Photoemission (2) Surface Science

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Surface/Interface in scales

10^6 m
(10^3 km)

10^3 m
(km)

10^0 m
(m)

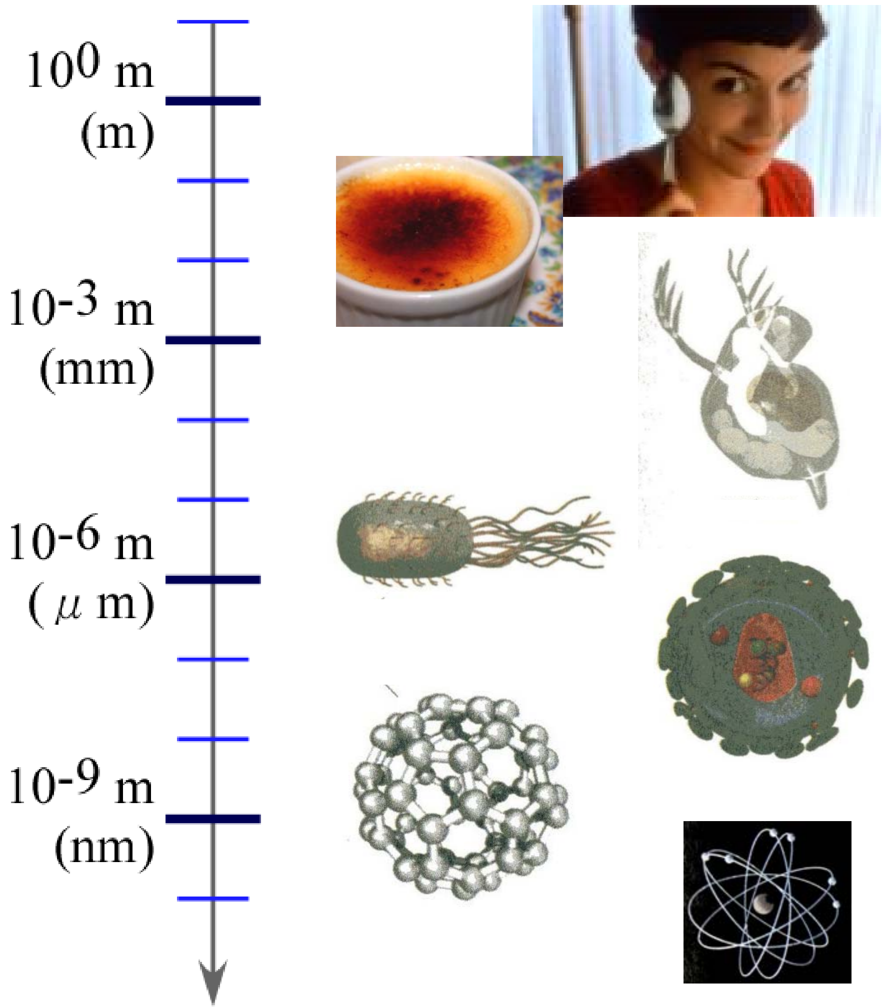
10^{-3} m
(mm)

Space
The Earth/Vacuum interface

Climates
Sea/Air interface

Skins
Face/Air interface

Surface/Interface in scales



Goods
(solid/air interface)

Cooking
(Oil/water interface)

Biomaterials surviving
in various environments

Molecules and atoms
in various conditions

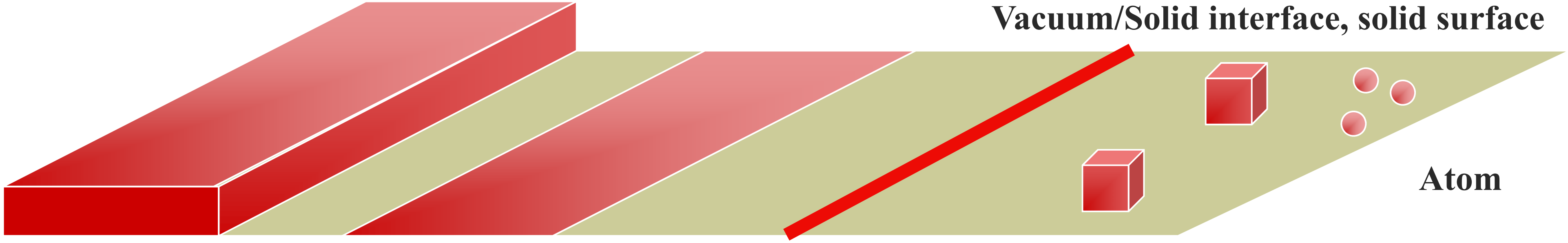
Surface/Interface in scales

- 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
- ....

My playground



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

Chemistry

- Catalysis reaction
- Ecology
- Solutions for energy-shortage problem

Physics

- Low-dimensional physics
- Quantum dynamics
- New physics

Applied 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…)**

Surface Analyses

Varieties of Surface analysis techniques

Given examples…….

Nanoprobes

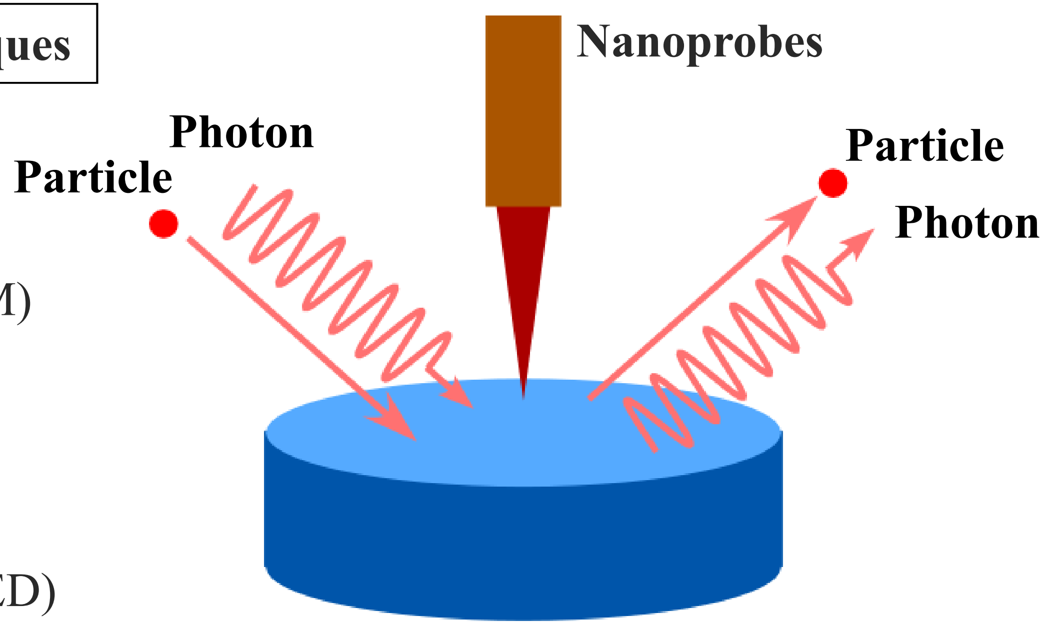
Scanning Tunneling Microscope (STM)
Atomic Force Microscope (AFM)

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

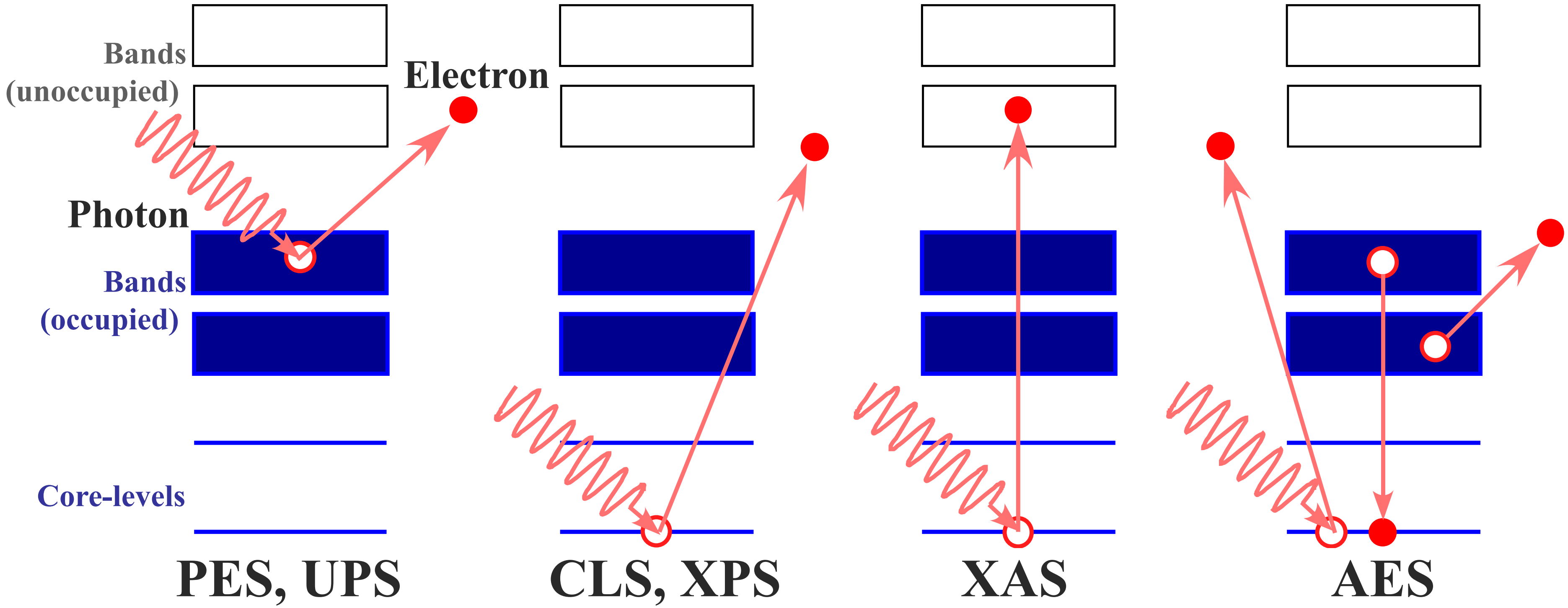
Grazing-angle incident X-ray Diffraction (GIXRD)



Surface Analyses

Photon-in / Particle-out

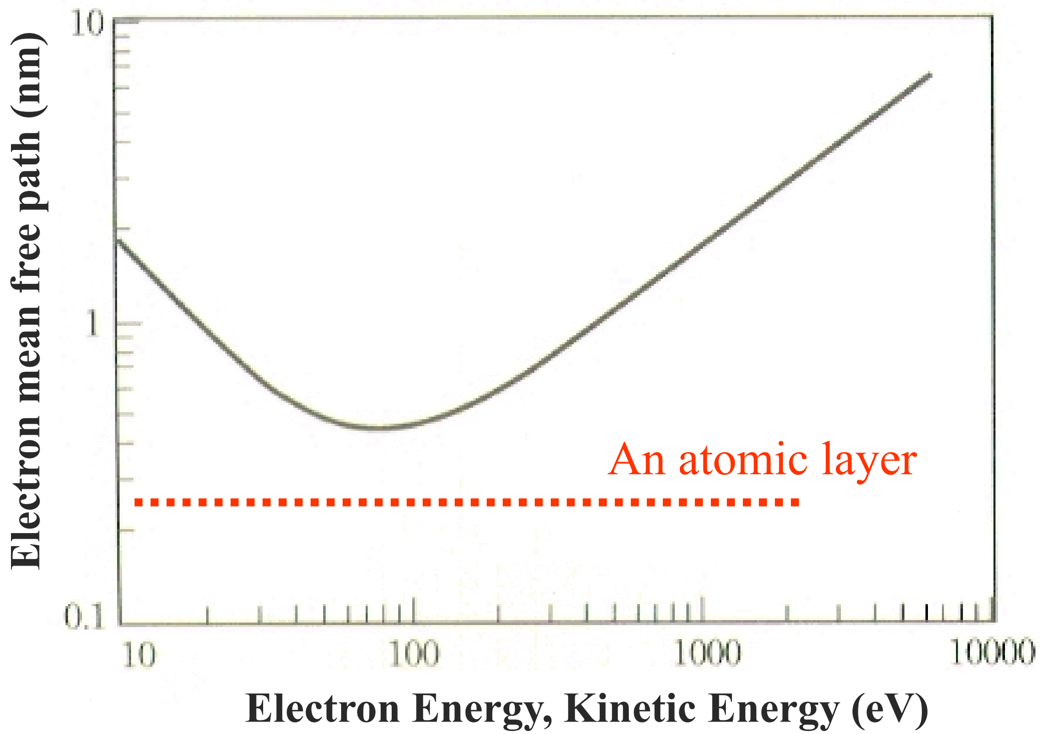
Photoemission Spectroscopy (PES), Ultraviolet Photoelectron Spectroscopy (UPS)
Core-level Spectroscopy (CLS), X-ray Photoelectron Spectroscopy (XPS)
X-ray Absorption Spectroscopy (XAS)
Auger Electron Spectroscopy (AES)



