Photoemission (2)
Surface Science

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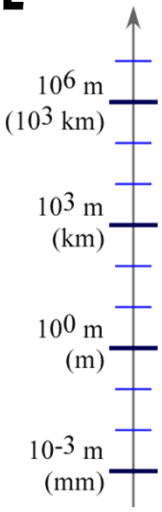
Surface/Interface in scales



Space
The Earth/Vacuum interface

Climates
Sea/Air interface

Skins
Face/Air interface

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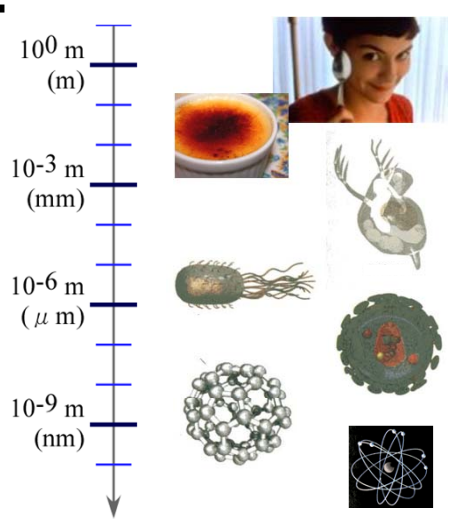
Surface/Interface in scales



Goods
(solid/air interface)

Cooking
(Oil/water interface)

Biomaterials surviving
in various environments

Molecules and atoms
in various conditions

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Surface/Interface in scales

- Things go on in a non-uniform system in any scale.

And there're always interfaces (surfaces) that play their roles.

- Solid/Liquid
- Solid/Gas
- Liquid/Gas
- Solid/Solid
- Solid/Vacuum
- ……..

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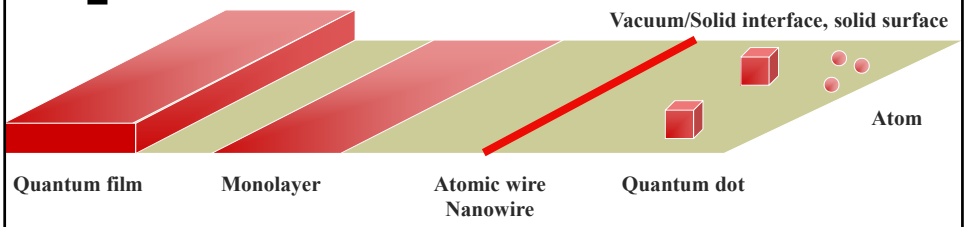
My playground



Nanometer-scale and atomic-scale structures on a solid surface.

Chemistry	Physics	Applied Physics
・Catalysis reaction ・Ecology ・Solutions for energy-shortage problem	・Low-dimensional physics ・Quantum dynamics ・New physics	・Bottom-up nanotechnology ・Atom technology ・New technological developments

Advantage of surface science:
- **Visualization of atomic configuration and electron density (LDOS) distribution in atomic scale**
- **Direct determination of electronic structure (band, Fermi surface, etc…)**

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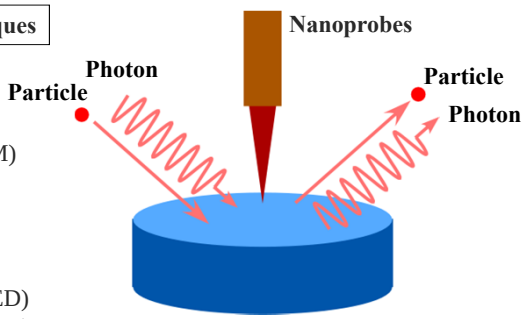
Surface Analyses

Varieties of Surface analysis techniques

Given examples…….



Nanoprobes

Scanning Tunneling Microscope (STM)
Atomic Force Microscope (AFM)

Particle-in / Particle-out

He scattering
Low-energy electron Diffraction (LEED)
Transmission Electron Diffraction (TED)
Refection High-Energy Electron Diffraction (RHEED)
Refection High-Energy Positron Diffraction (RHEPD)

Photon-in / Photon-out

Grazing-angle incident X-ray Diffraction (GIXRD)

