_0)-E_d/kT$$

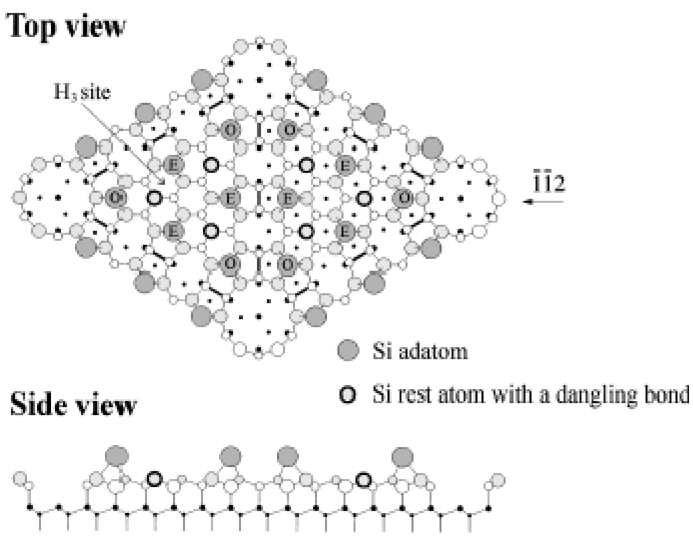


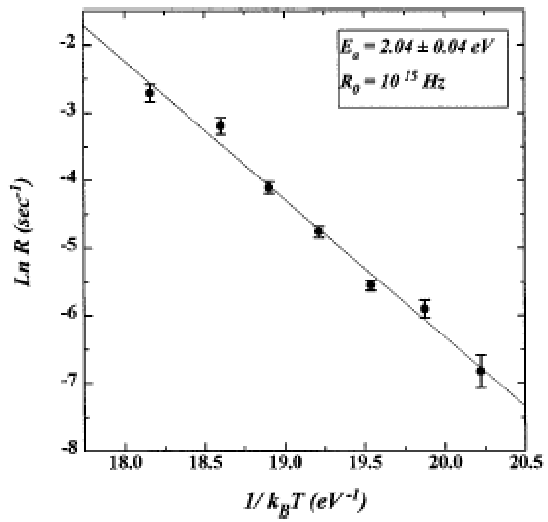
Surface Diffusion

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

350^{0}C







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

Nucleation and Epitaxial Growth

Fe/Fe(100)

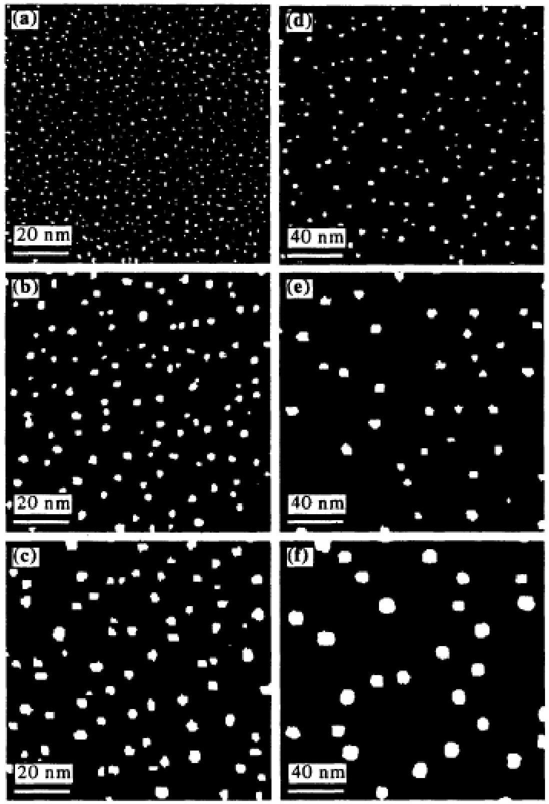
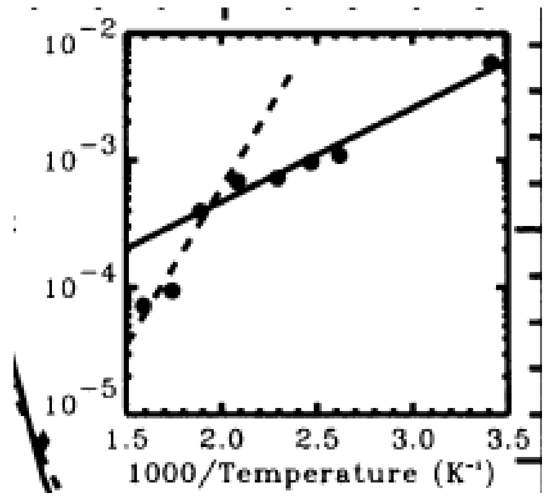


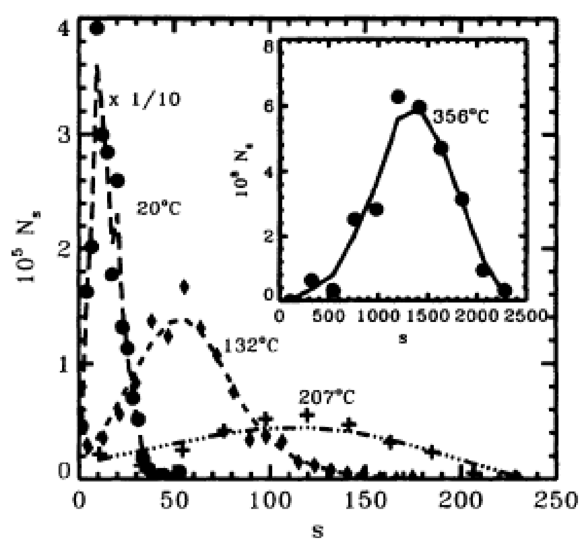
FIG. 1. STM images, 100×100 nm^2, of single-layer Fe islands (white) on the Fe(001) surface (black). Sample temperatures during growth are (a) 20 °C, (b) 108 °C, (c) 163 °C, (d) 256 °C, (e) 301 °C, and (f) 356 °C. Fe was deposited for a fixed time for all measurements with a flux of $1.4\pm0.3\times10^{13}$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

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

E_d : activation energy

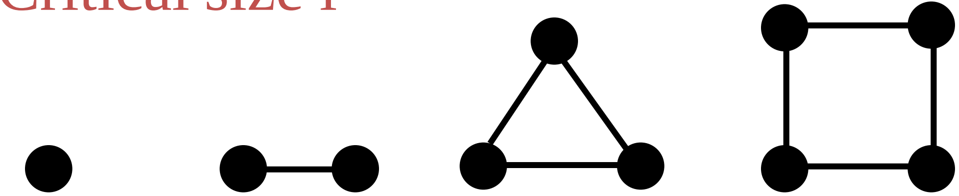
E_i : binding energy of critical size i





Phys. Rev. B 49, 8522 (1994)

Critical size i



i=0 monomer

i=1 dimer

i=2 trimer

i=3 tetramer

Scaling theory

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

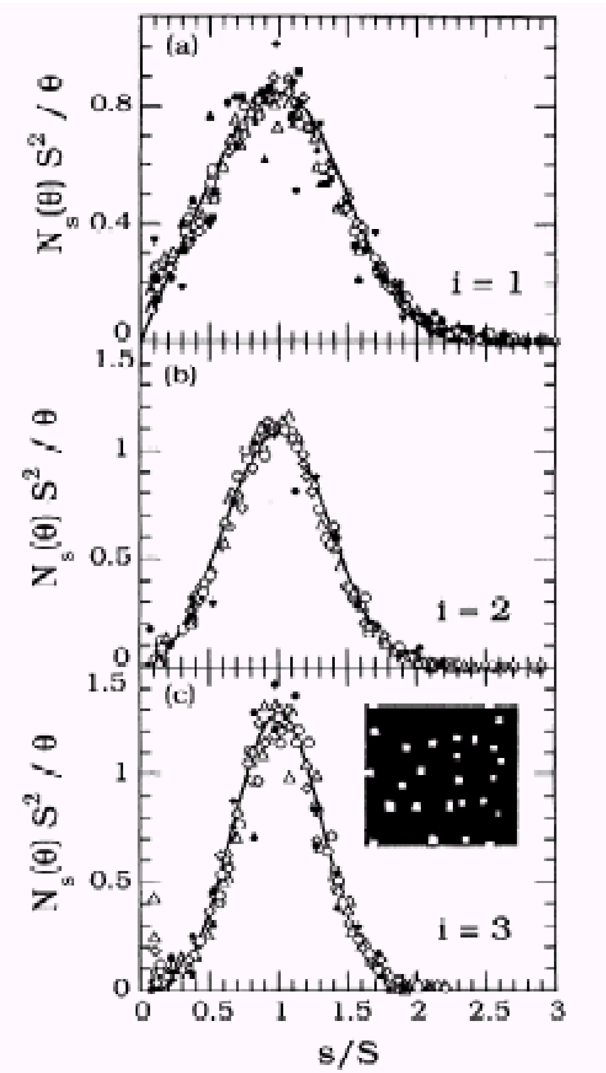
Ns : island density at size s

θ : coverage

S : average island size

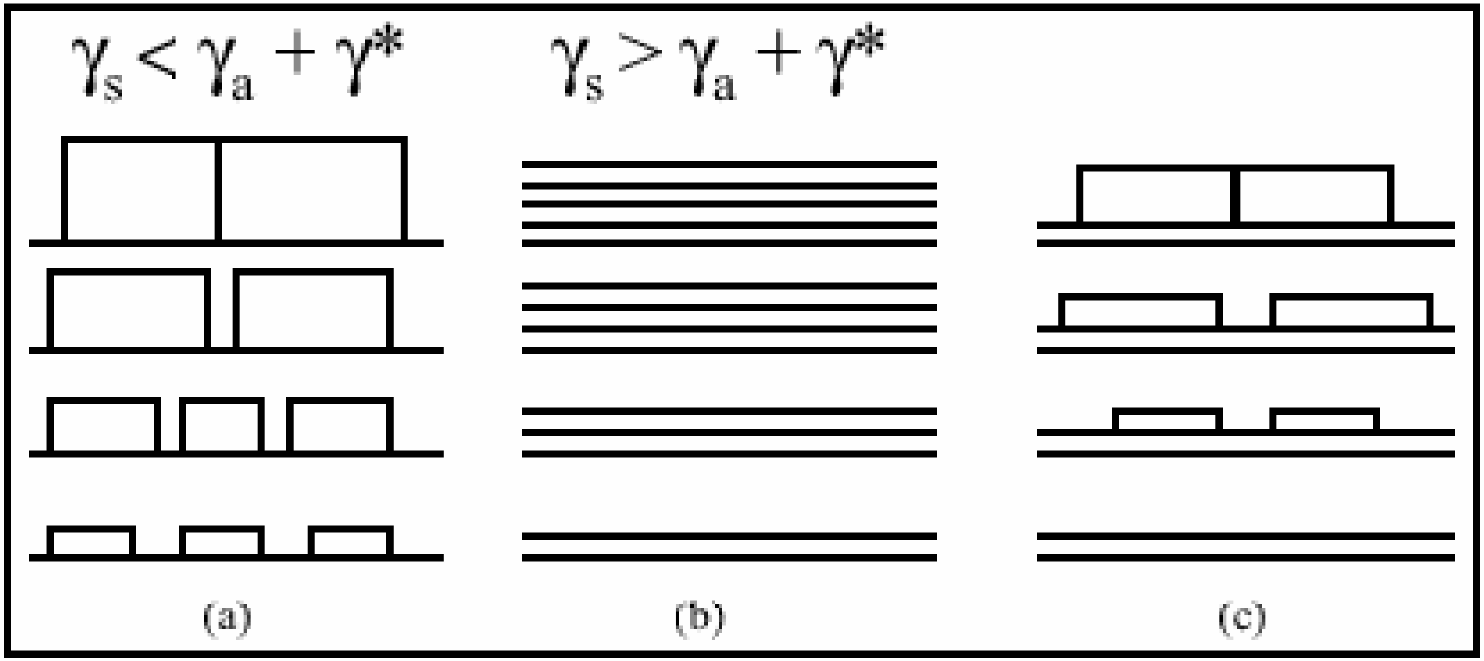
$$Ns\ S^2/\ \theta = f_i\,(s/S)$$

$f_i\,(s/S)$ 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)