Spectroscopy with VUV~SX

- Electron mean free path

surface-sensitive ~ bulk sensitive



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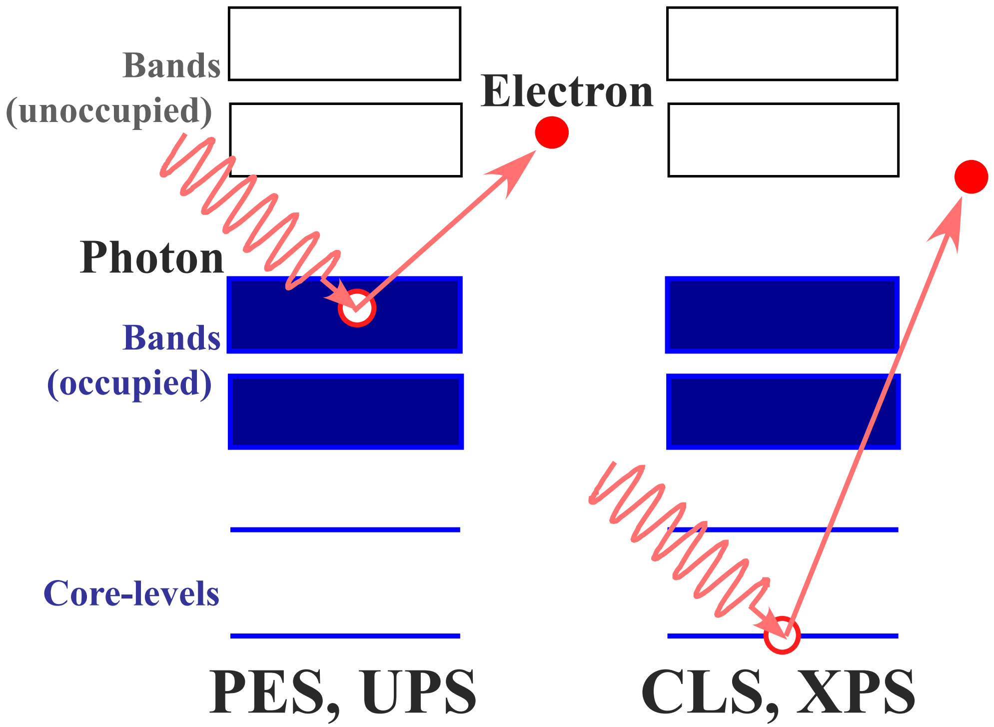
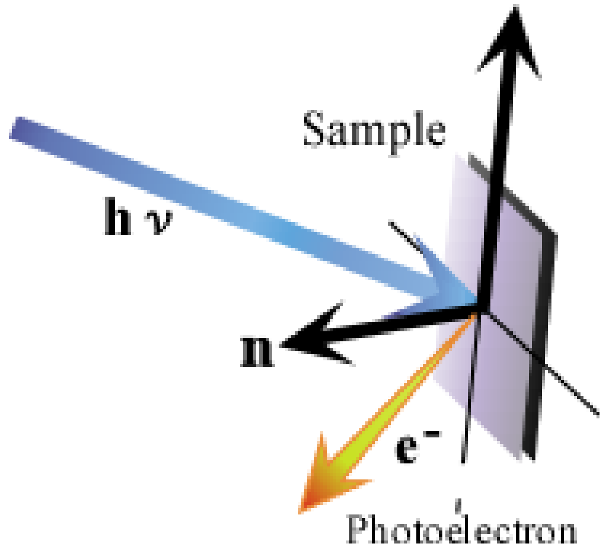
Probing electronic states

- Photoelectron spectroscopy

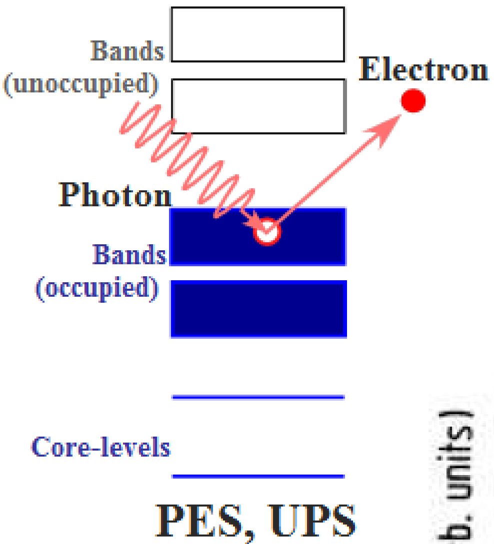


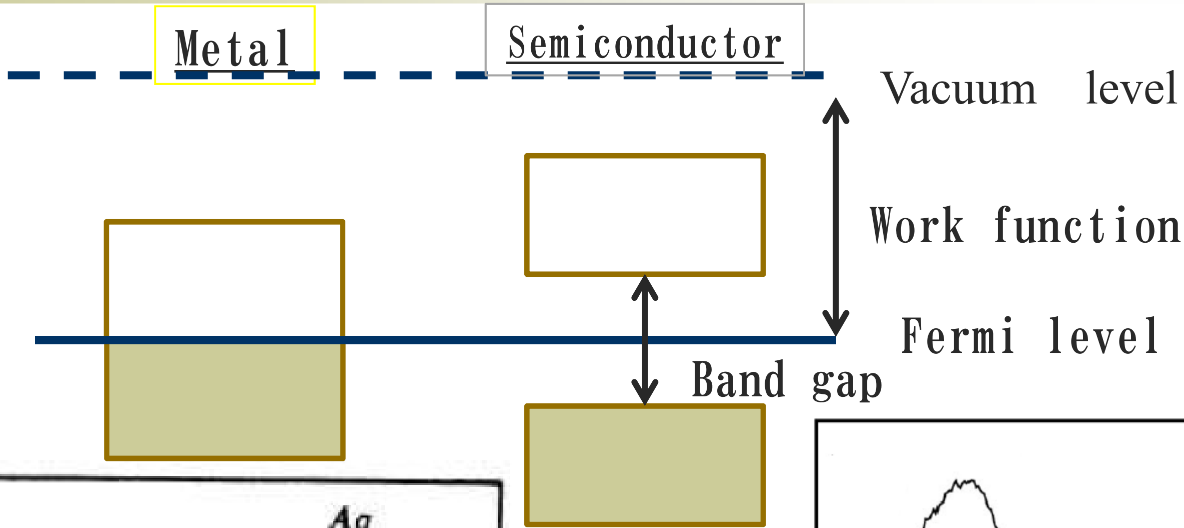


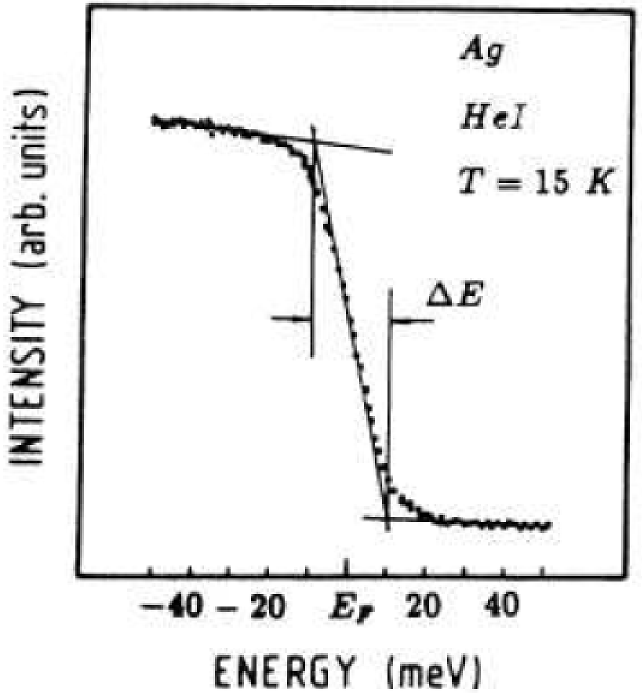
$E_k = h\nu - \Phi - E_B$

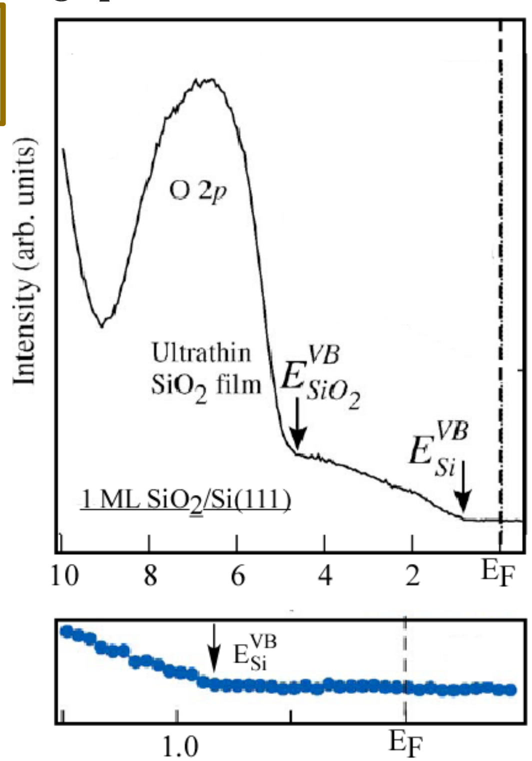
work function (Φ), binding energy (E_B)

Probing electronic states









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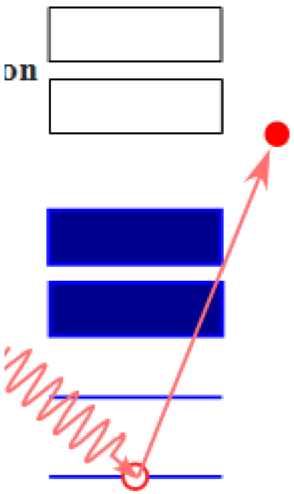
Probing electronic states

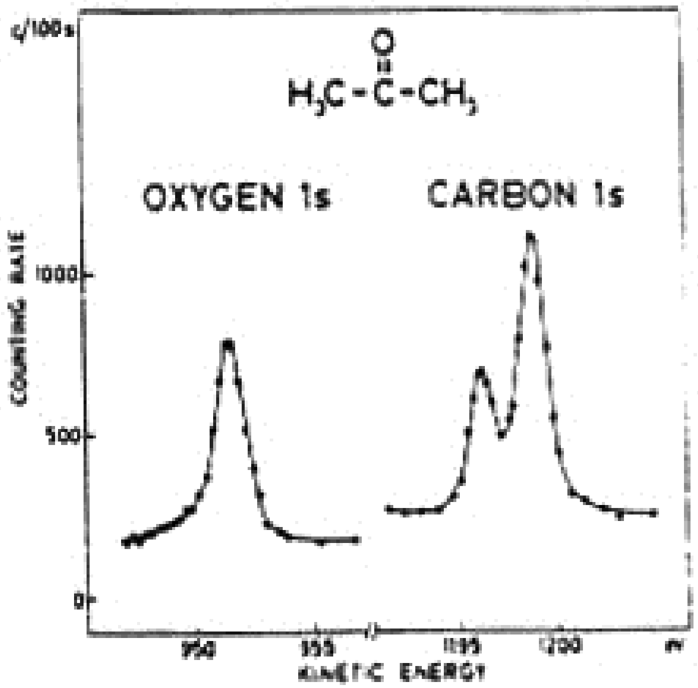
CLS, XPS

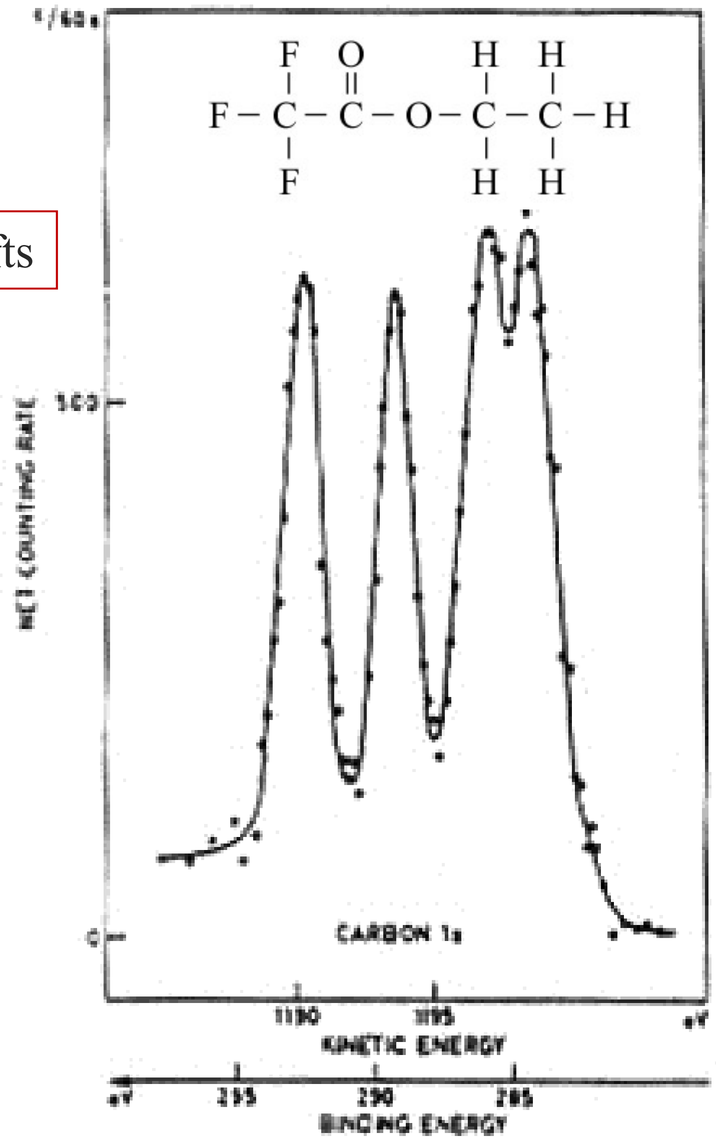
ESCA (Electron Spectroscopy for Chemical Analysis)