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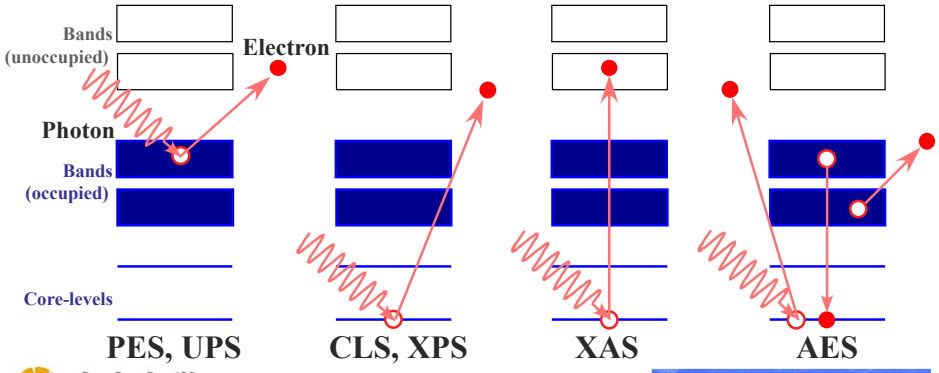
Surface Analyses

Photon-in / Particle-out

Photoemission Spectroscopy (PES), Ultraviolet Photoelectron Spectroscopy (UPS)
Core-level Spectroscopy (CLS), X-ray Photoelectron Spectroscopy (XPS)
X-ray Absorption Spectroscopy (XAS)
Auger Electron Spectroscopy (AES)



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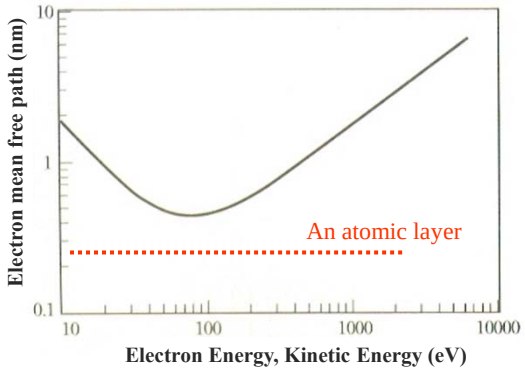
Spectroscopy with VUV~SX

- Electron mean free path

surface-sensitive ~ bulk sensitive



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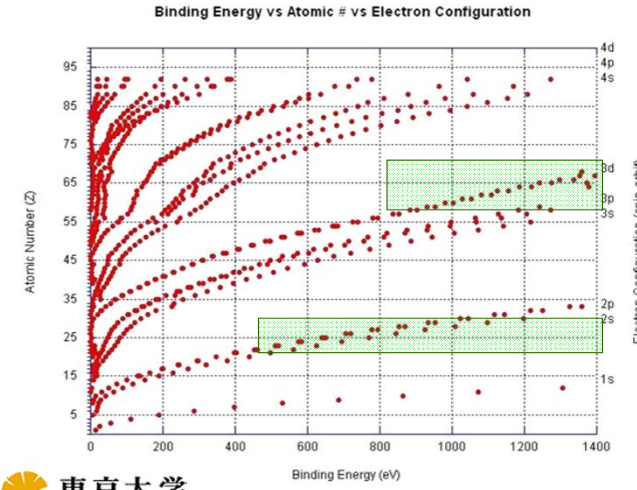
Spectroscopy with VUV~SX

- Absorption edge, resonance effect



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Spectroscopy with VUV~SX

- **Energy range to probe**
  - **- atomic structure**
  - **- electronic structure**
  - **- spin structure**

- Diffraction
- Absorption (EXAFS,NEXAFS,MCD)
- Photoemission (ARPES, CLS, Spin-resolved PES, PED)
- X-ray emission

- surface sensitive ~ bulk sensitive
- specification of all elements
- structure determination with high accuracy
- spin magnetic moment, orbital magnetic moment
- direct determination of spin-resolved electronic structure

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Cutting a Si(111) crystal

Atomic structure

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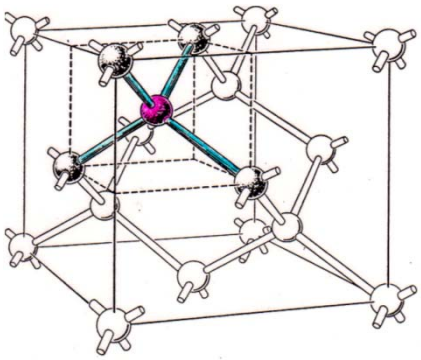
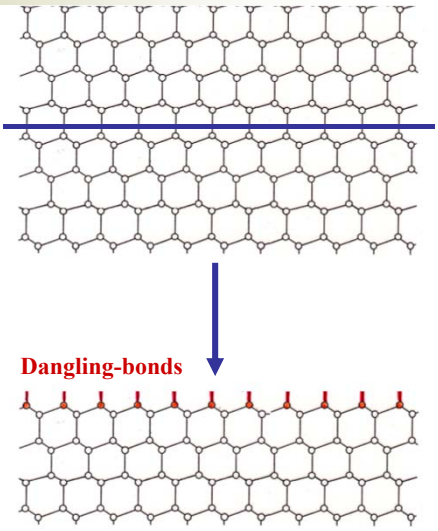
Cutting (expectation)