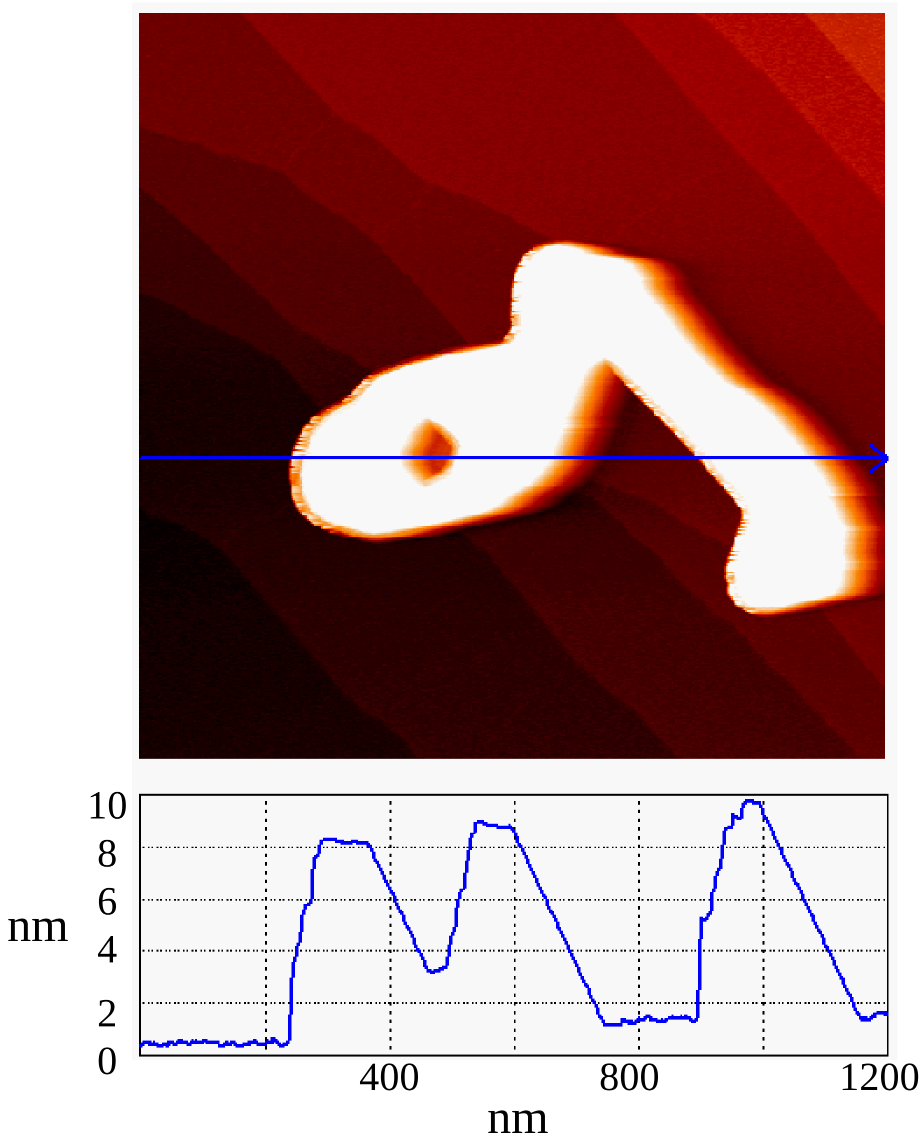
Stranski-Krastonov (SK)

γ_s : surface free energy of substrate

γ_a : surface free energy of adsorbate

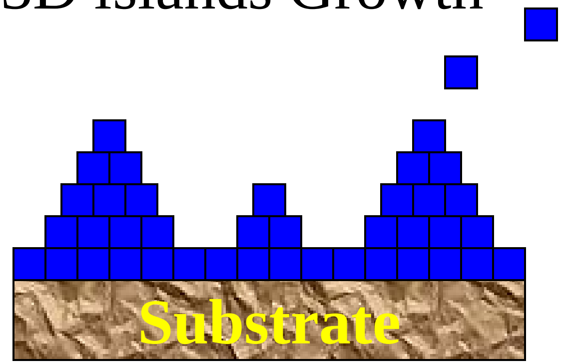
γ^* : interfacial free energy

Pb/Si(111) at RT



Stranski-Krastanov growth mode

3D islands Growth

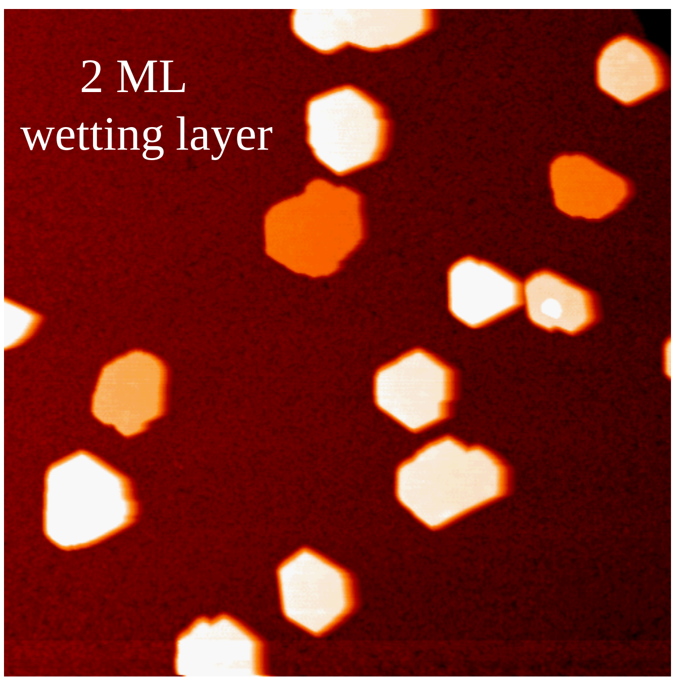


Layer + Island (SK) Growth

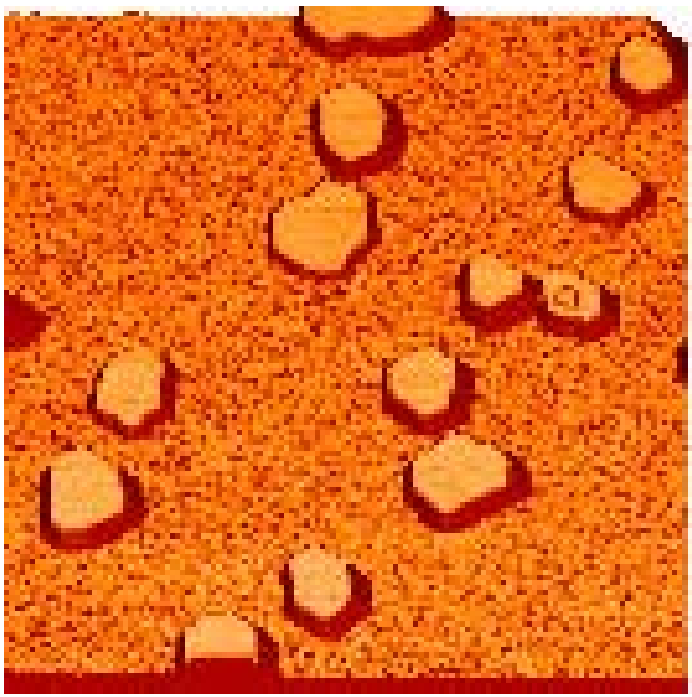
The Growth of 2D Pb islands on Si(111)7×7 surfaces at Low Temperature