Chemical shifts



CLS, XPS





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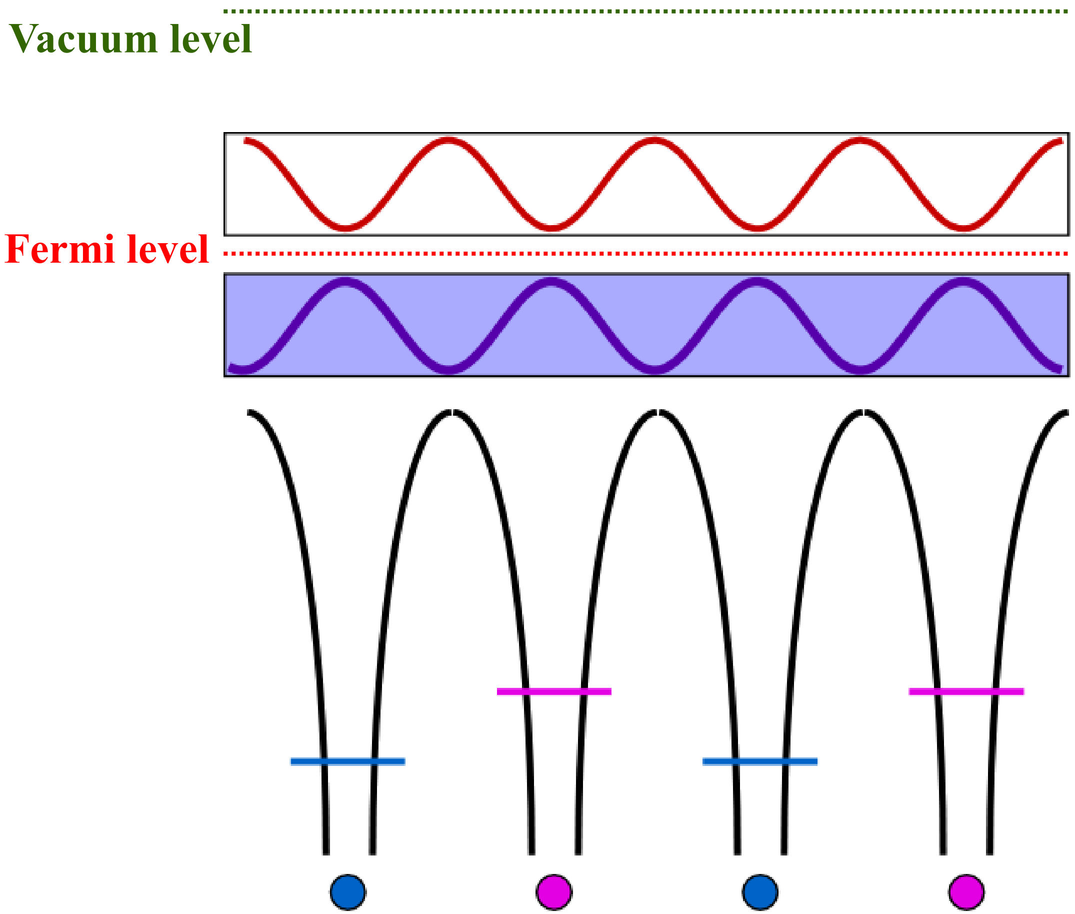
What can be probed by photoemission



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

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

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

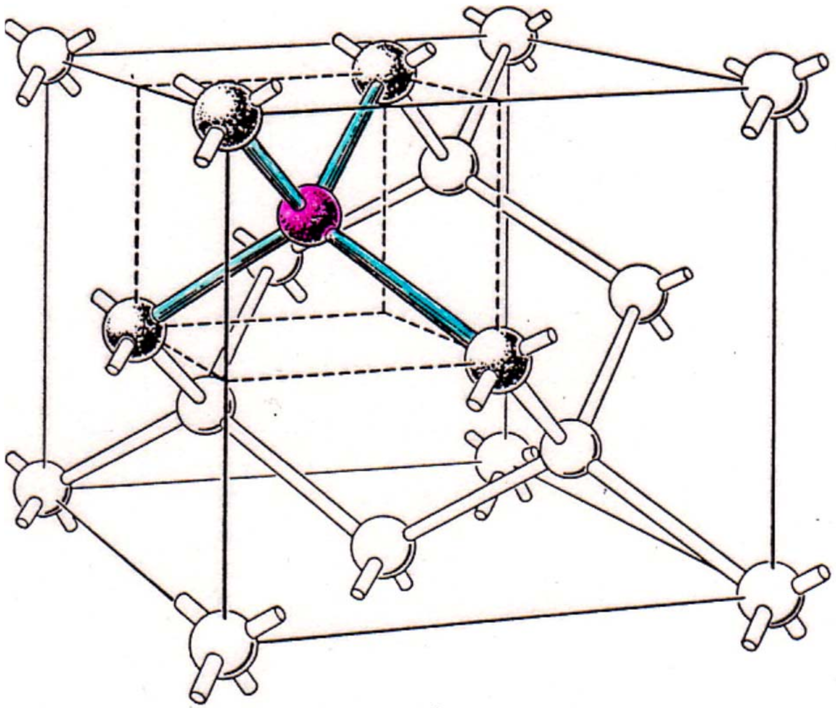
Semiconductor surface

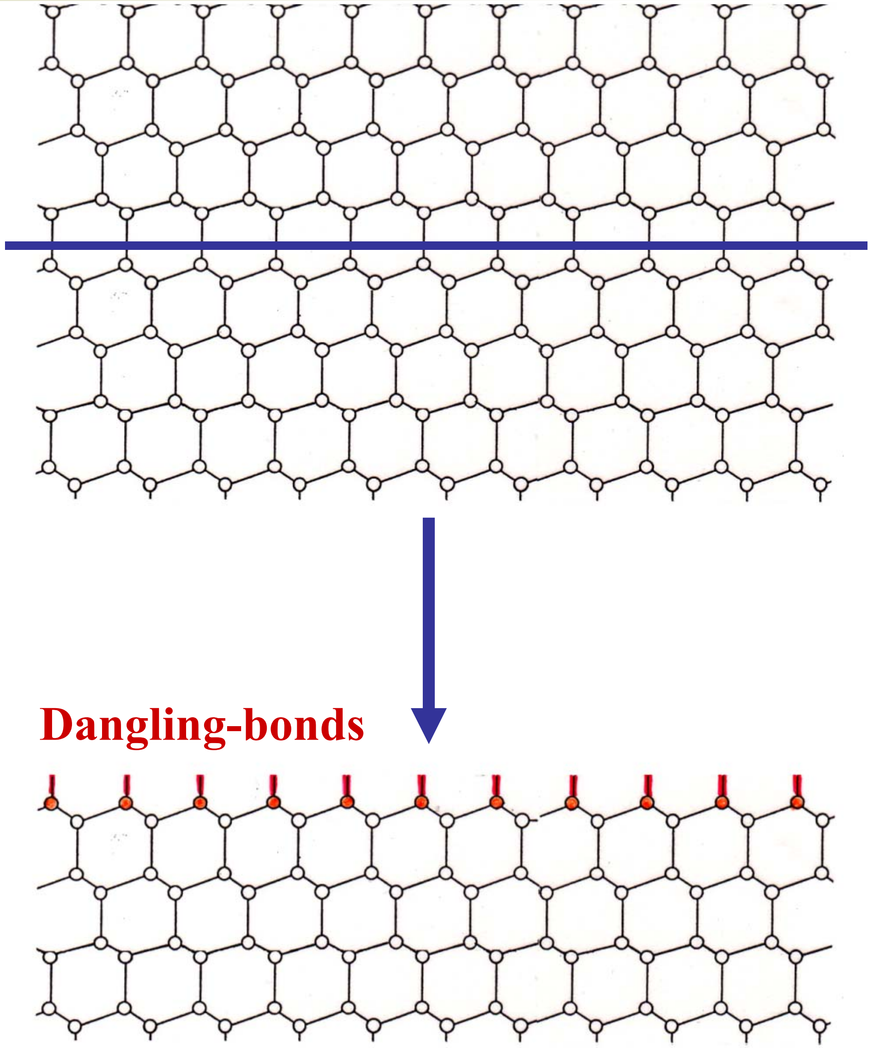
Atomic structure

Cutting (expectation)

Silicon (Si)

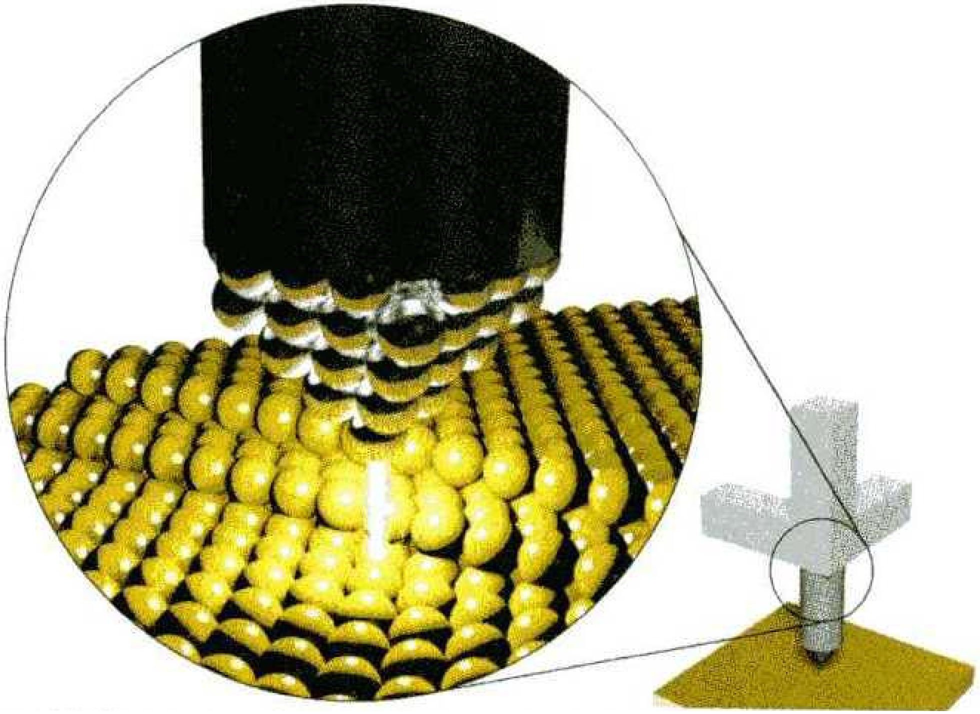
Diamond structure



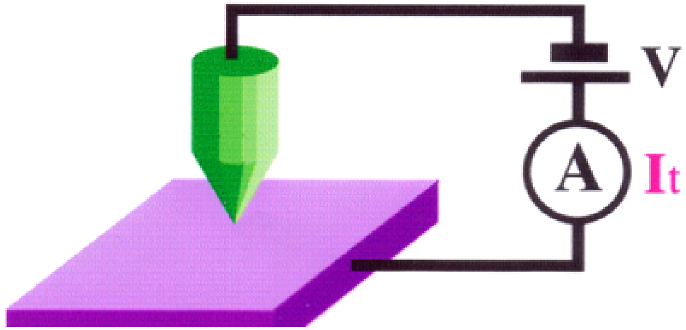


Scanning Probe Microscope

Scanning Tunneling Microscope (STM)