Silicon (Si)
Diamond structure





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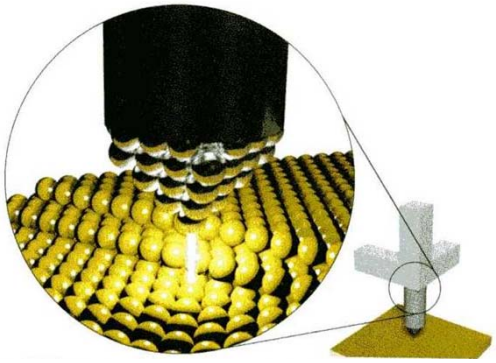
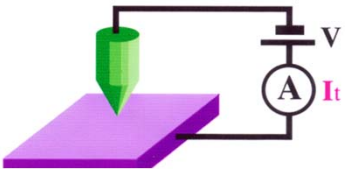
Scanning Probe Microscope

Scanning Tunneling Microscope (STM)



Rohrer and Binnig (1982)



Tunneling Current $It \propto f(v) \cdot e^{-\sqrt{\Phi} \cdot d}$

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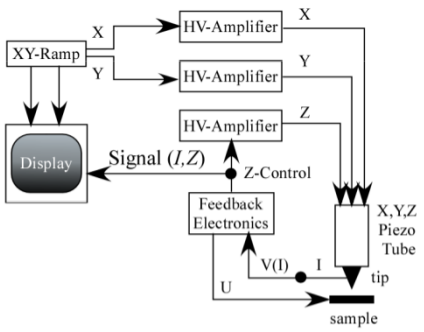
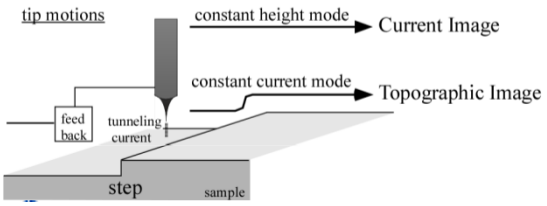
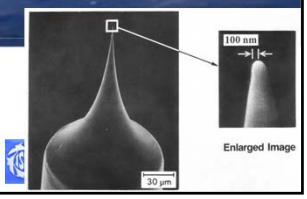
STM

Scanning Tunneling Microscope (STM)



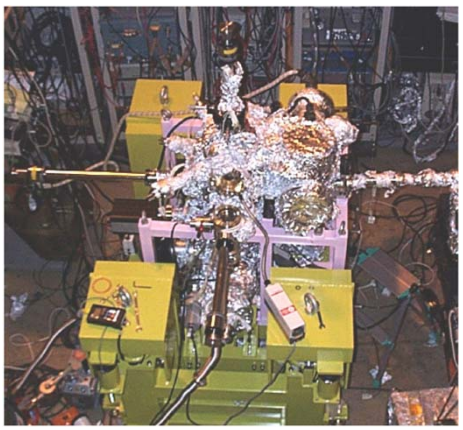




Scanning Tunneling Microscope

An experimental chamber

- the Ultra High Vacuum condition
- Isolation of vibration
- Sample surface preparation



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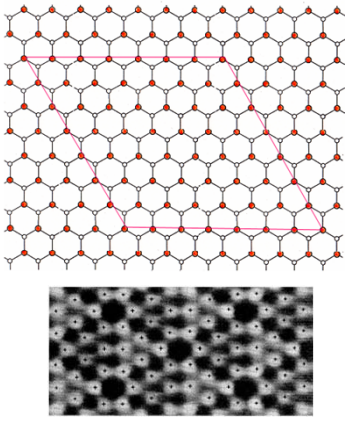
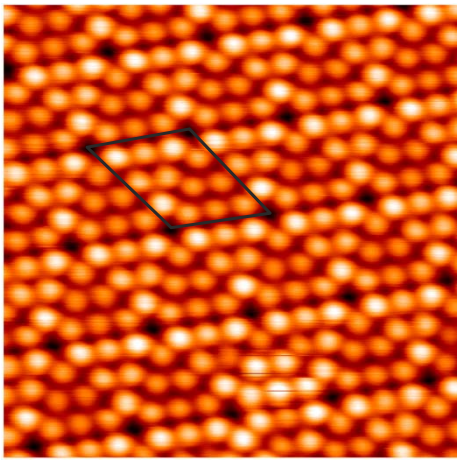
An STM image