T=208K, θ = 3.2 ML Pb

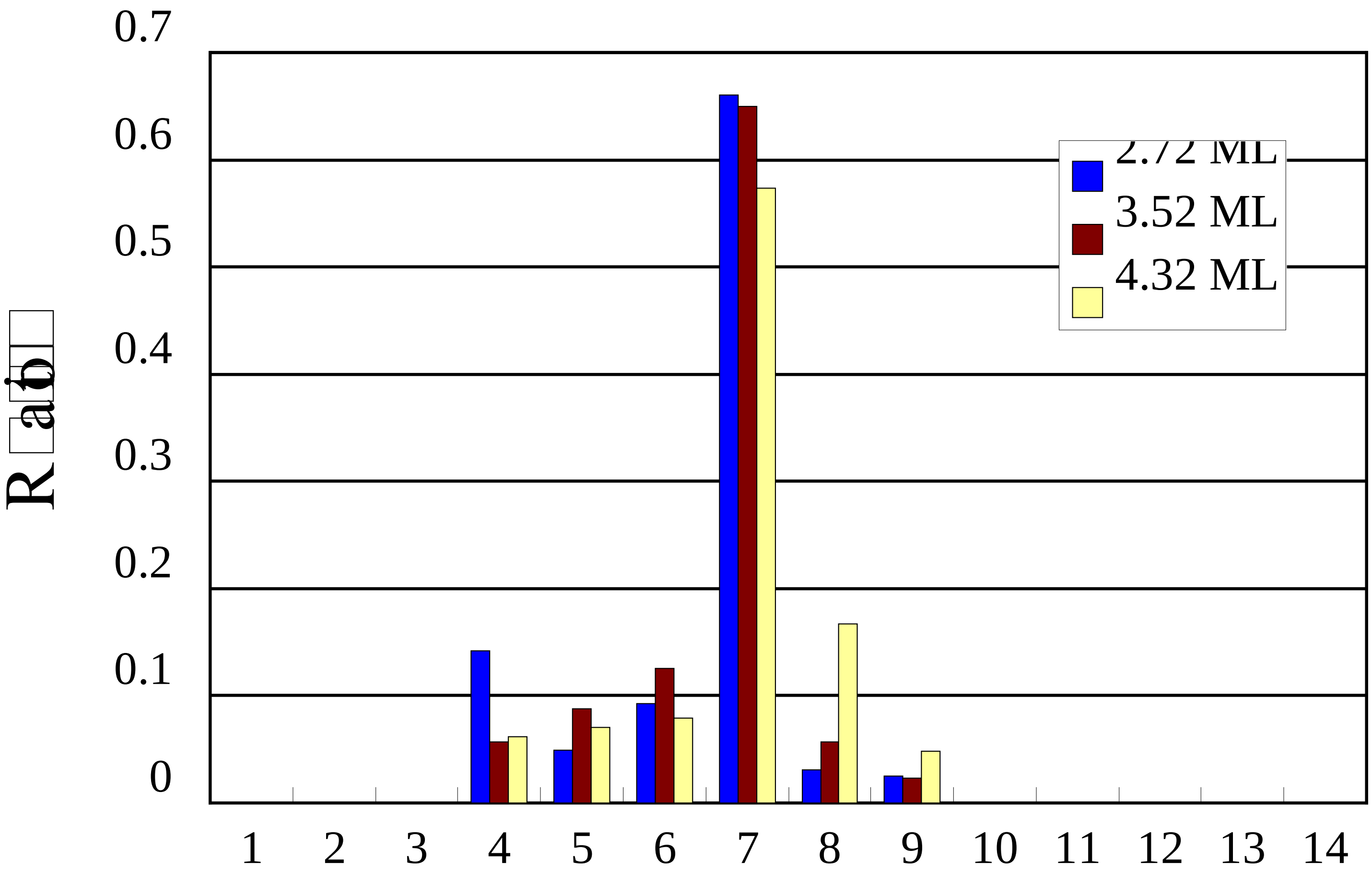
Topography



3D image of topography

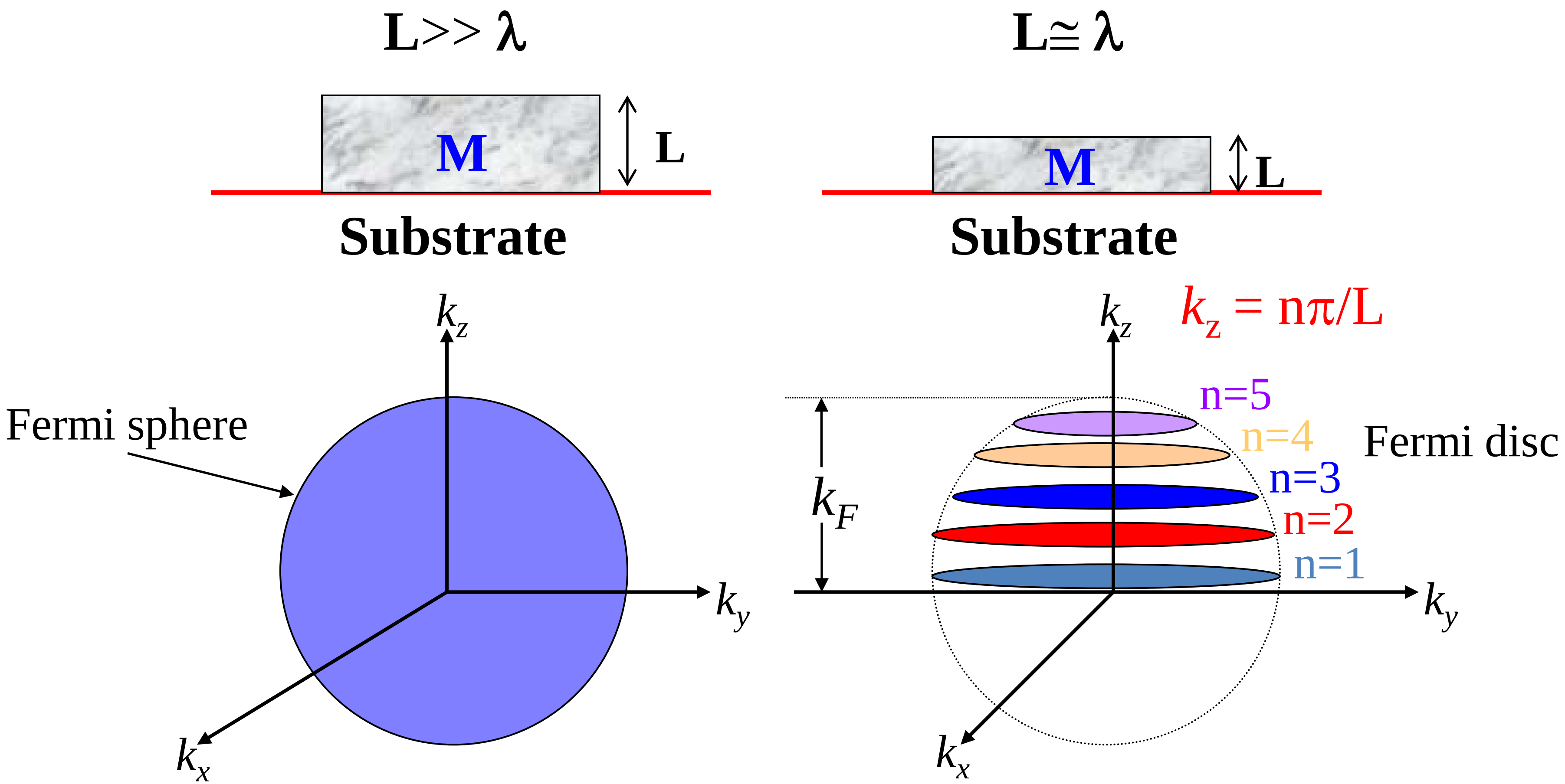


Phys. Rev. Lett. 86, 5116 (2001)

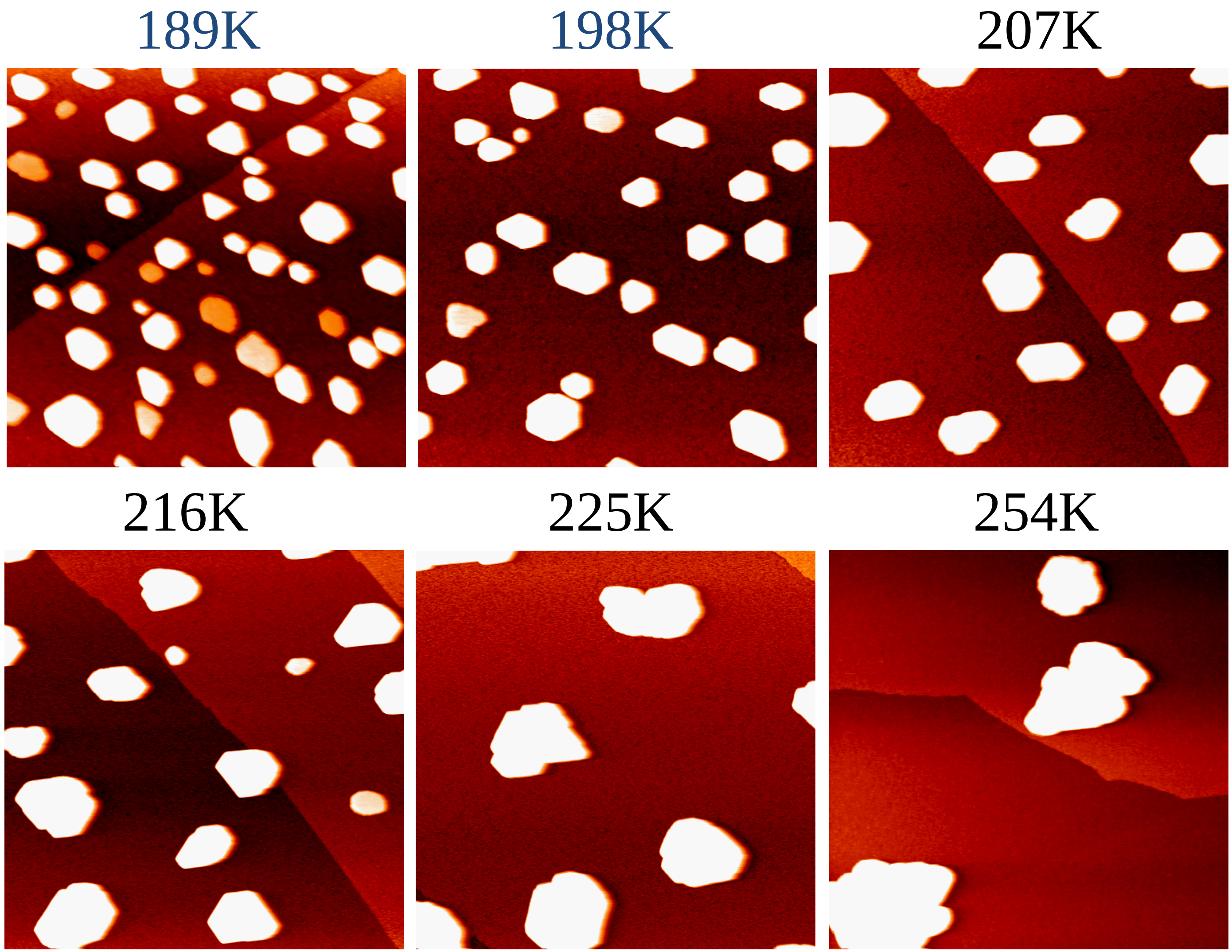

0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
2.72 ML
3.52 ML
4.32 ML
1
2
3
4
5
6
7
8
9
10
11
12
13
14