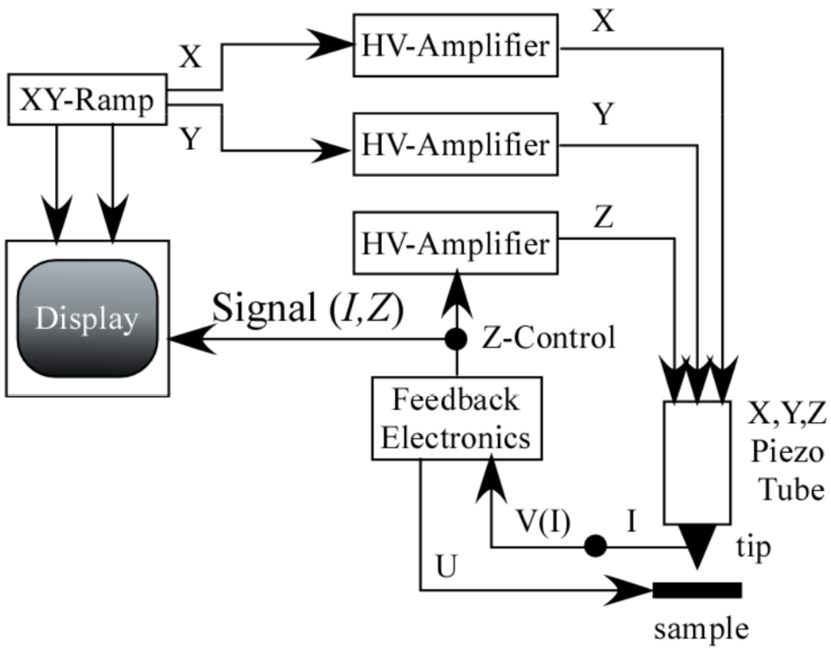
Rohrer and Binnig (1982)

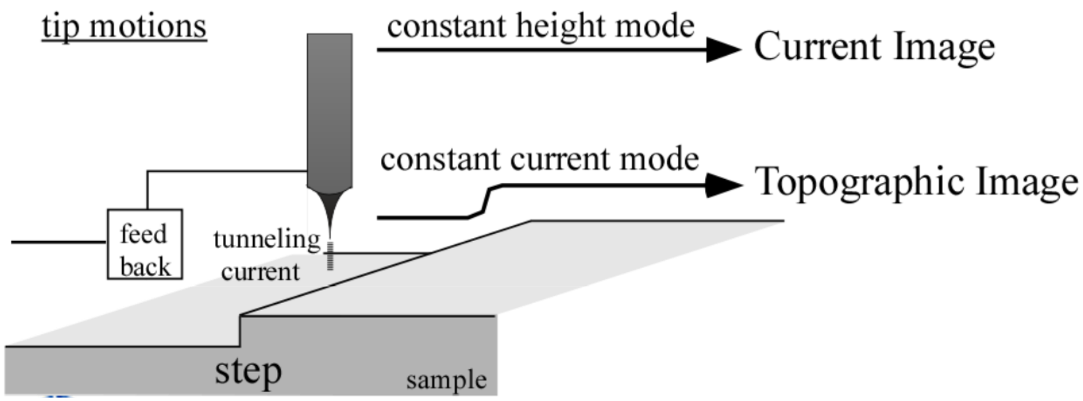


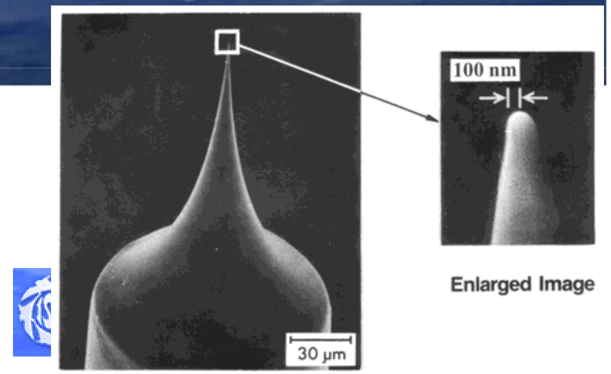
Tunneling Current $I_t \propto f(v) \cdot e^{-\sqrt{\Phi} \cdot d}$

「STM

Scanning Tunneling Microscope (STM)



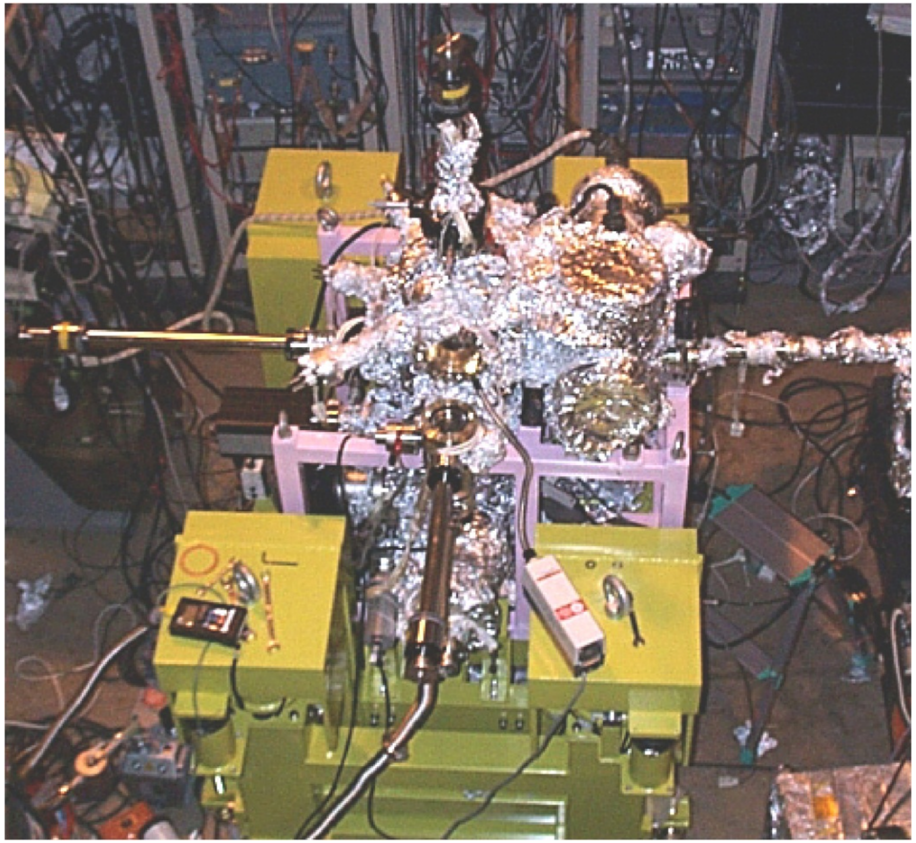




Scanning Tunneling Microscope

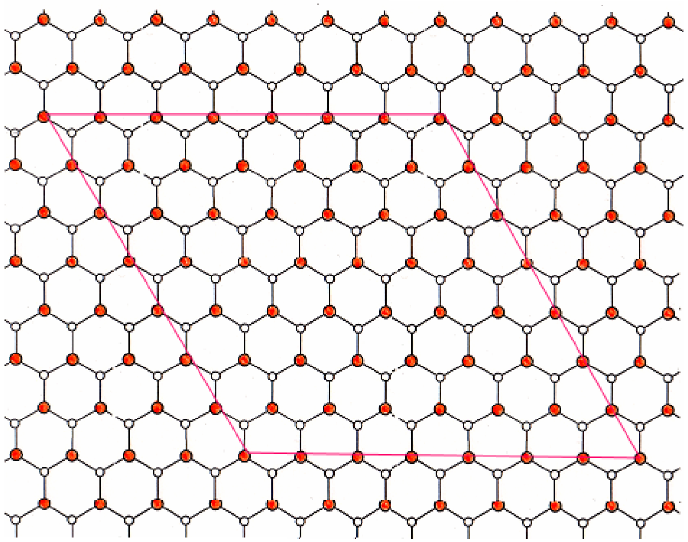
An experimental chamber

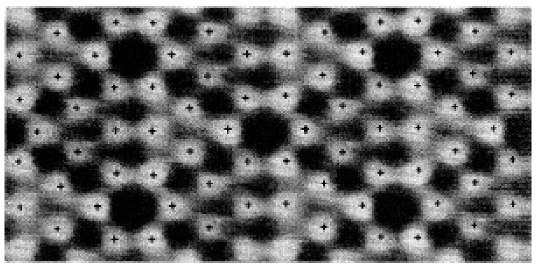
- the Ultra High Vacuum condition
- Isolation of vibration
- Sample surface preparation



An STM image

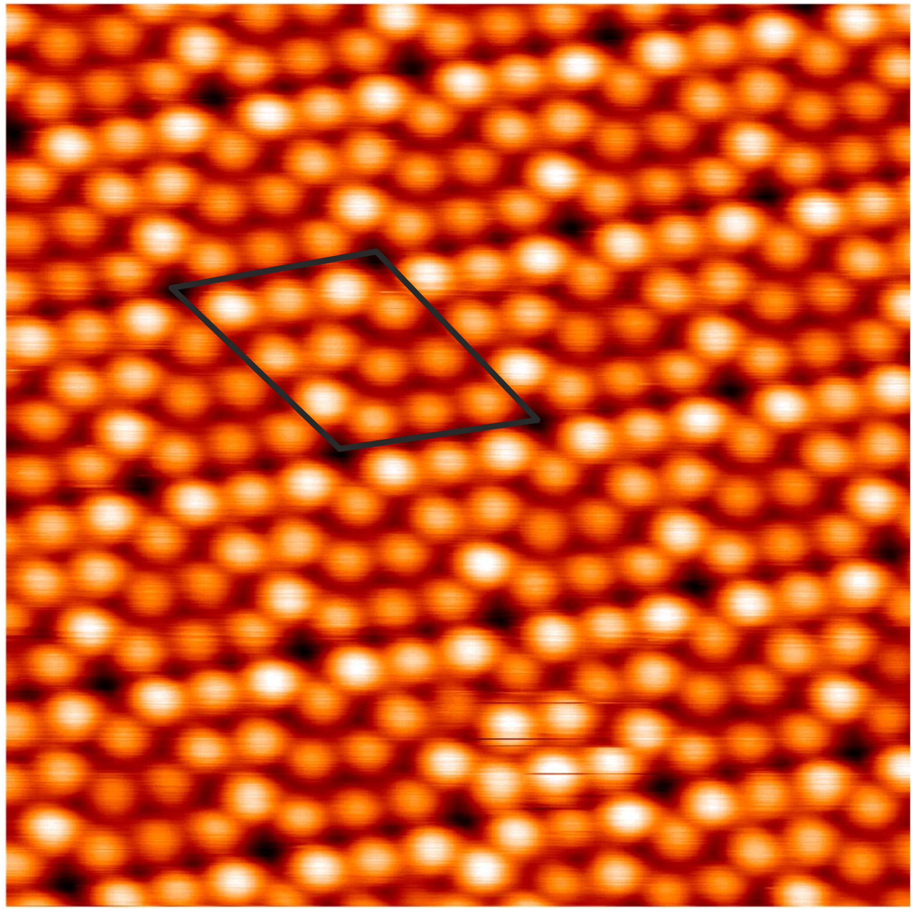
Ideal surface





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

Real surface (STM image)



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

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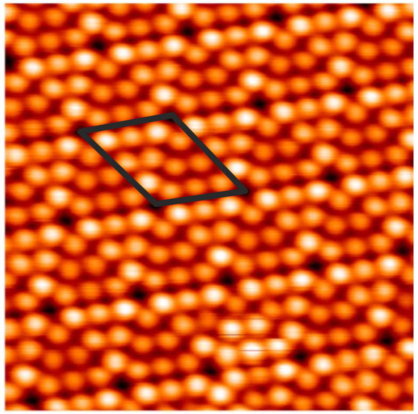
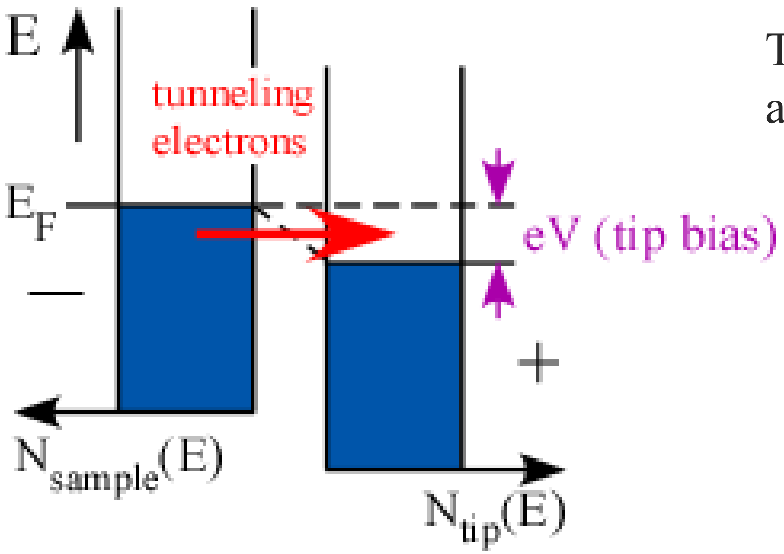
Scanning Tunneling Microscope



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).