Ideal surface



Real surface (STM image)



G. Binnig, H. Rohrer *et al*., Phys. Rev. Lett. **50** (1983) 120.

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The $7a_{1x1}$ (a_{1x1}:3.8Å) periodicity:
The Si(111)7x7 surface

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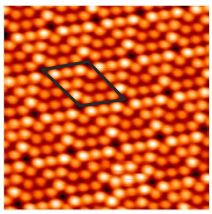
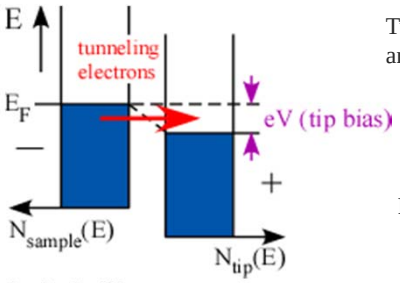
Scanning Tunneling Microscope



It's just an image of atomic scale protrusions measured through tunneling currents.

What are them?



Tunneling currents between unoccupied states and occupied states near Fermi level (EF).

Protrusions in STM could be surface atoms

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Cutting a Si(111) crystal

Electronic structure

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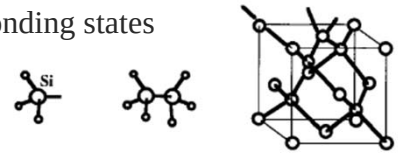
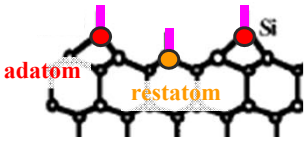
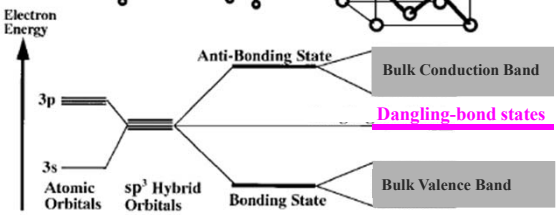
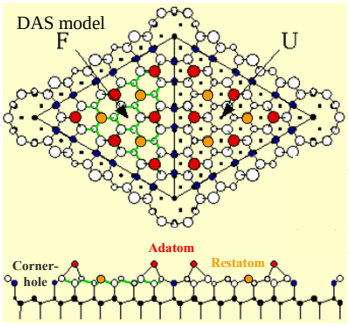
Electronic states of Si(111)7x7

- Bonding states









# of dangling bonds in the 7x7 unit cell

adatom: 12
restatom: 9
corner-hole: 1

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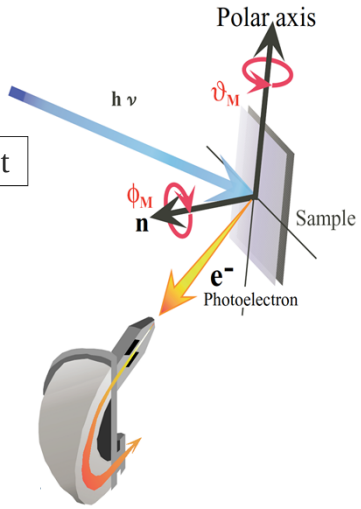
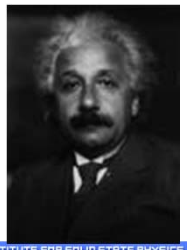
Probing electronic states

photoelectric effect



Dr. Albert Einstein



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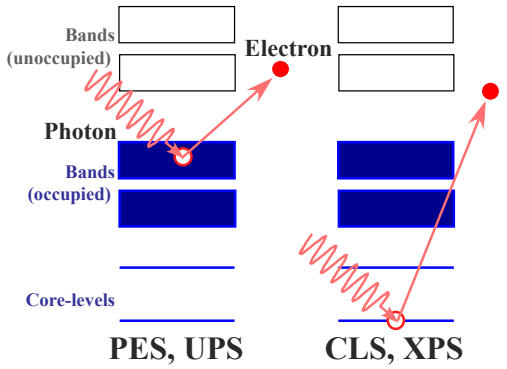
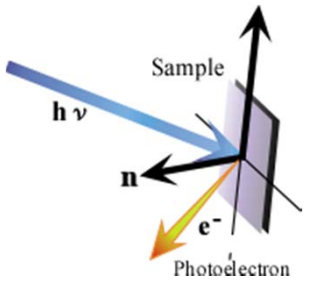
Probing electronic states