Quantum Size Effect-Driven Epitaxial Growth

λ = de Broglie wavelength of electron



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



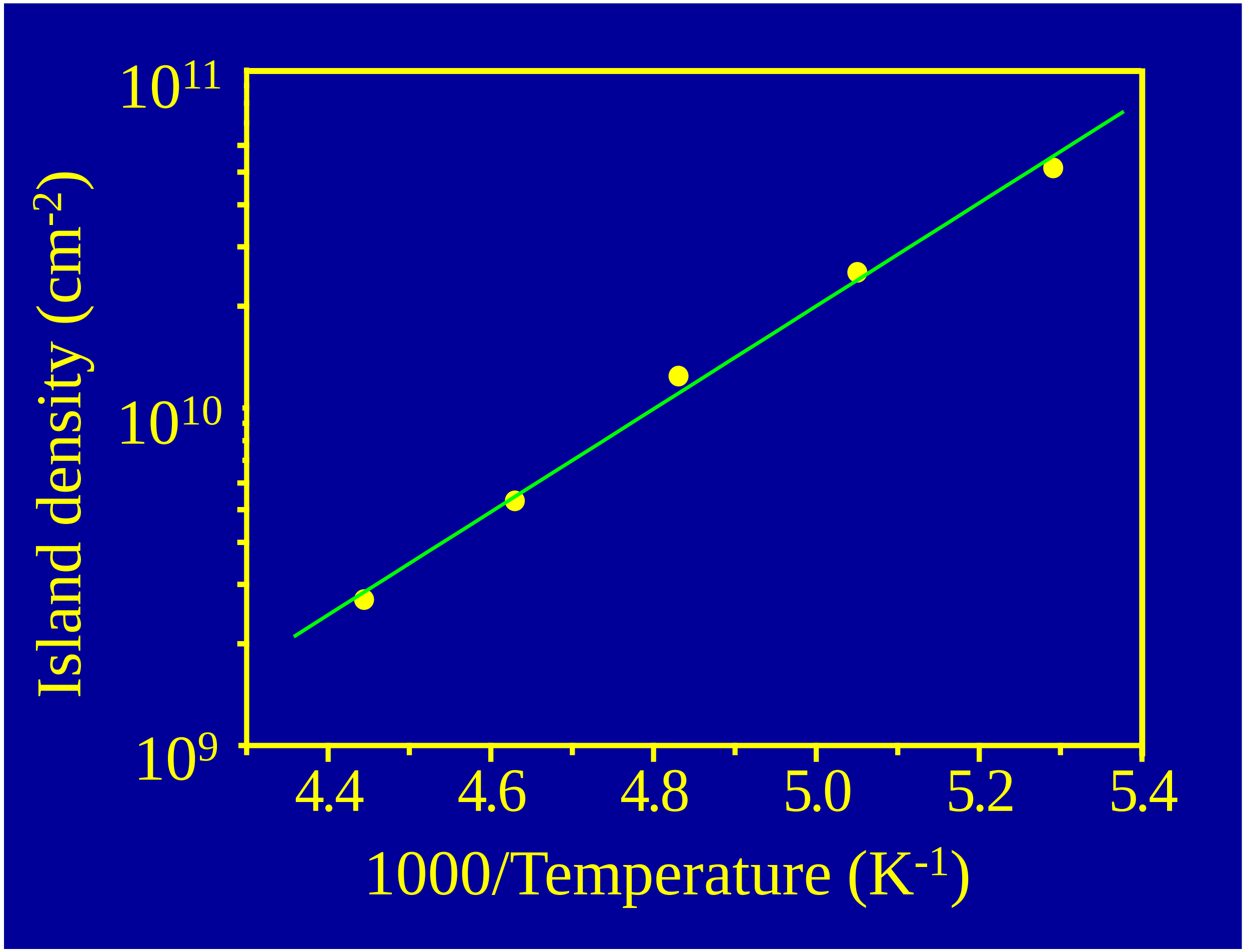
$$N \sim \exp[(iE_d+E_i)/(i+2)k_BT]$$

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

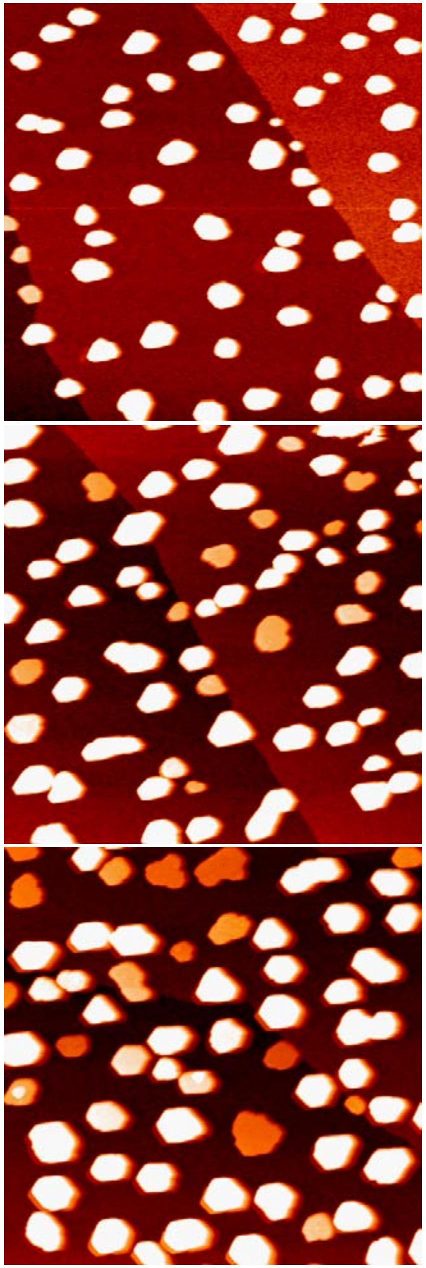


- The nucleation and the quantum size effect are two independent factors in the formation of an island, the former results in the creation of an island and the latter determines the thickness of the created island.

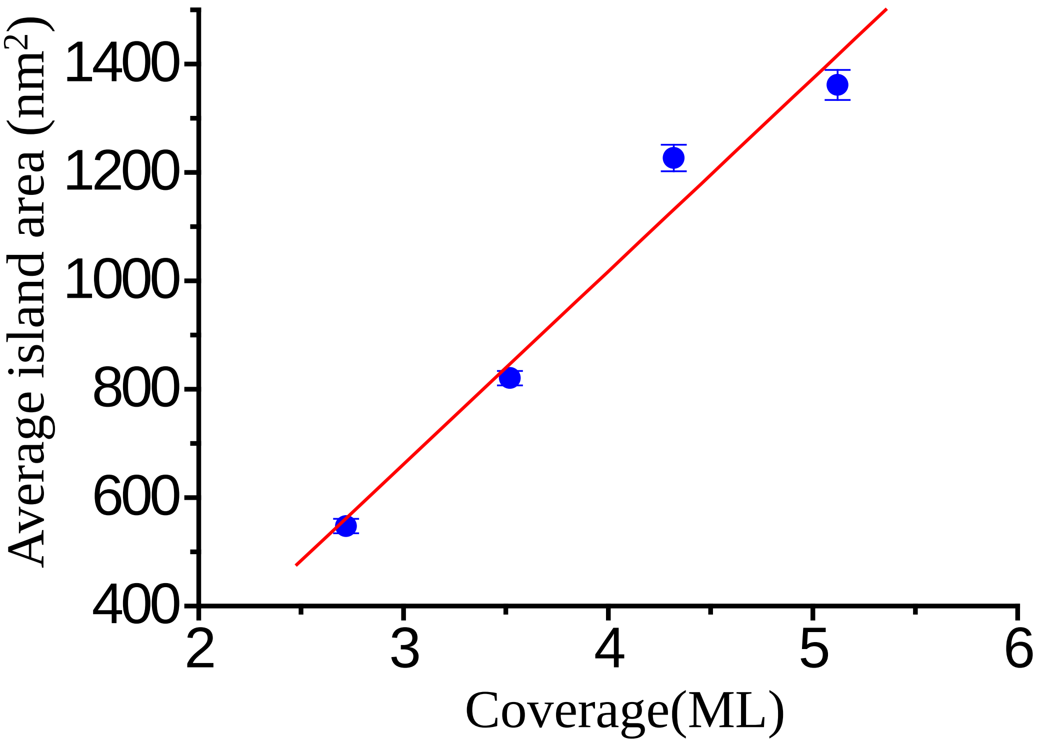
2.72 ML

3.52 ML

4.32 ML

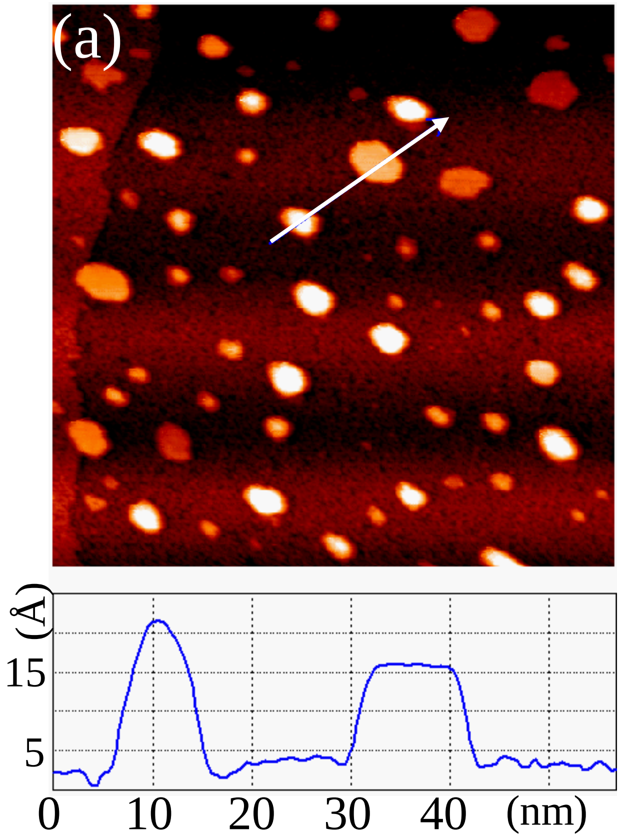


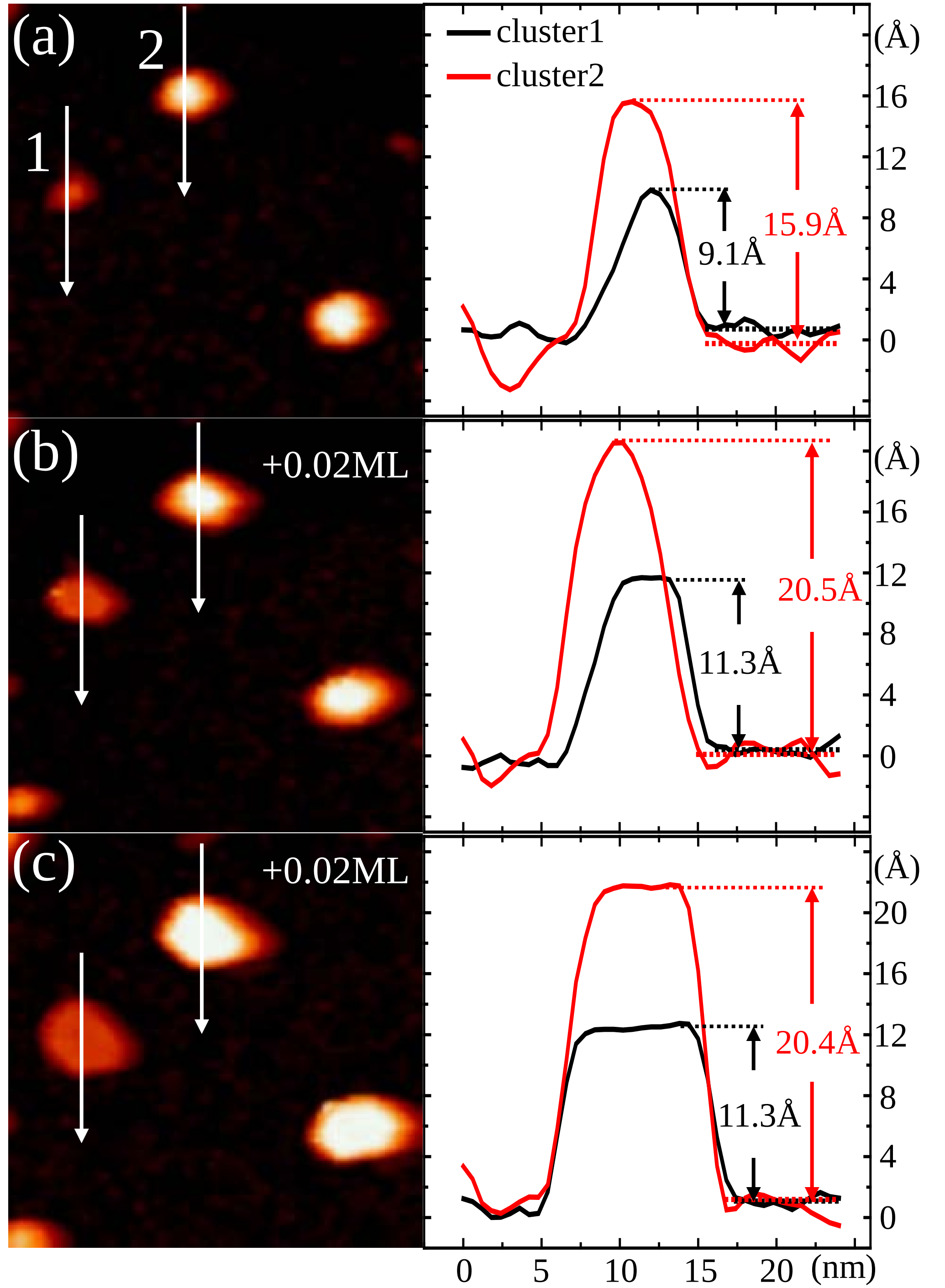
(500×500 nm^2)