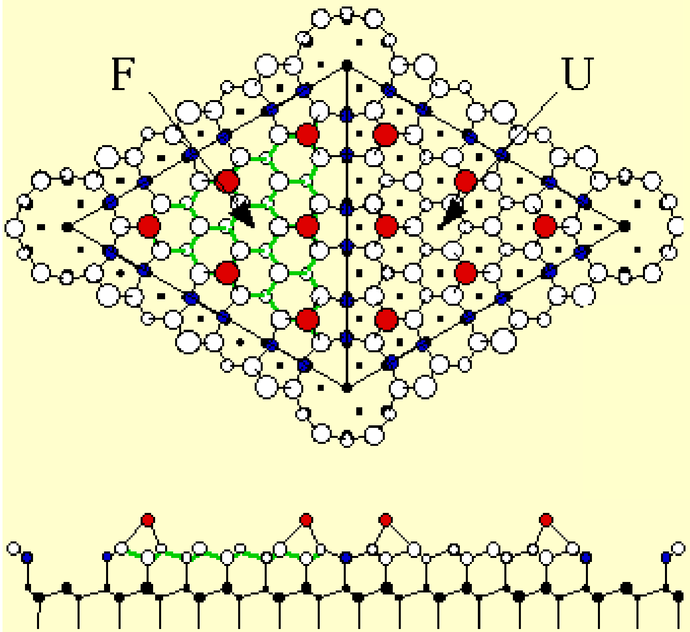
↓

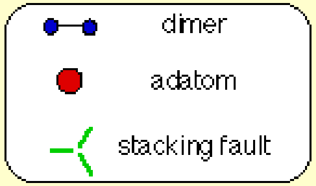
Protrusions in STM could be surface atoms

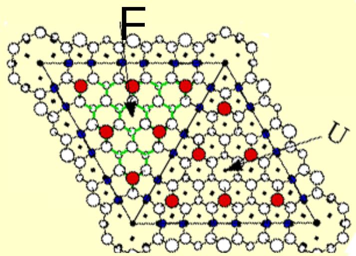
Atomic Structure

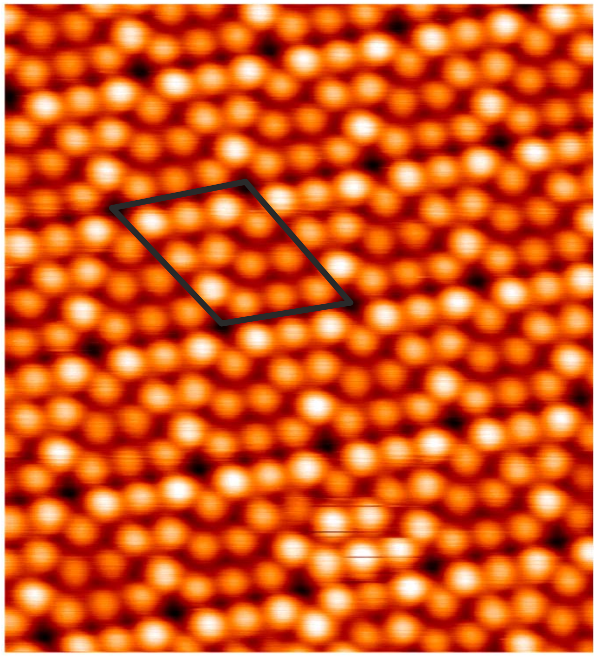
Dimaer-Aadatom-Stacking Fault (DAS) model

K. Takayanagi *et al.*,
Surf. Sci. **164**, 367 (1985).



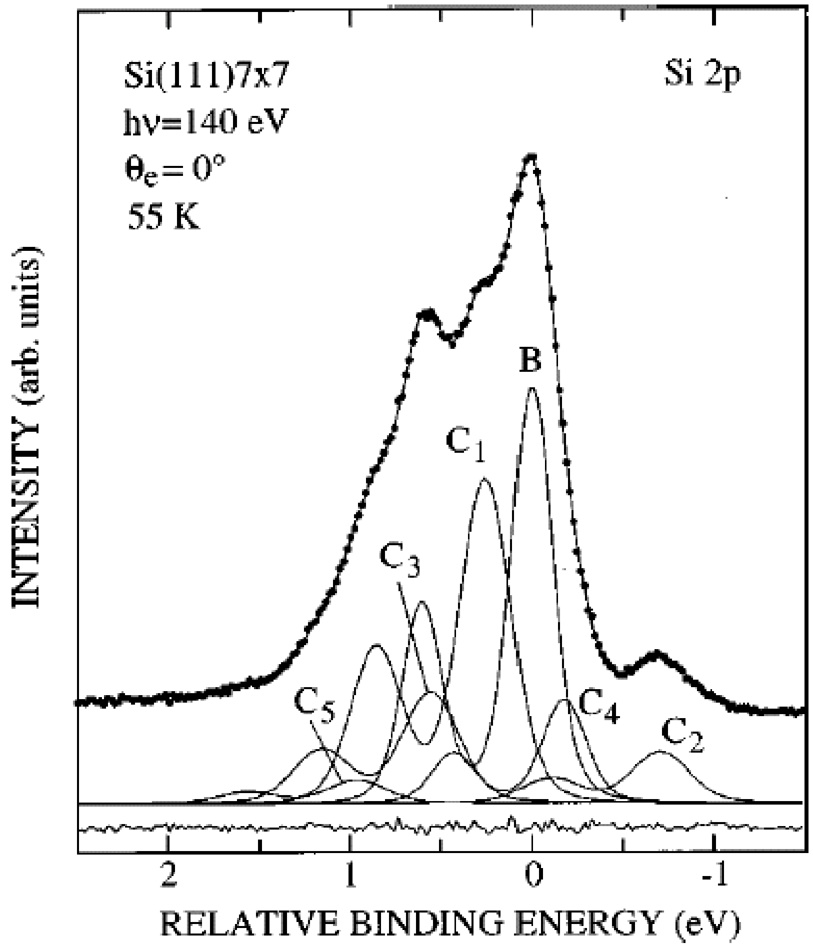






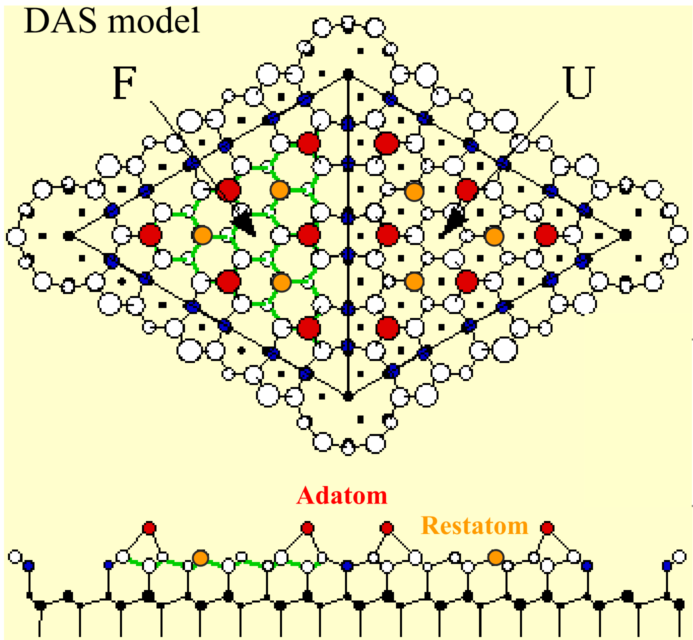
Si(111)7x7

Core-levels



<u>Surface components</u>

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).

Semiconductor surface

Electronic structure

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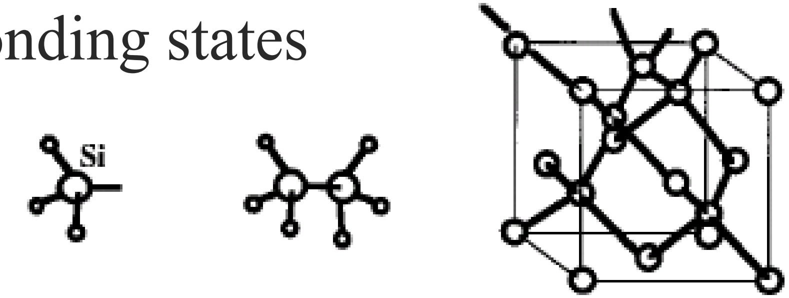
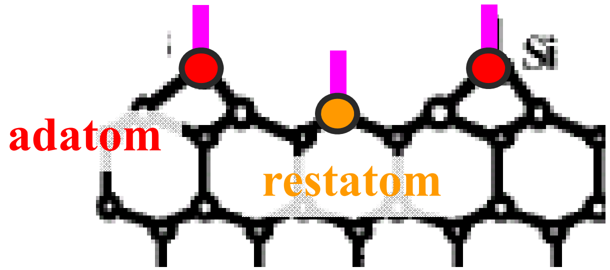
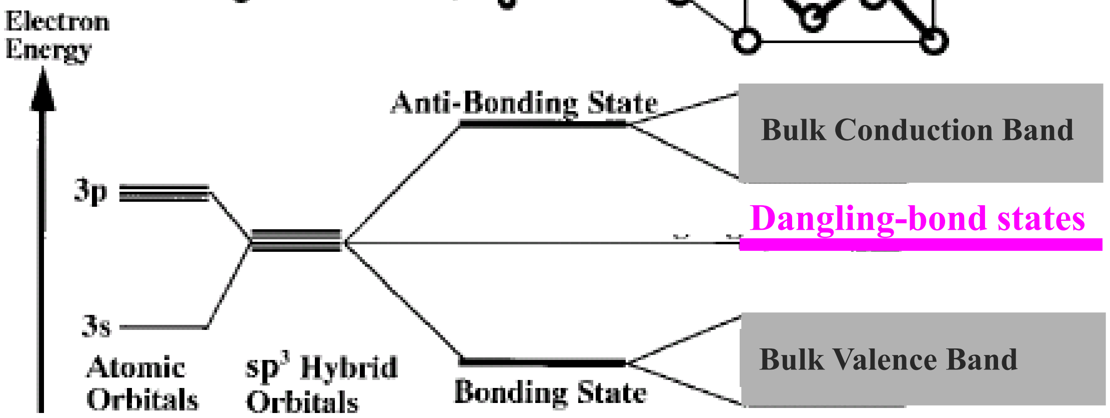
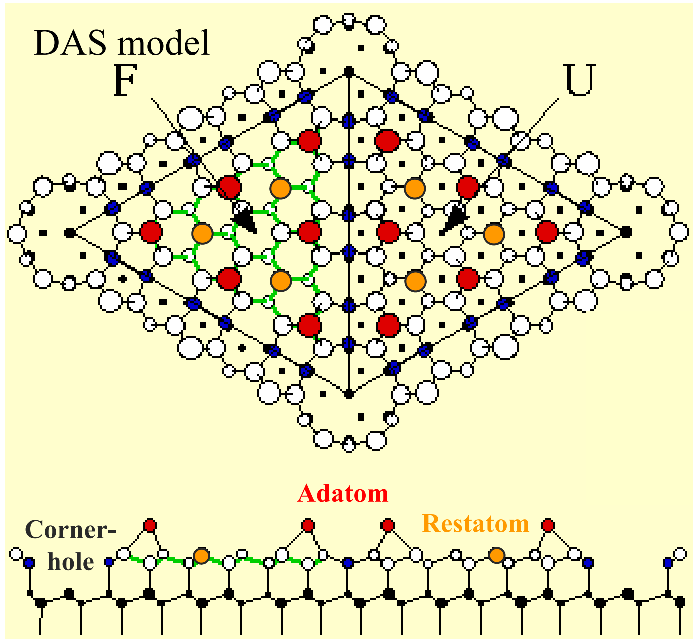
Electronic states of Si(111)7x7

- Bonding states









<u># of dangling bonds</u>
<u>in the 7x7 unit cell</u>

adatom: 12
restatom: 9
corner-hole: 1

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Band mapping

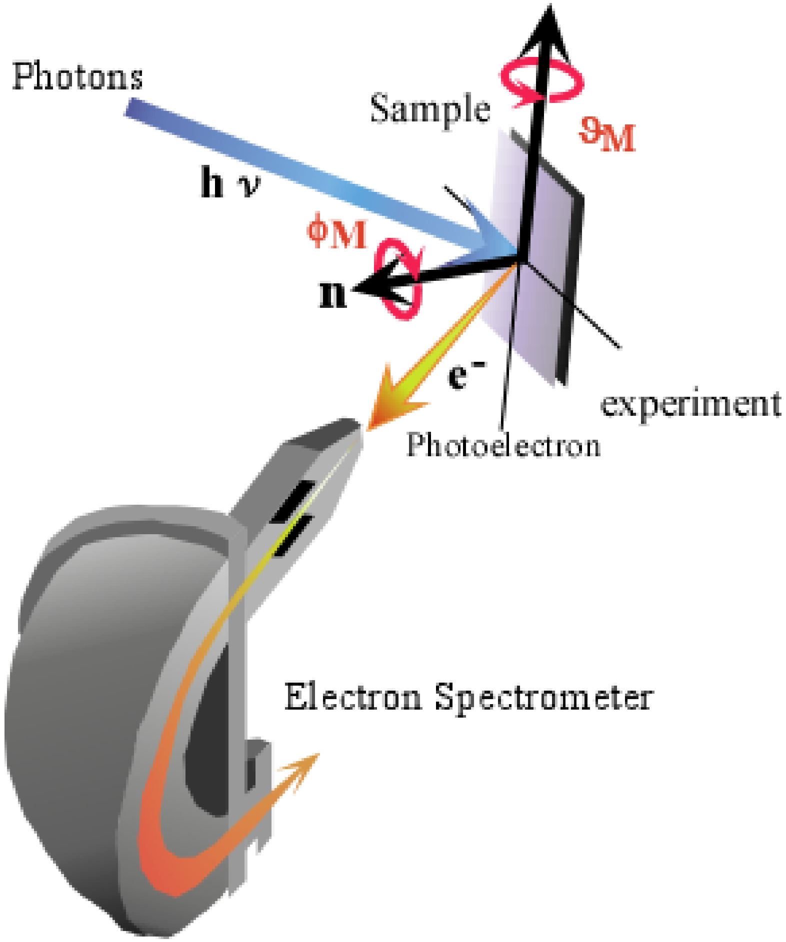
- Angle-resolved photoemission spectroscopy (ARPES)