- Photoelectron spectroscopy





$E_k = h\nu - \Phi - E_B$

work function binding energy

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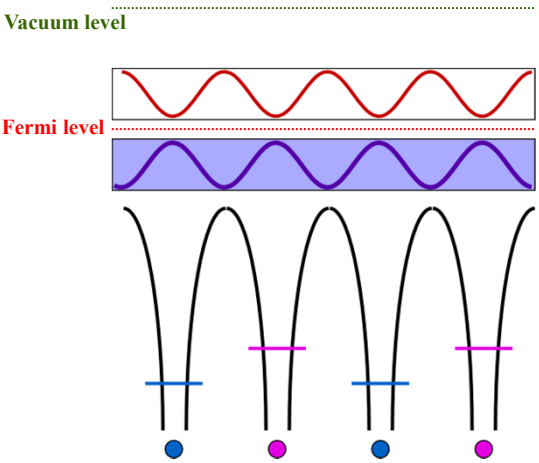
What can be probed by photoemission



Band Dispersions of
- partially occupied states (metal)
- fully occupied states (semicpnductor)

Energy shift of core-levels
- Different elements
- Different chemical sites (environments)

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Band mapping

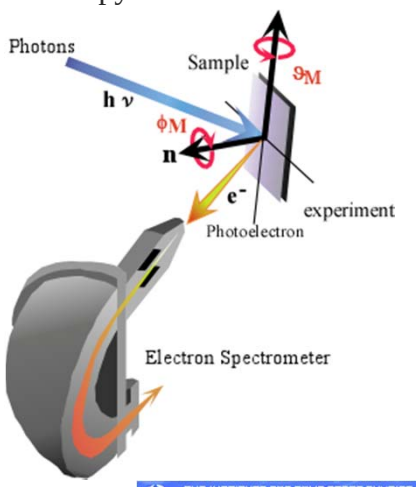
- Angle-resolved photoemission spectroscopy (ARPES)

$$E_k = h\nu - \Phi - E_B$$

work function, binding energy

$$k_{\parallel}(\text{Å}^{-1}) = 0.512\ \{(h\nu - \Phi - E_B)\}^{1/2} \cdot \sin\theta_e$$

→ Band dispersion $(E, k_{//})$



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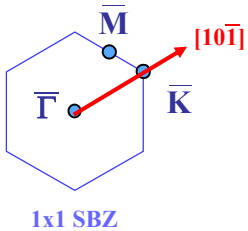
ARPES measurement

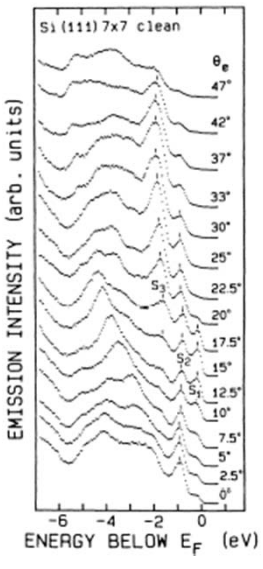
Si(111)7x7

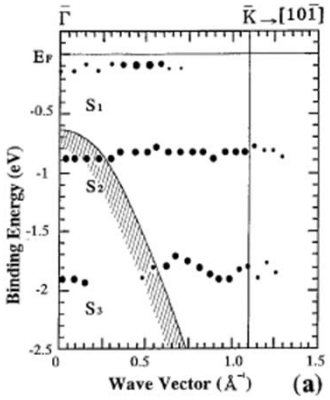
Conventional measurements

Energy spectra at various angles along symmetric crystal axis



1x1 SBZ





P. Martensson *et al.*, Phys. Rev. B **36**, 5974 (1987).

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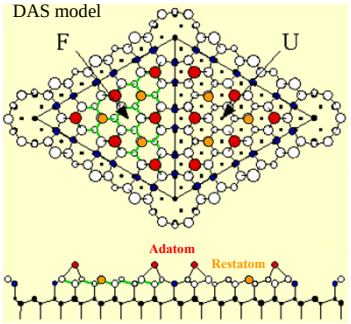
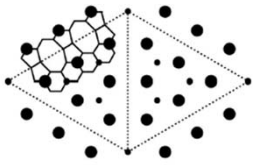
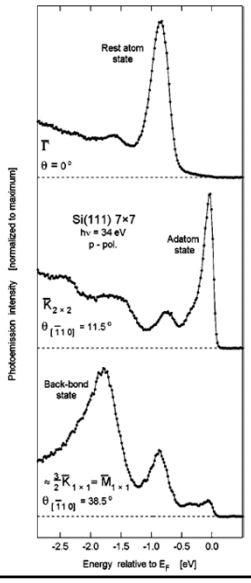
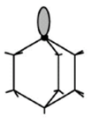
Dangling bonds