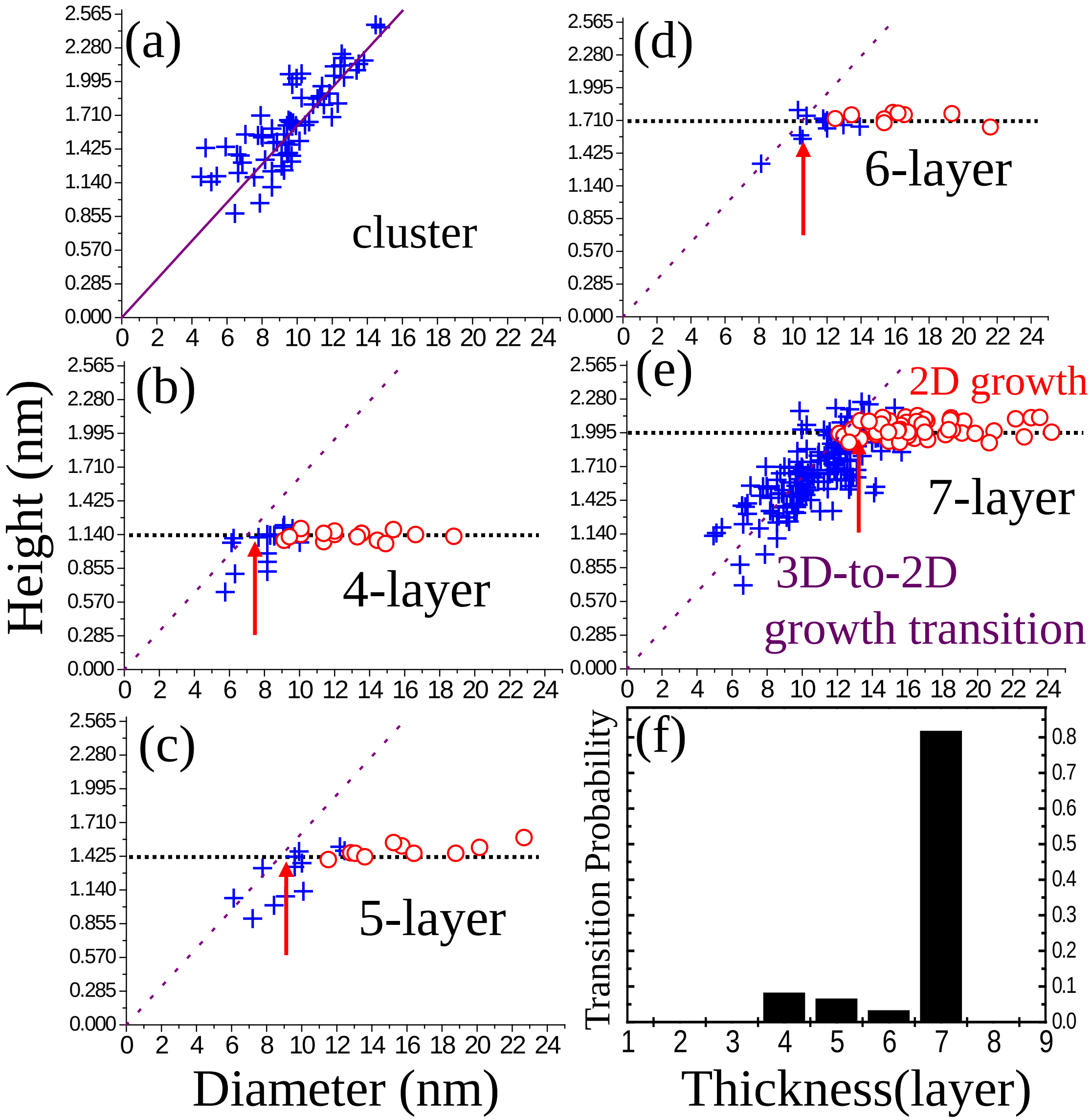
2D Growth driven by the quantum size effect

2.3 ML, 170 K





Phys. Rev. B 68, 033405 (2003)



- Growth transition induced by the quantum size effect

- Independent transition pathway:

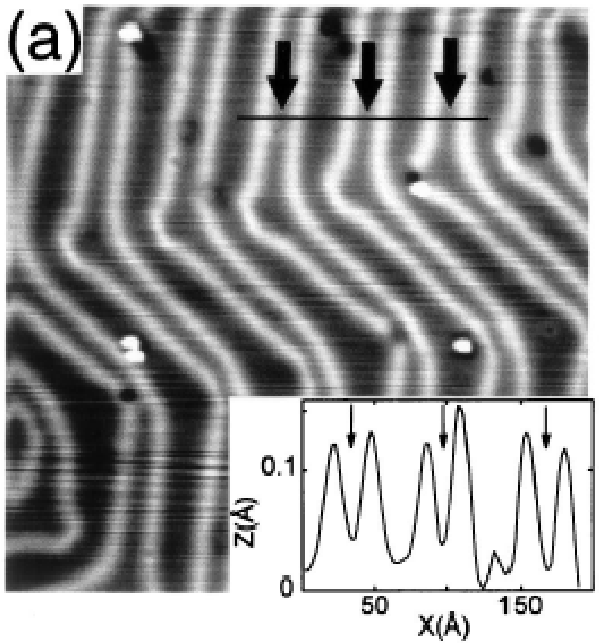
  N-layer thickness island is transformed from N-layer height cluster

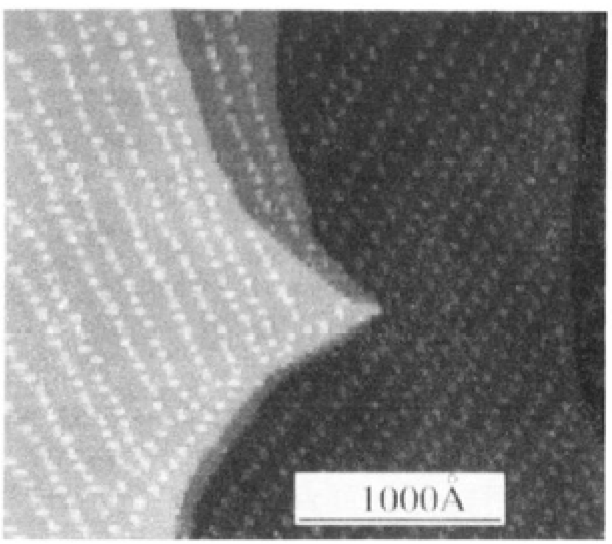
- Identical cluster can be of different electronic structure (quantum size effect).

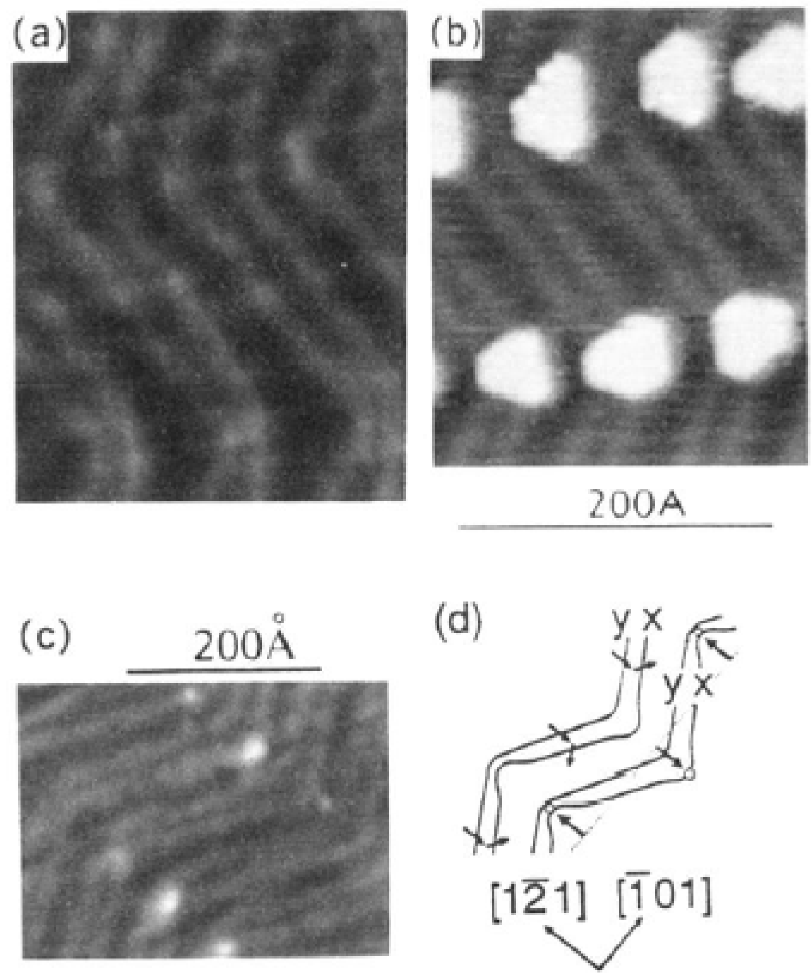
Phys. Rev. B 71, 073304 (2005)

Self-Assembly

Ni cluster on reconstructed Au(111)



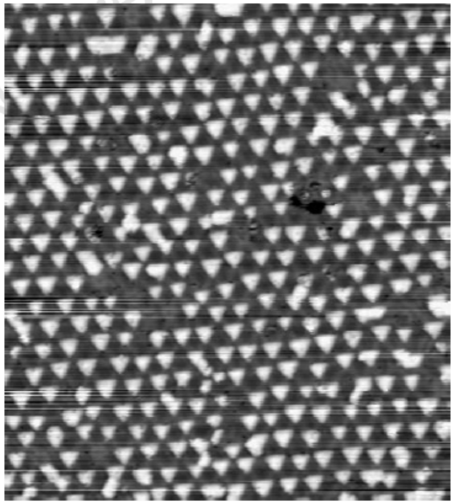




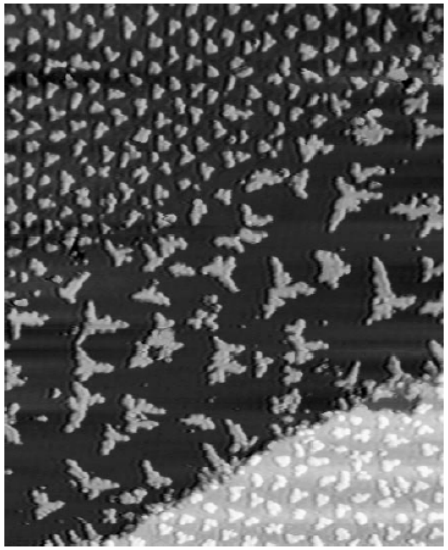
Phys. Rev. Lett. 66, 1721 (1991).

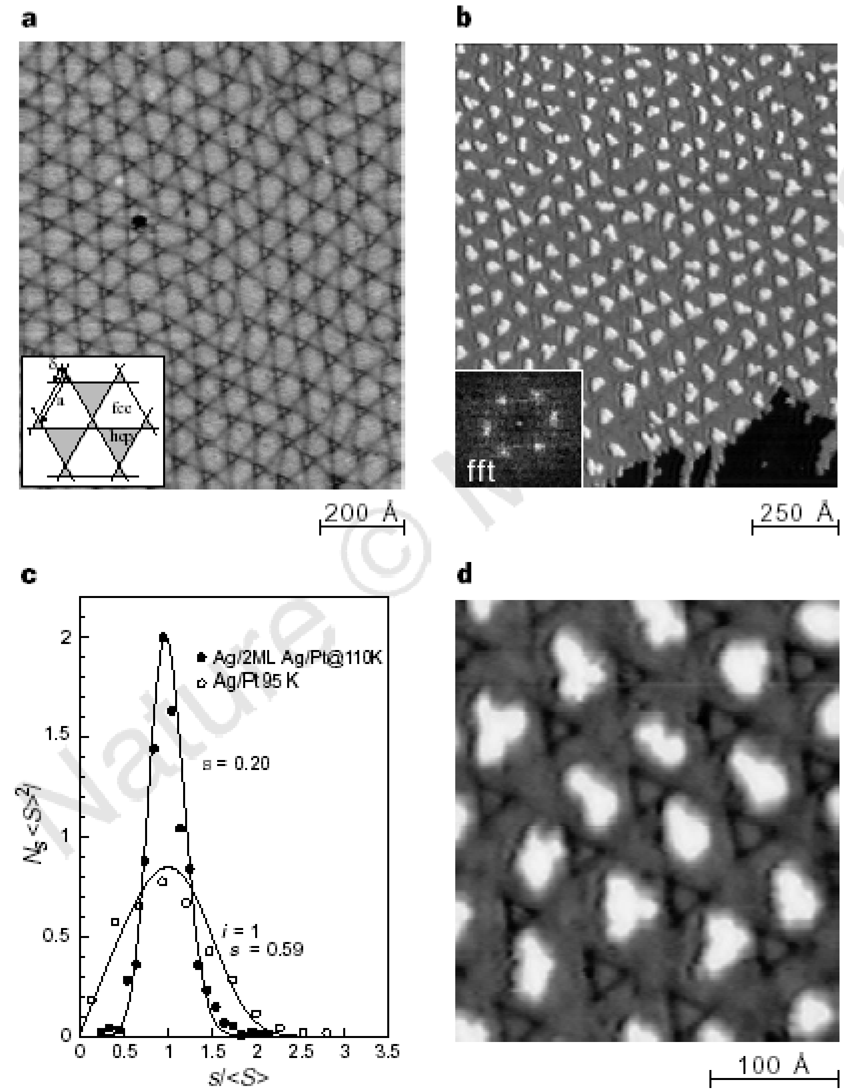
Self-organized growth of nanostructure arrays on strain-relief patterns