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

work function　　binding energy

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

→ Band dispersion $(E, k_{//})$



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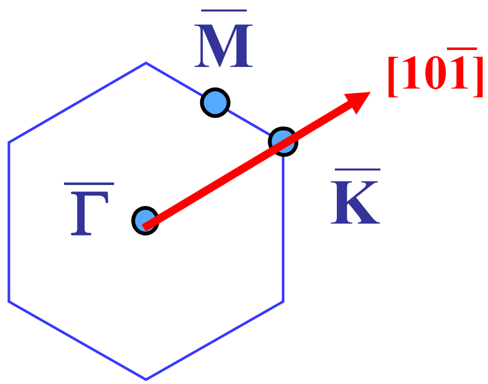
ARPES measurement

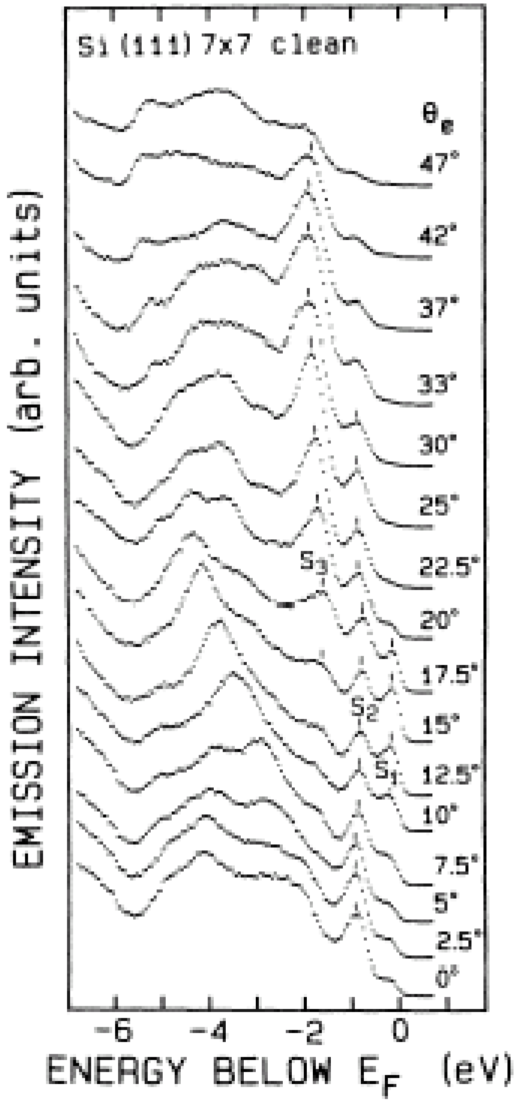
Si(111)7x7

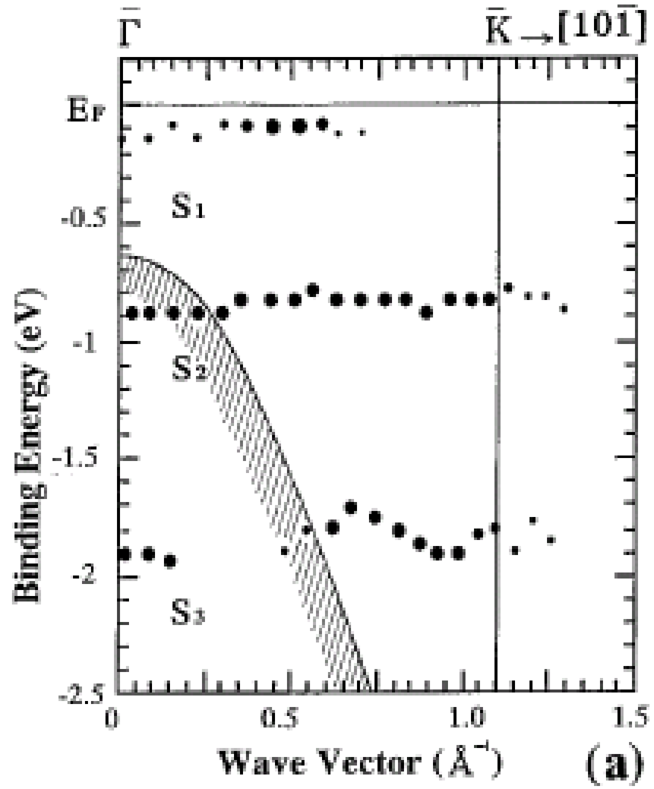
Conventional measurements

Energy spectra at various angles along symmetric crystal axis



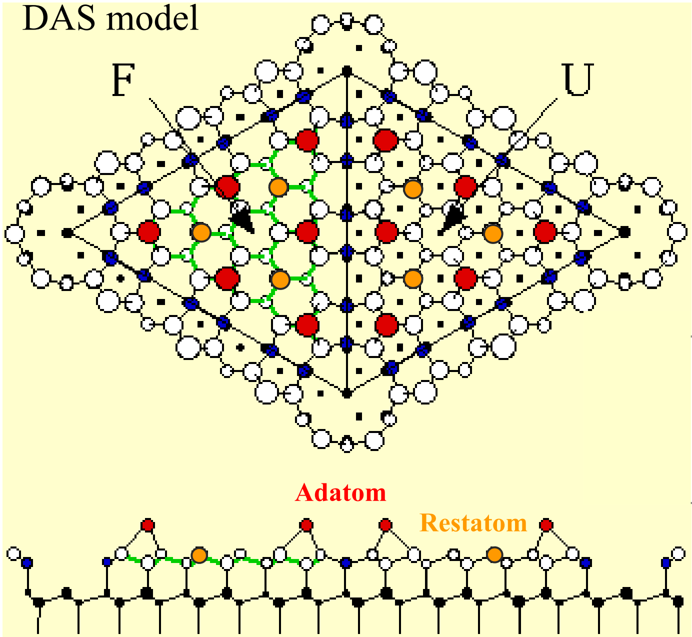
1x1 SBZ

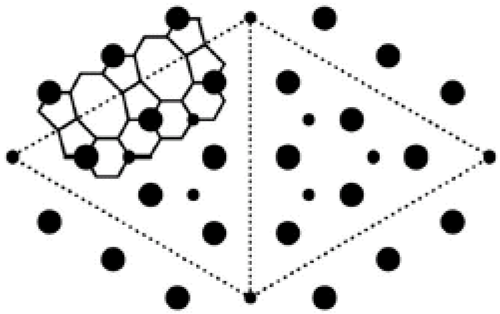


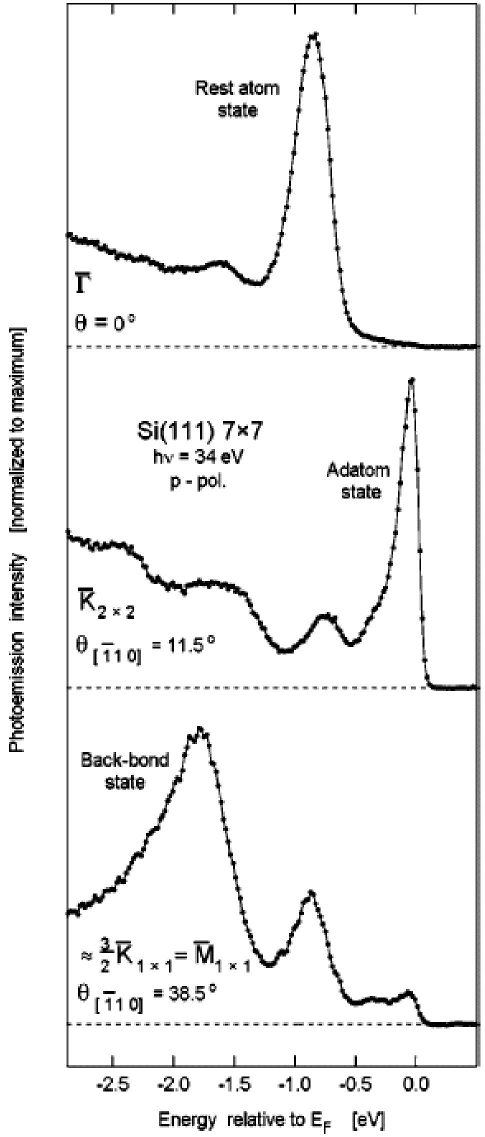


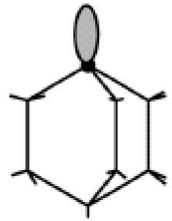
P. Martensson *et al.*, Phys. Rev. B **36**, 5974 (1987).

Dangling bonds

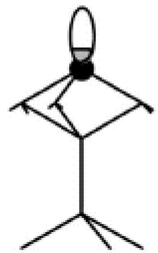








Rest atom state
(Fully occupied)



Adatom state
(Partially occupied)

- **Charge transfer**
- **Metallic surface**

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

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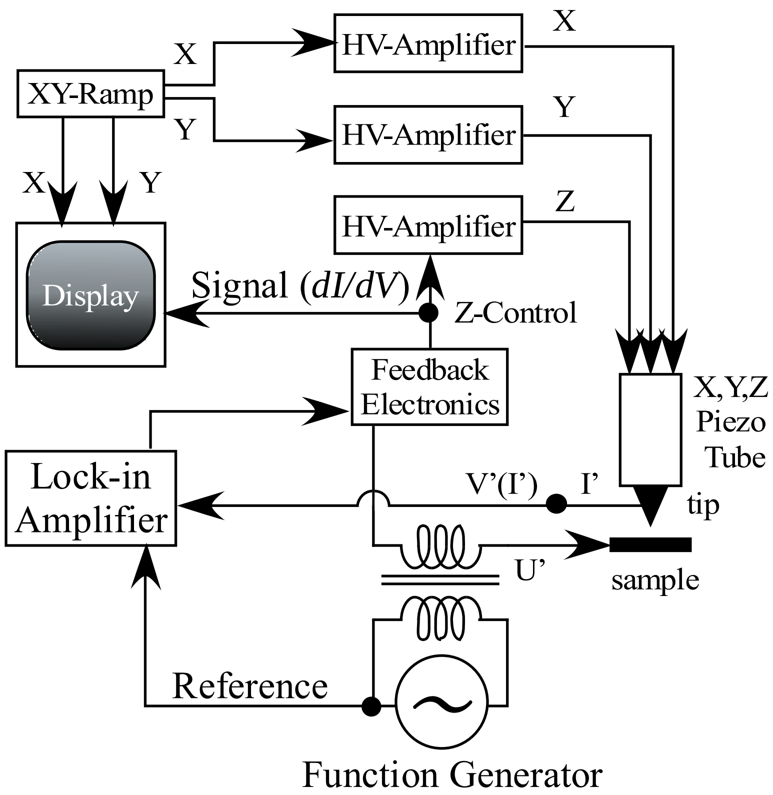
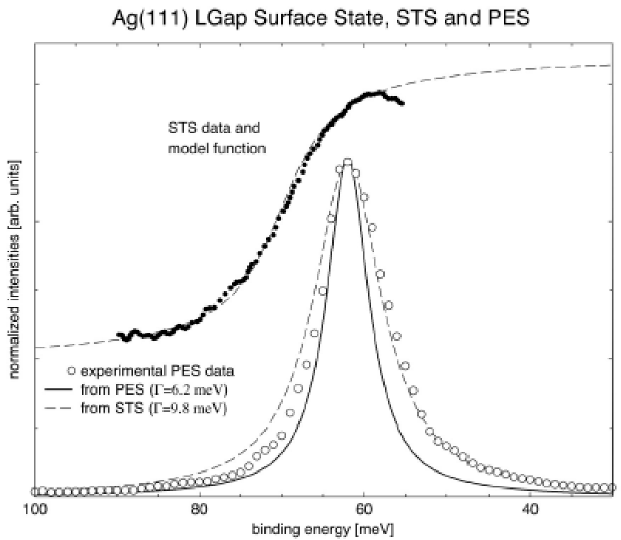
Scanning Tunneling Spectroscopy