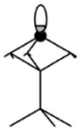








Rest atom state
(Fully occupied)



Adatom state
(Partially occupied)

- Charge transfer
- Metallic surface

R. Losio *et al.*,
Phys. Rev. B **61**, 10845 (2000).

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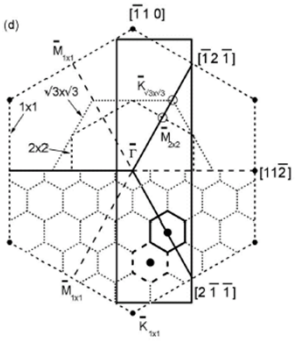
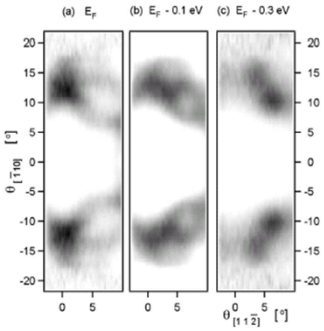
Fermi surface mapping

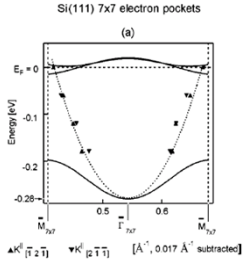
- Adatom state

Si(111)7x7

Photoemission intensity mapping
Intensity of a certain energy taken at various emission angles







R. Losio *et al.*,
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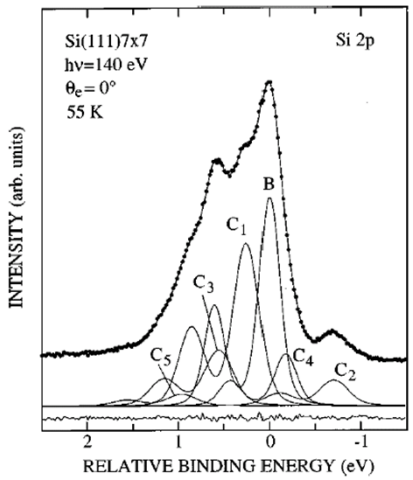
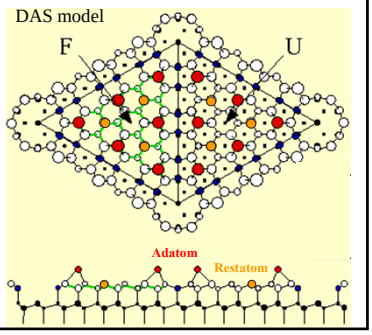
Core-levels



Surface components

C_1: Atom binding to the adatom
C_2: Rest atom
C_3: Adatom
C_4: Dimer atom
C_5: Surface impurity atom



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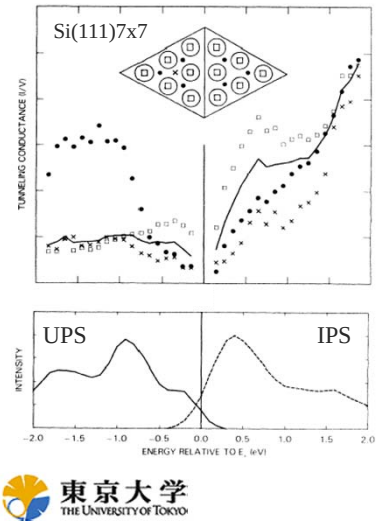
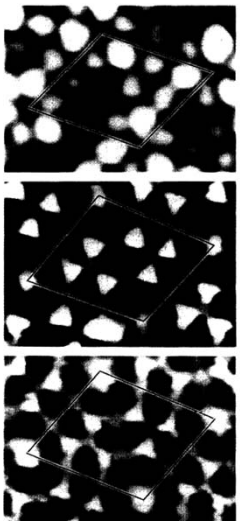
R. I. G. Uhrberg *et al.*,
Phys. Rev. B **58**, R1730 (1998).