Fe islands/Cu/Pt(111)



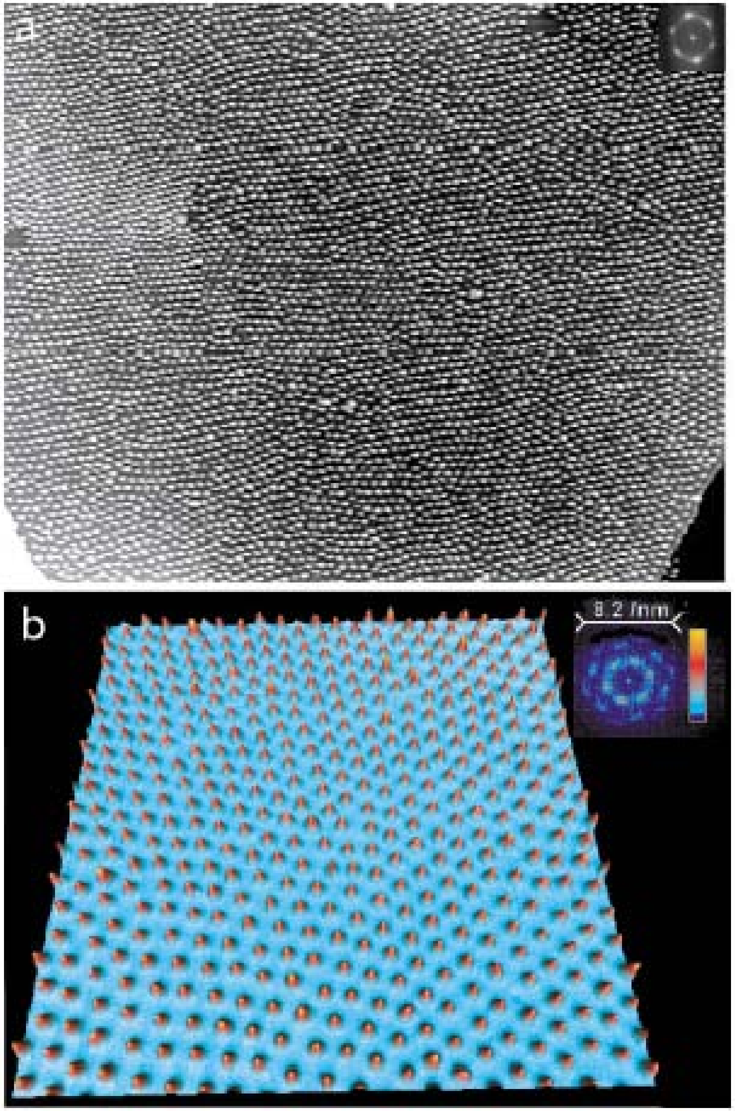
Ag island/Ag/Pt(111)



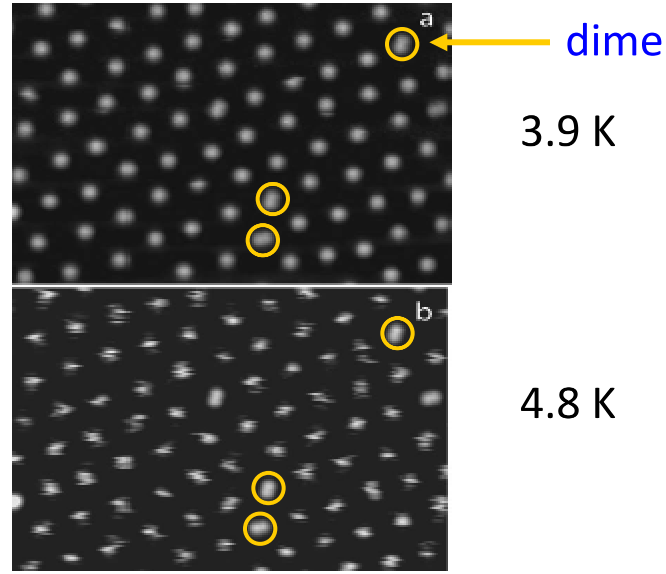


Nature 394, 451 (1998)

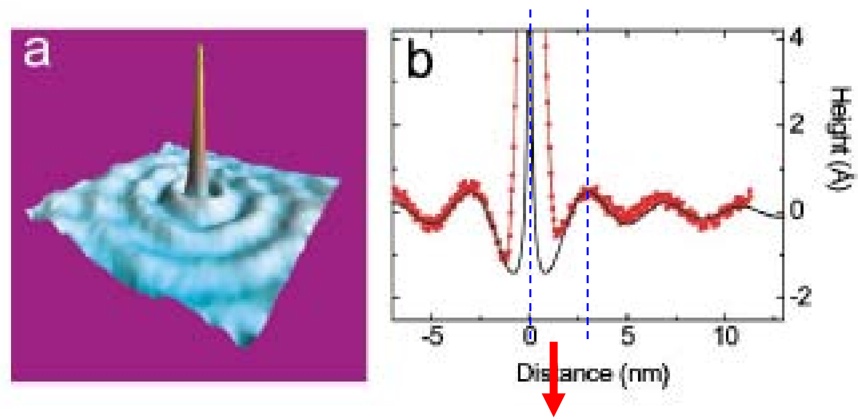
Ce atomic superlattice on Ag(111) at 3.9 K



Lattice constant=32 Å



lattice disappear at 10 K

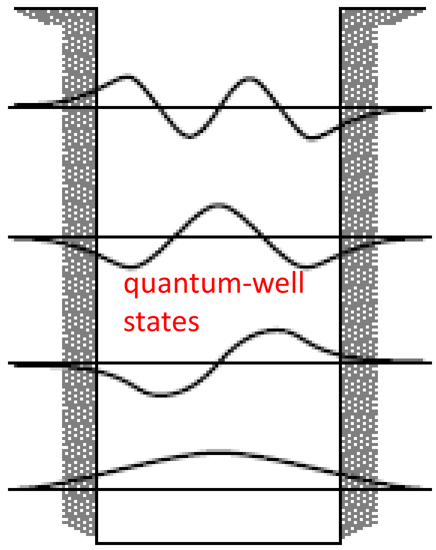


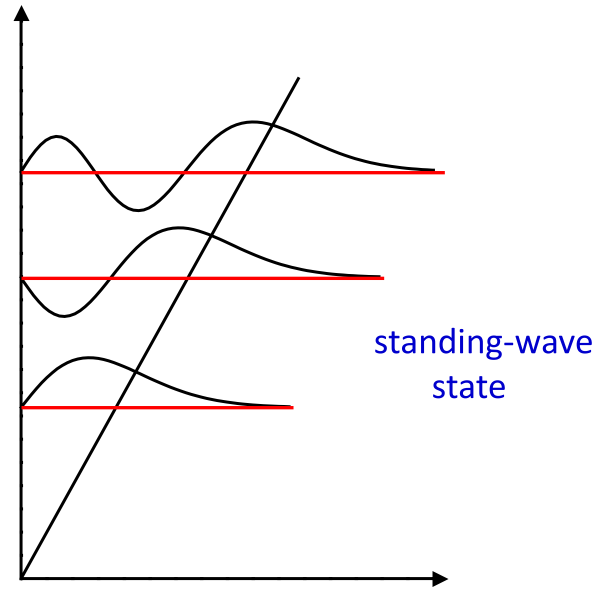
Ce superlattice is created by standing wave formed around Ce atoms.

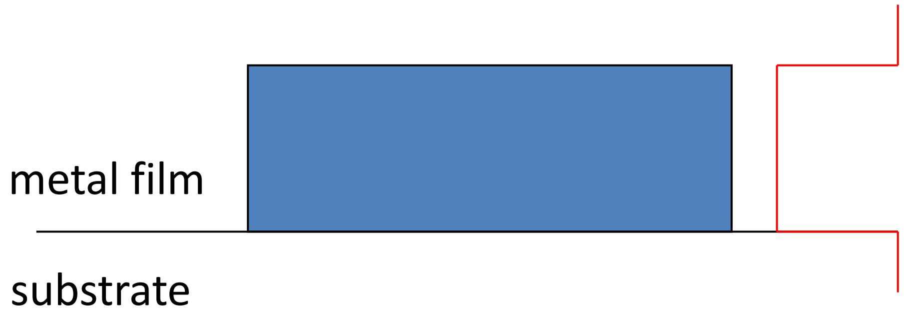
Ce: Cerium (鈰), 稀土族, 原子序:58

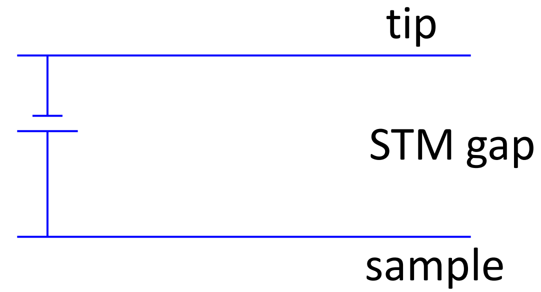
Phys. Rev. Lett. 92, 016101 (2004).