Scanning Tunneling Spectroscopy (STS), dI/dV



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



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

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

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

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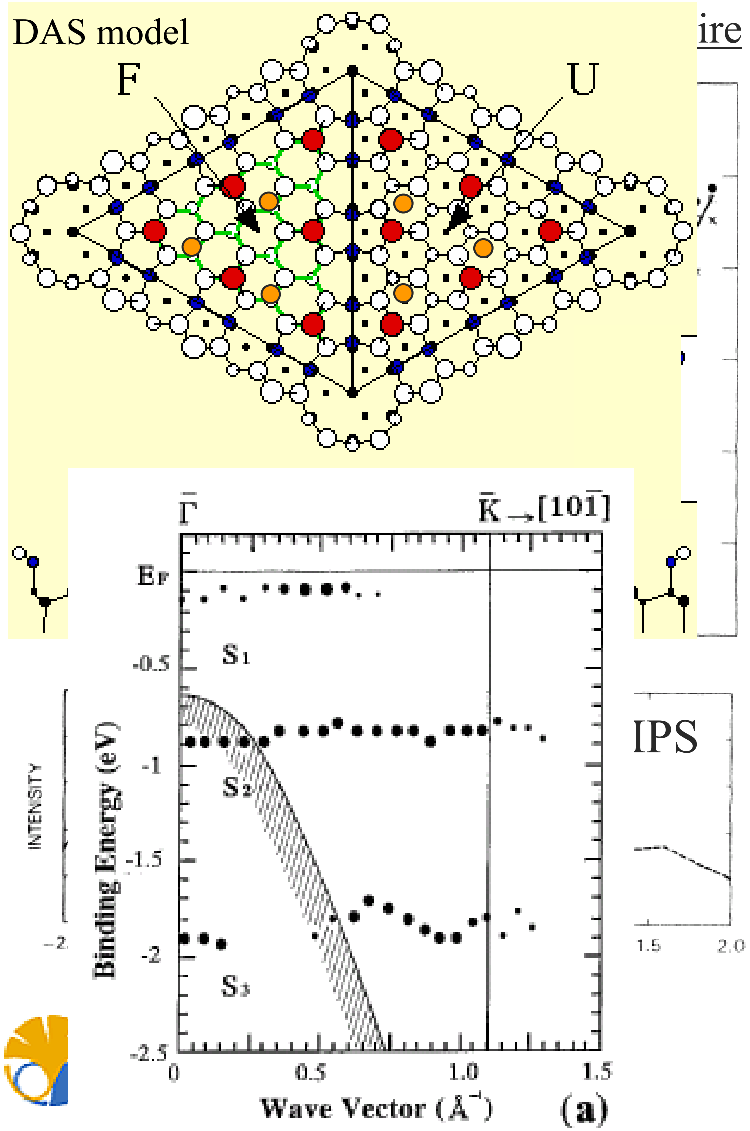
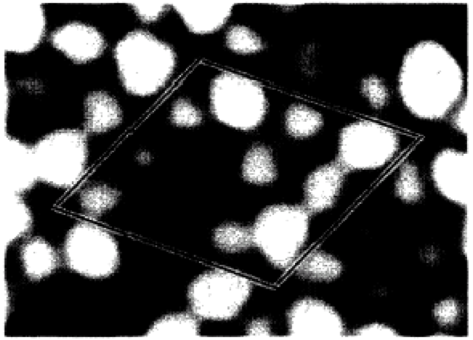
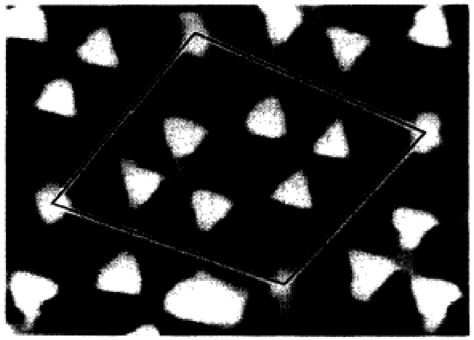
Scanning Tunneling Spectroscopy



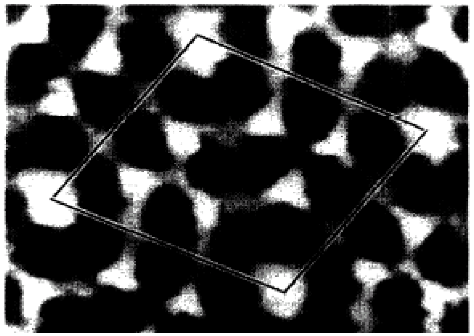
Differential Current Imaging Tunneling Spectroscopy



Adatom state @ - 0.35 V



Rest atom state @ - 0.8 V



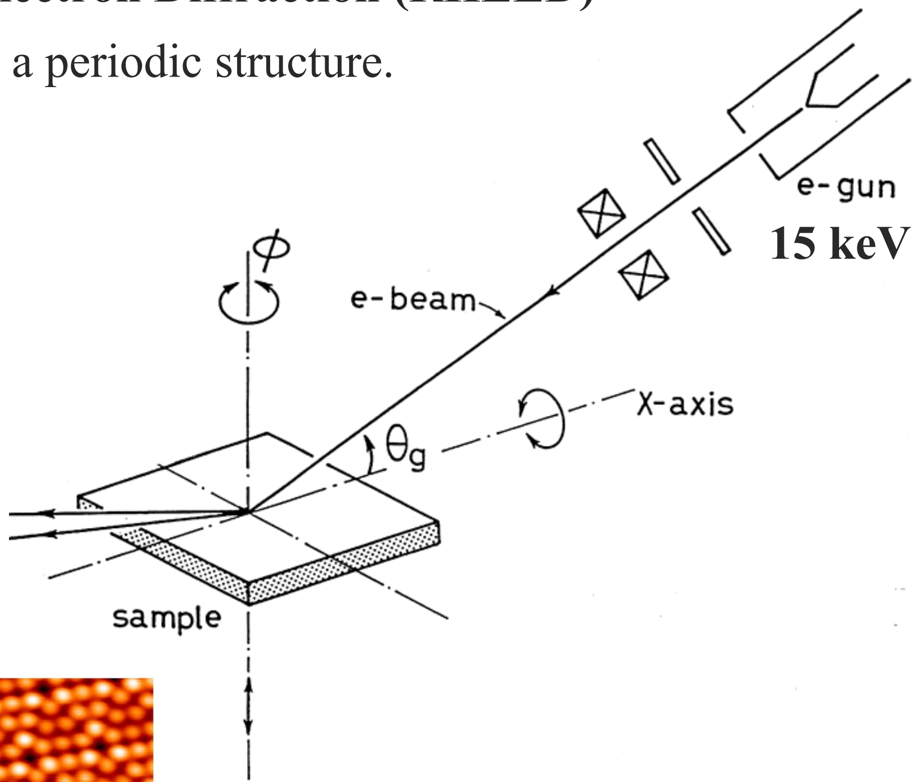
Back bond state @ - 1.7 V

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

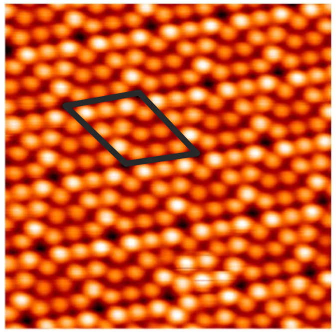
Electron Diffraction

Reflection High-Energy Electron Diffraction (RHEED)

(Electron) Wave diffracts at a periodic structure.



Si(111)7x7



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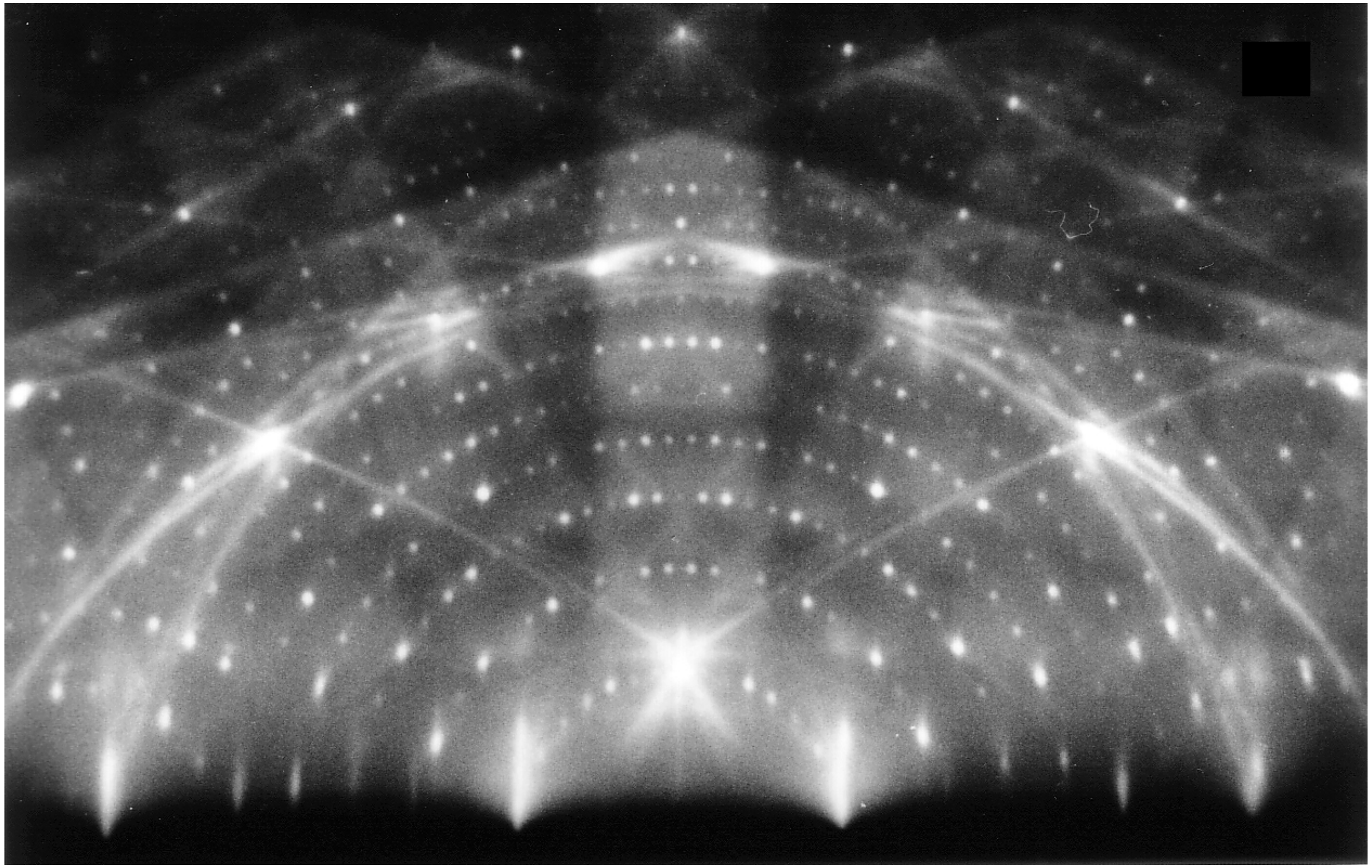
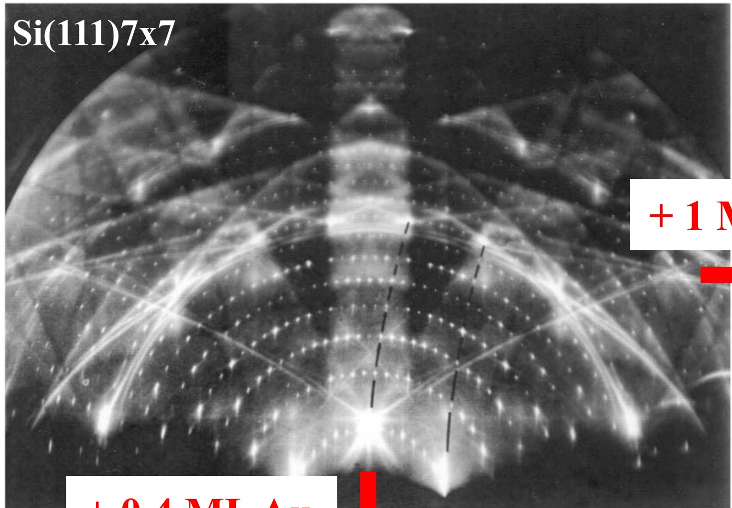
Reflection High-Energy Electron Diffraction