Scanning Tunneling Spectroscopy

Tunneling Spectroscopy at different sire



Differential Current Imaging Tunneling Spectroscopy



Adatom state @ - 0.35 V

Rest atom state @ - 0.8 V

Back bond state @ - 1.7 V

R. J. Hamers *et al.*,
Phys. Rev. Lett. **56**, 1972 (1986).

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Cutting a Si(111) crystal

Adsorption

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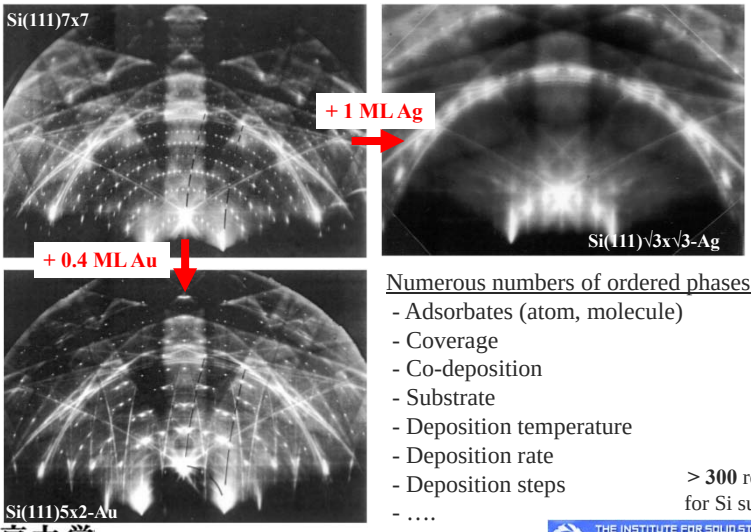
Variations of ordered surface phases



Numerous numbers of ordered phases
- Adsorbates (atom, molecule)
- Coverage
- Co-deposition
- Substrate
- Deposition temperature
- Deposition rate
- Deposition steps
- ….

> 300 reported for Si substrate

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S. Hasegawa *et al.*, Prog. Surf. Sci. **60**, 89 (1999).

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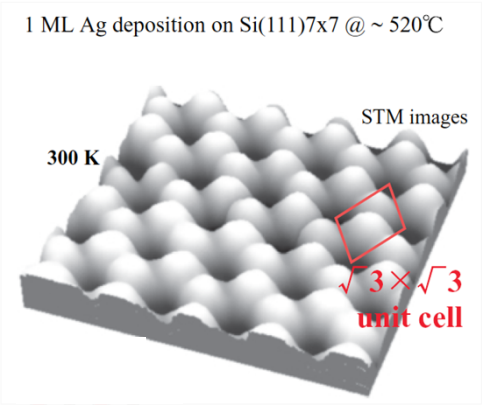
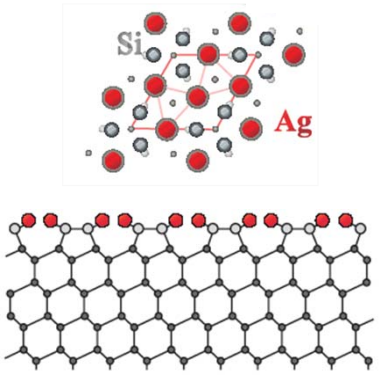
Si(111)√3x√3-Ag

- Atomic Structure and STM image





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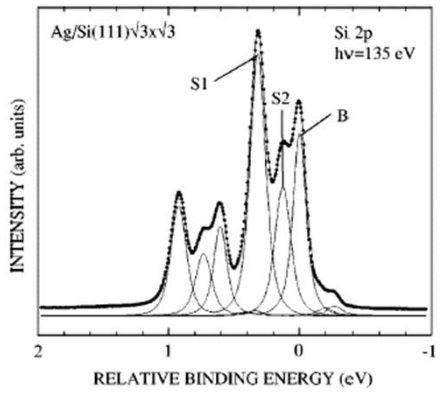
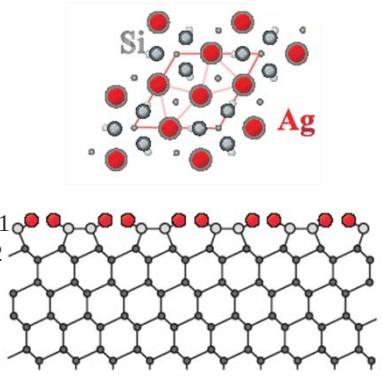
Si(111)√3x√3-Ag

- Atomic Structure and CLS spectra





R.I.G Uhrberg *et al.*, Phys. Rev. B **65**, 081305(R) (2002).

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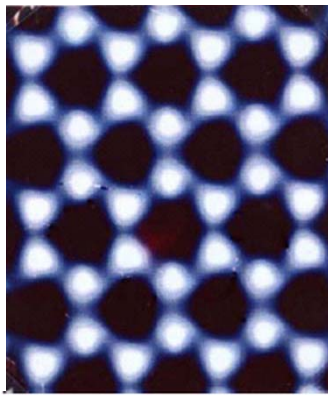
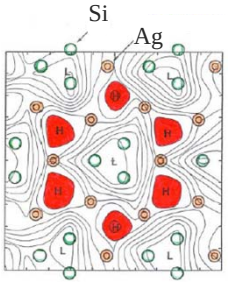
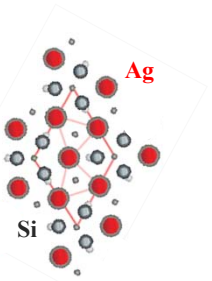
Si(111)√3x√3-Ag

- STM simulation





Tunneling current distribution



Structure model

STM protrusions do not match the atom positions.