Quantum Confinement Effect



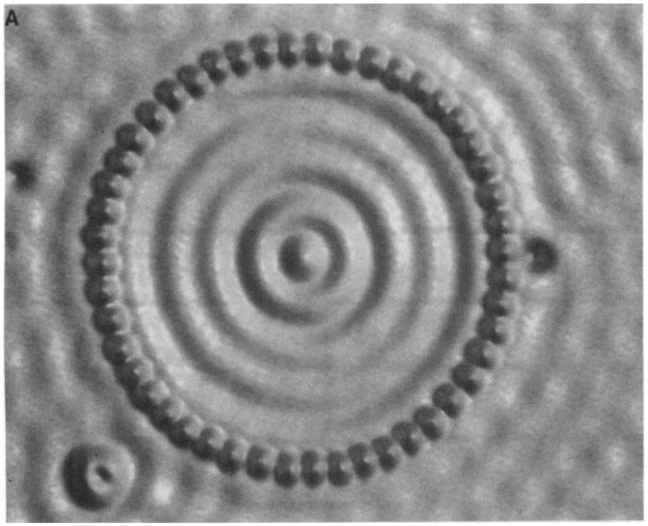






Visualization of quantum confinement effect with STM & STS

STM

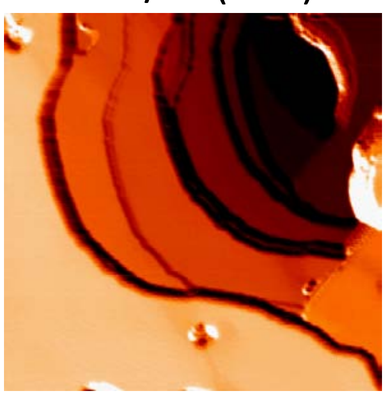


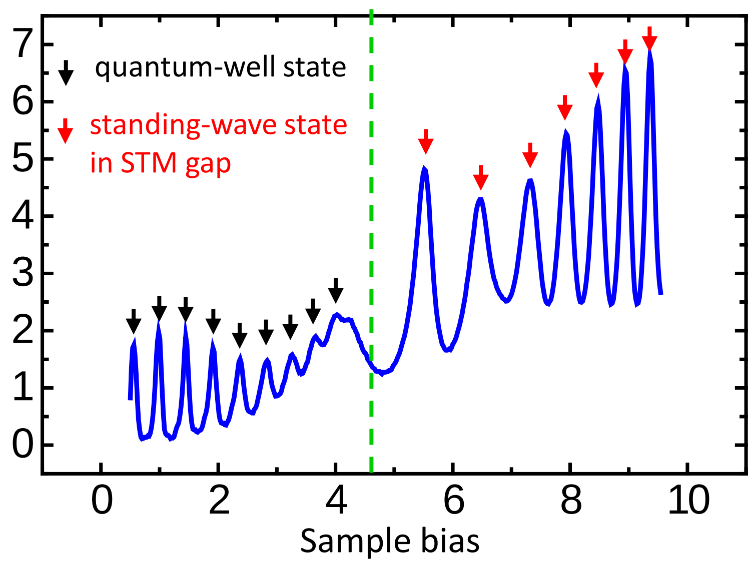
Quantum corral by Eigler et al. in IBM

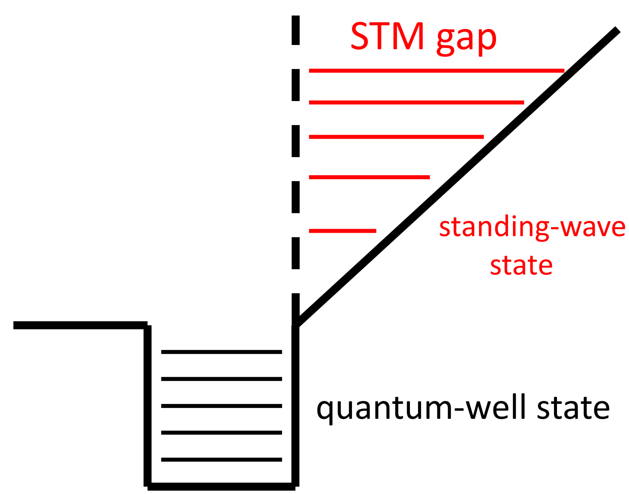
2D electron gas on Cu(111)

STS

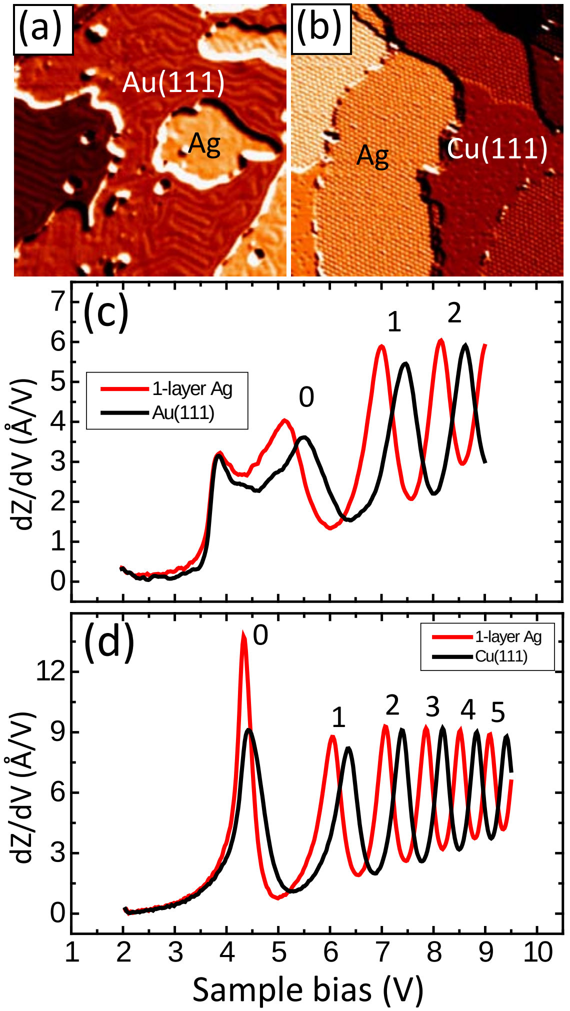
Pb/Cu(111)

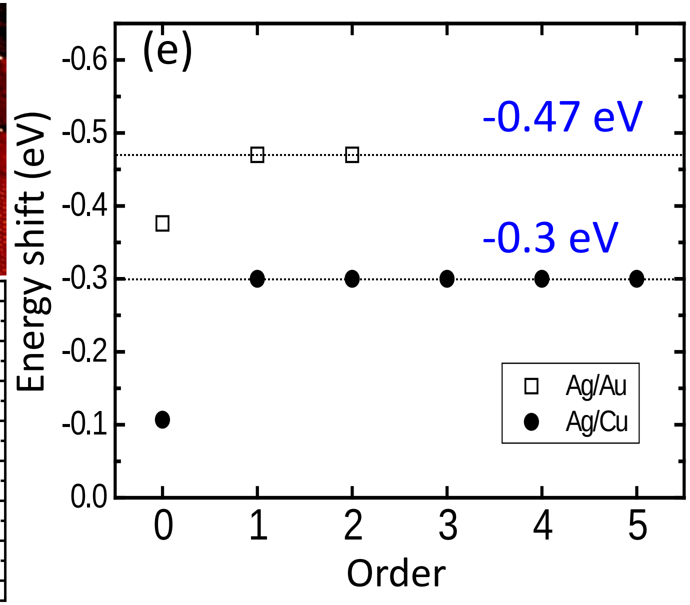




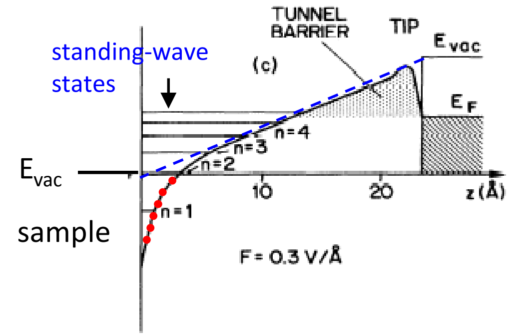


Application of standing-wave state in STM gap on work function measurement of thin metallic film

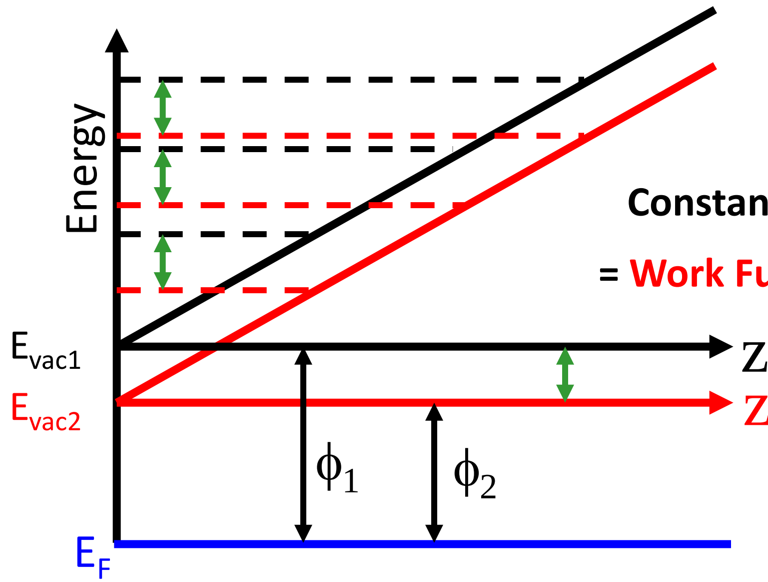




Phys. Rev. Lett. 99, 216103 (2007)



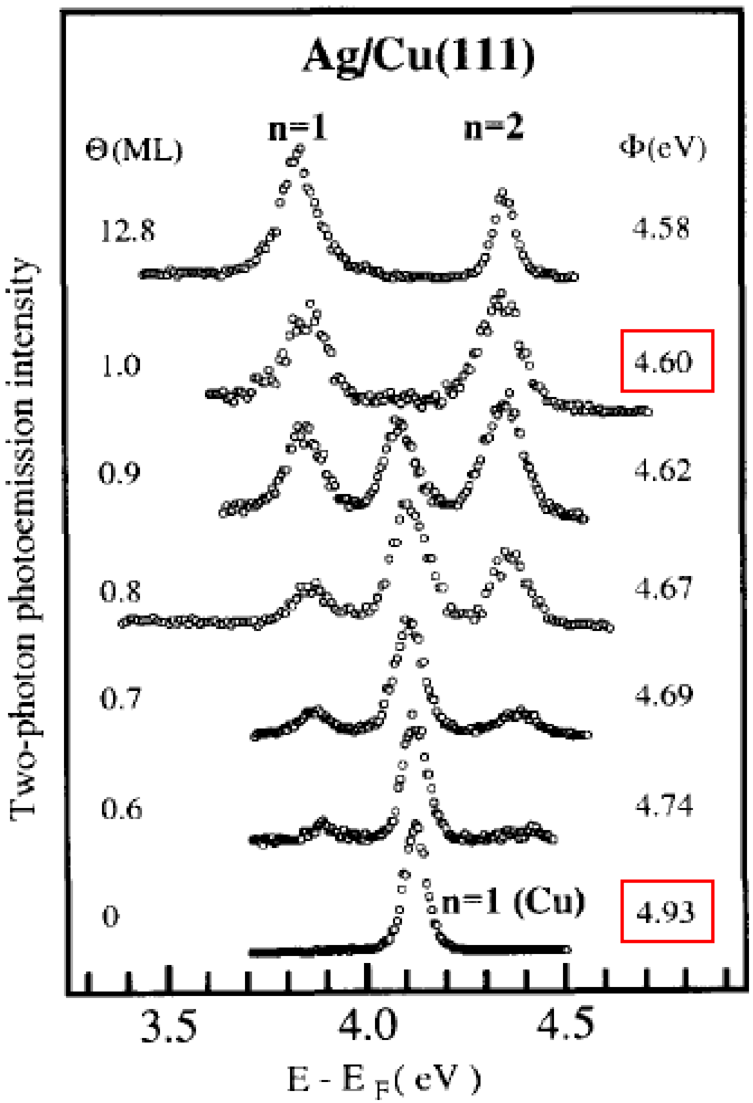
Superposition of image potential and applied potential