S. Watanabe *et al.*, Phys. Rev. B **44**, 8330 (1991).

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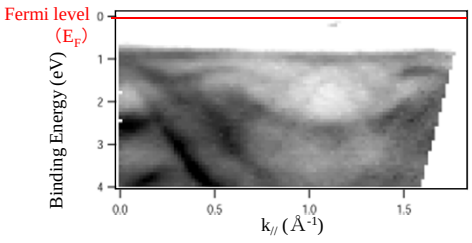
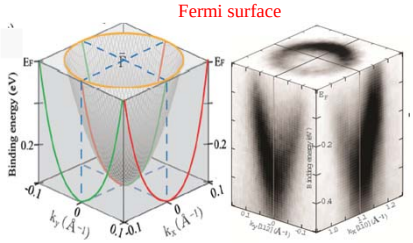
Si(111)√3x√3-Ag

- Electronic Structure



Fermi surface



$E = \frac{\hbar^2 k^2}{2m^*}$ 2D Free-Electron-Like State

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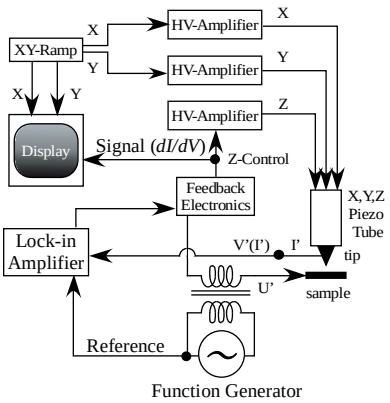
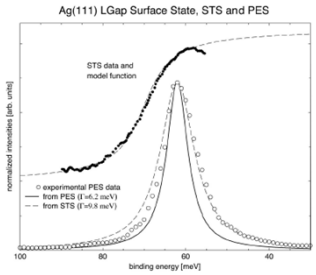
Scanning Tunneling Spectroscopy

G. Nicolay *et al.*, Phys. Rev. B **62** 1631 (2000).

Scanning Tunneling Spectroscopy (STS), dI/dV





Bias Modulation: $V' = V + \varepsilon \sin\omega t$

Current Modulation: $I(V + \varepsilon \sin\omega t) = I(V) + \frac{dI}{dV}\varepsilon \sin\omega t$

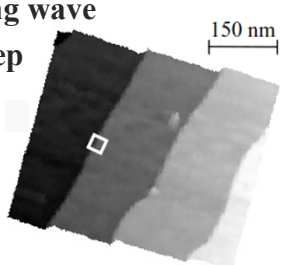
Detection by phase matching

$\frac{dI}{dV} \propto$ LDOS (Local Density Of States)

C. Bai, *Scanning Tunneling Microscopy and its Application* (Springer,1992)

Si(111)√3x√3-Ag

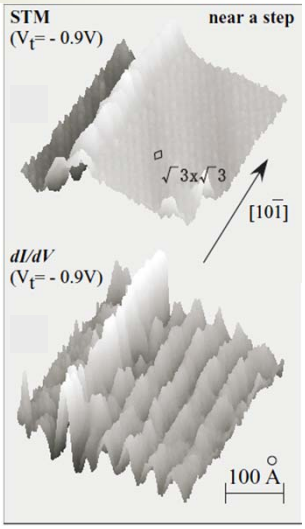
- **Electron Standing wave at monatomic step**



$1+|R|^2+2|R|\cos(2k_x x - \eta)$

$Re^{i\eta}e^{-ik_x x}$

$e^{ik_x x}$



I. Matsuda *et al.*, Phys. Rev. Lett. **93**, 236801 (2004).

Summary

- Surface Science is everywhere. Global to Atomic scale.
- For solid/vacuum interface (solid surface), we have advantages of
  - **Visualization of atomic configuration and electron density (LDOS) distribution in atomic scale**
  - **Direct determination of electronic structure (band, Fermi surface, spin, etc…)**
- A combinations of nanoprobe techniques, electron diffraction, and spectroscopy with synchrotron radiation

→ **Proper and detailed understandings of surface phenomenon in atomic scale**

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