Constant Energy Shift

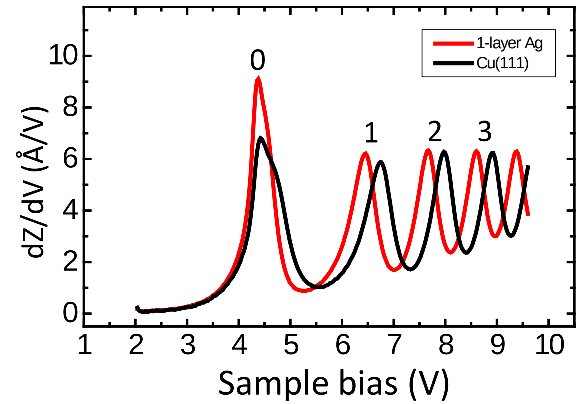
= Work Function Difference

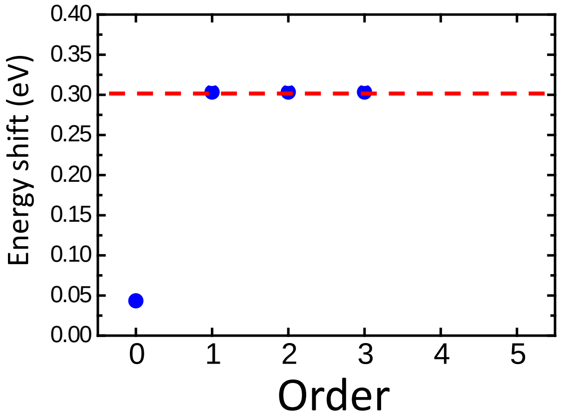
Photoemission (-0.33 eV)



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

Standing-wave states (-0.3 eV)



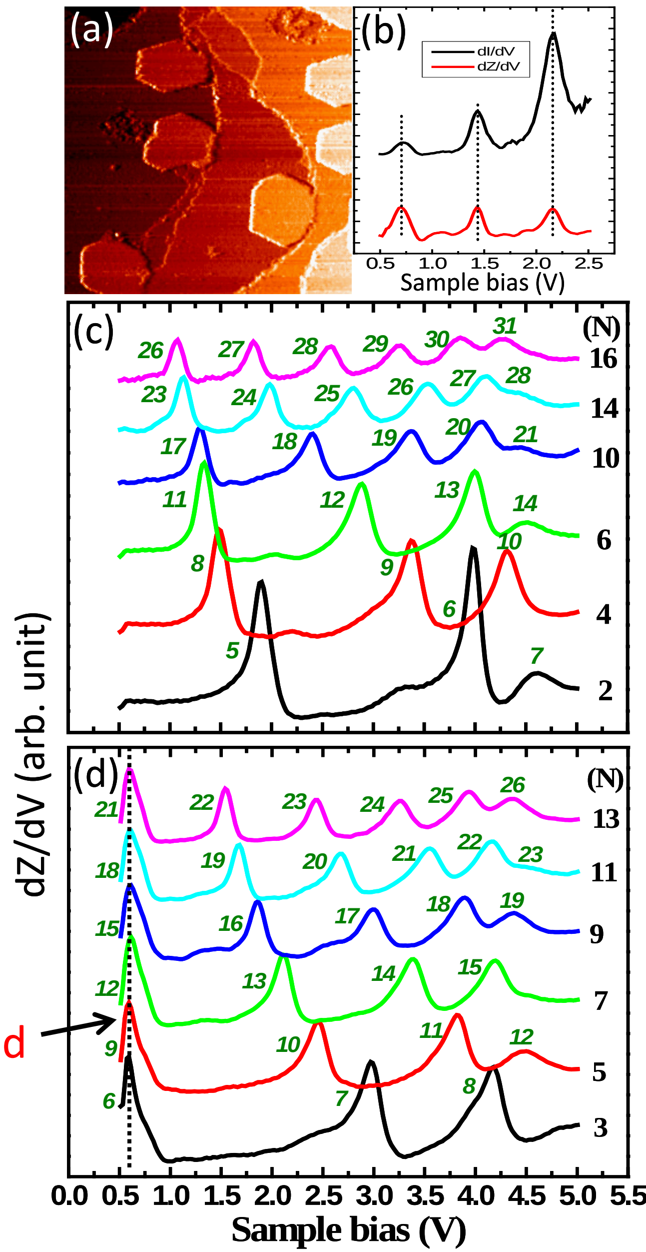


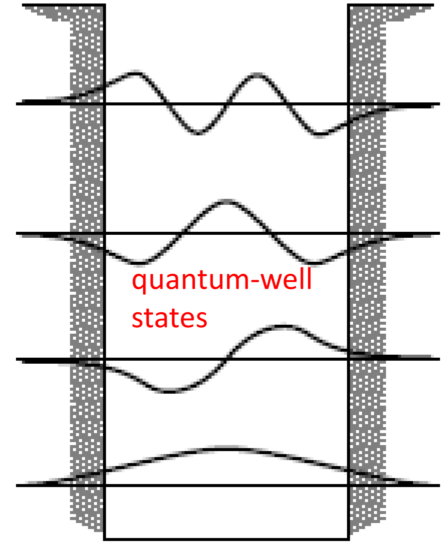
Both techniques are consistent.

Precision can be better than 20 meV.

Influence of image potential effect on empty quantum well states

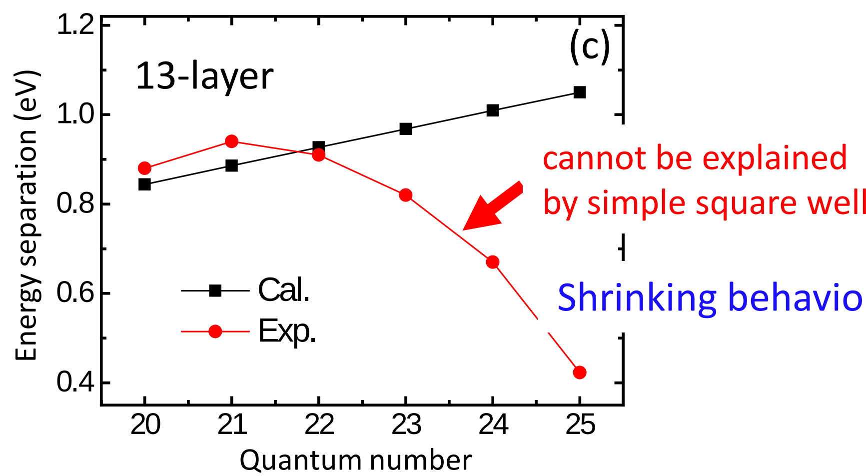
Pb island/Cu(111)





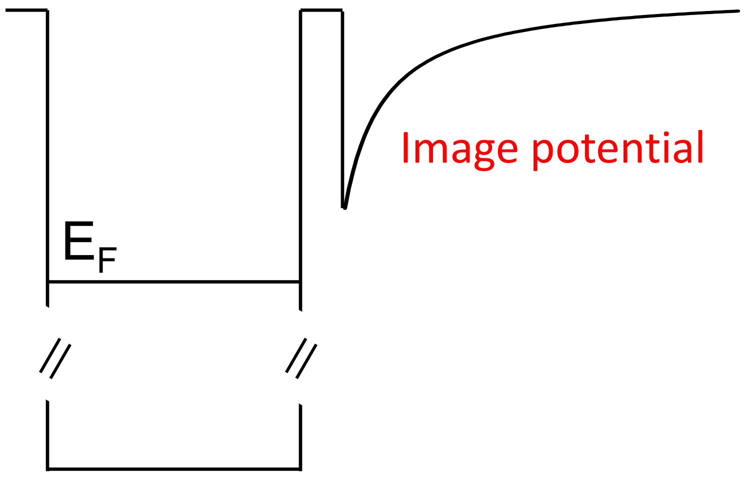
$$2k(N+1)d=2n\pi$$

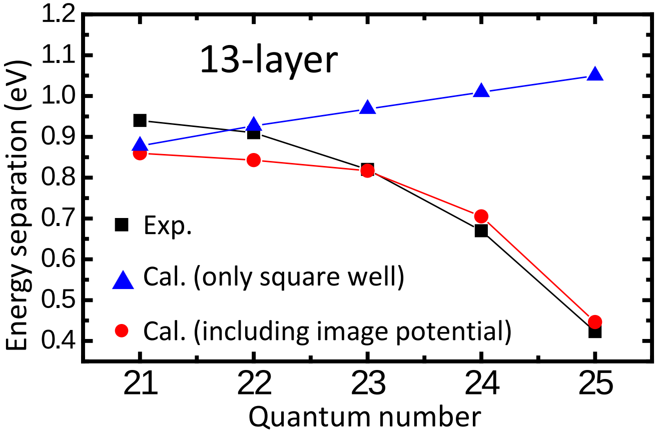
$$\Delta E= \hbar^2(2n+1)\pi^2/2m^*(N+1)^2d^2$$



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

Manifestation of image potential effect through Empty Quantum Well States





E_V=4.6 eV above E_F

$$\hbar^2k^2/2m^*=E+E_F$$

$$m^*=1.14\ m_0$$

For simple square well:

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

Including phase ϕ_B contributed from image potential

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

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

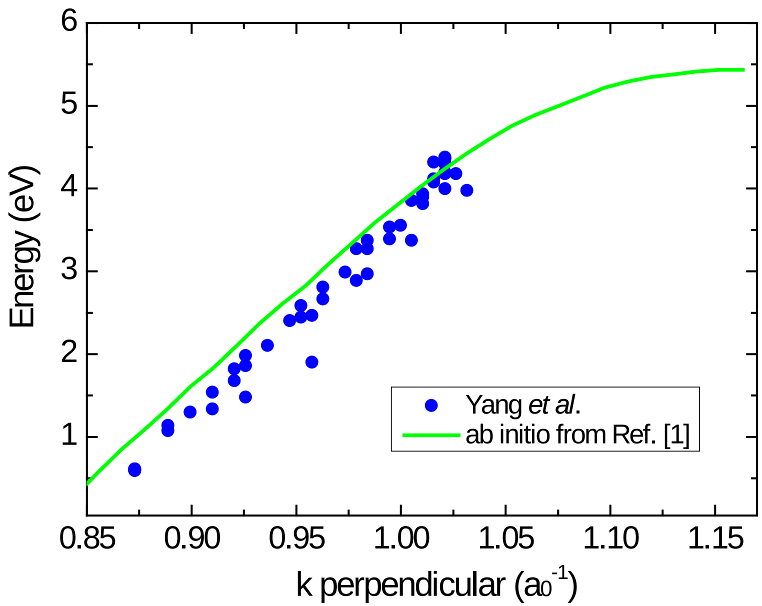
E: energy of quantum well state

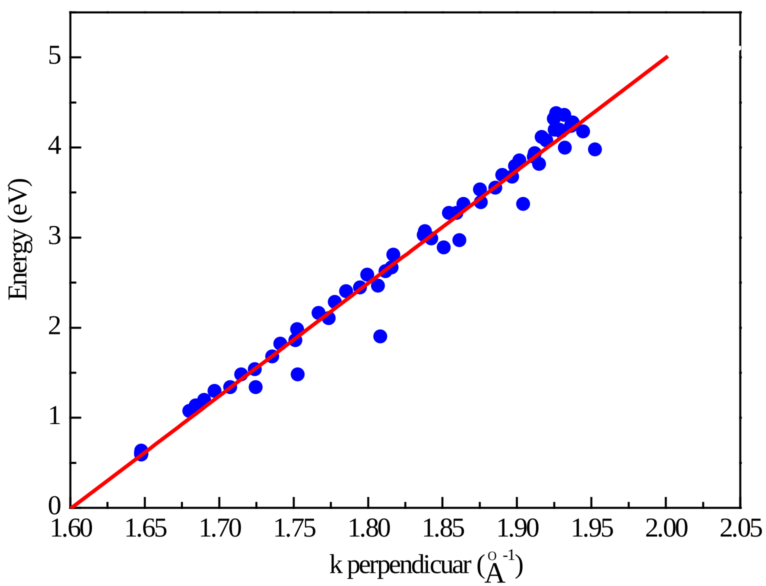
E_V: vacuum level

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

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

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





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

$k_F=1.6$ Å^{-1}

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