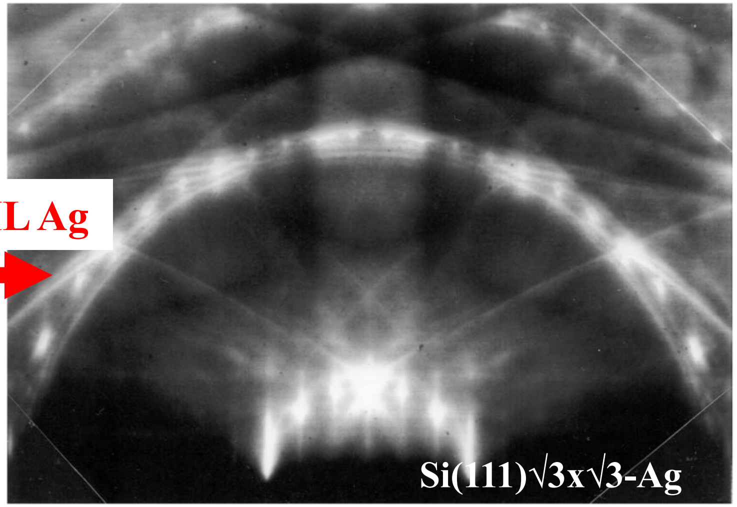
- RHEED pattern of Si(111)7x7 at 15 keV



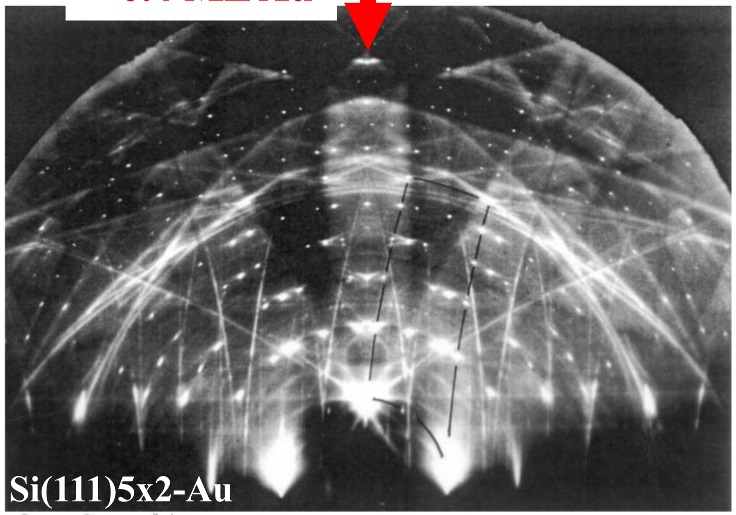
Variations of ordered surface phases



+ 1 ML Ag



+ 0.4 ML Au



<u>Numerous numbers of ordered phases</u>

- 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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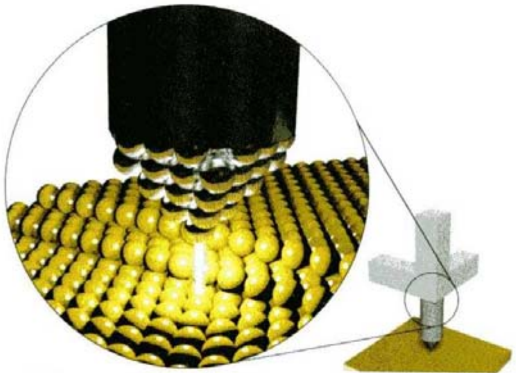
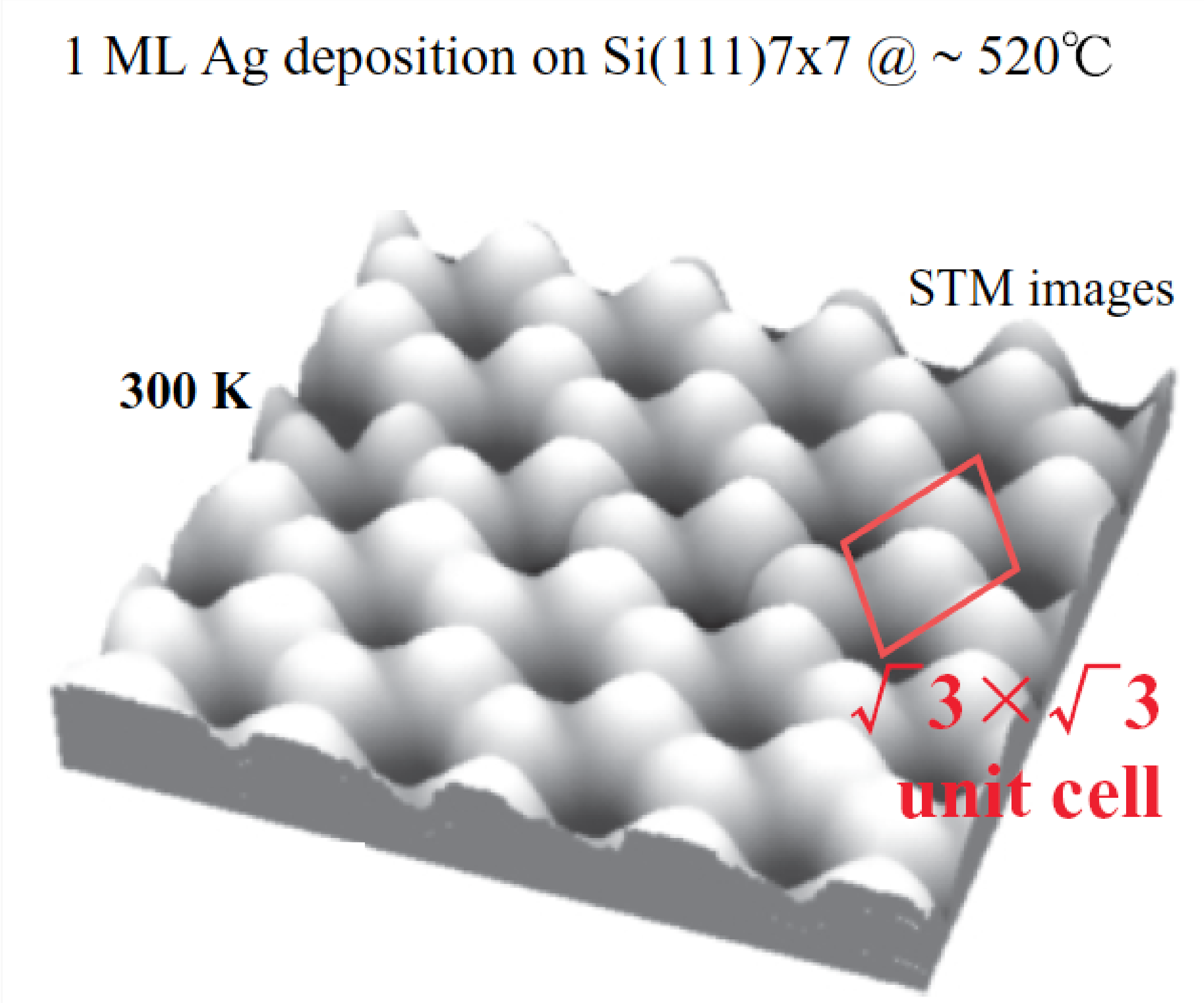
Si(111)√3x√3-Ag

- STM image





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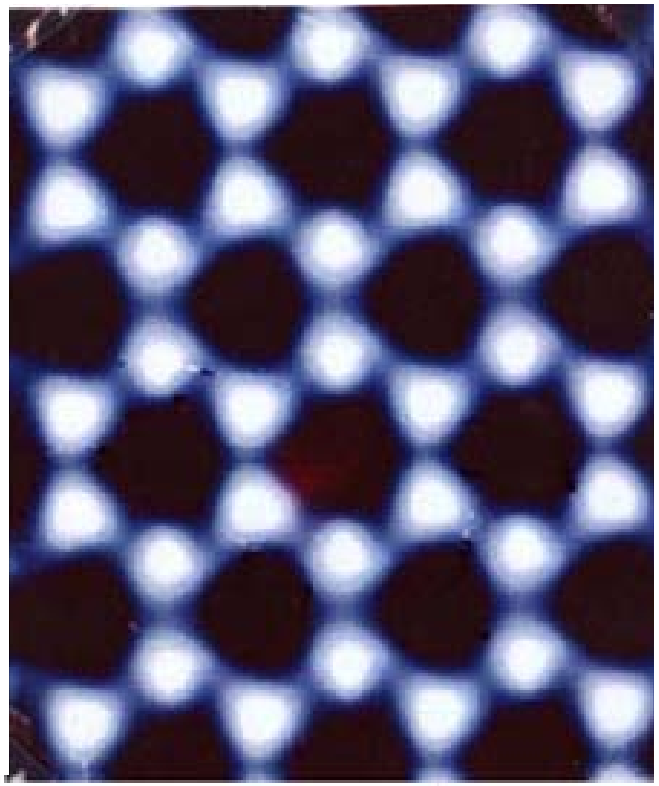
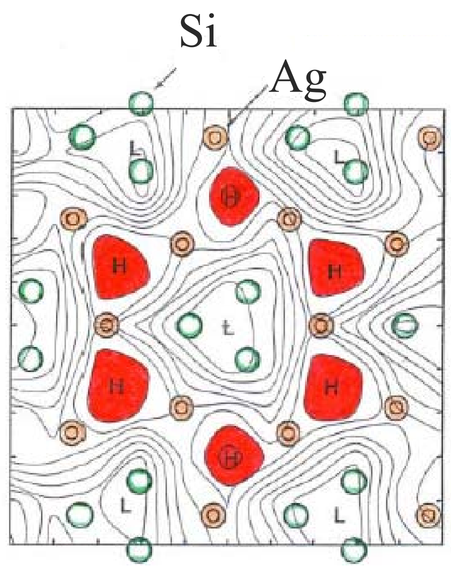
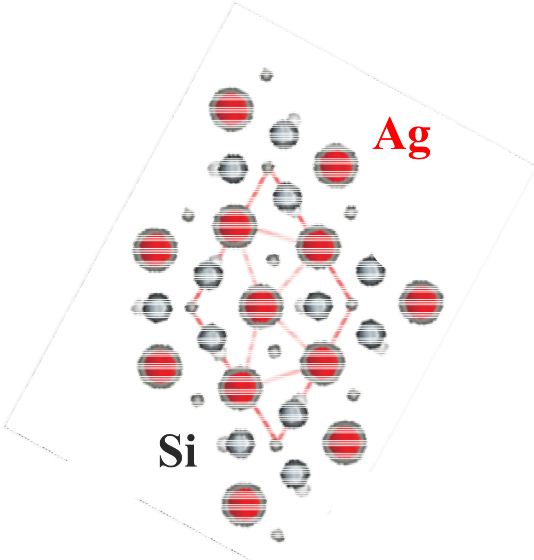
Si(111)√3x√3-Ag

- STM simulation





Tunneling current distribution



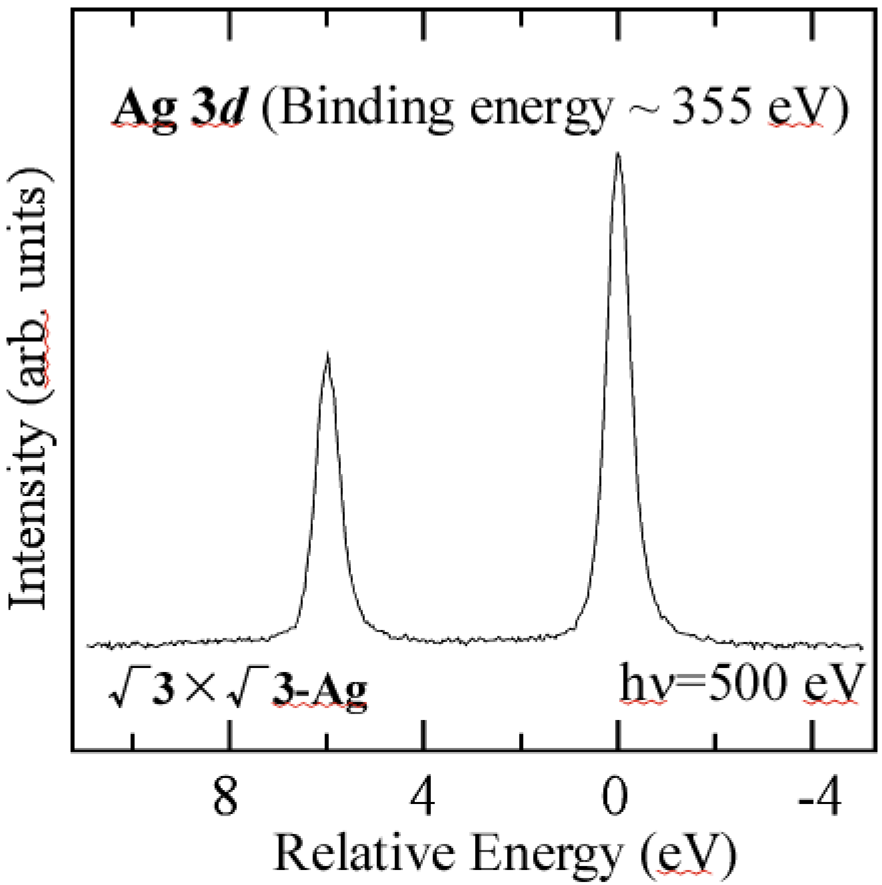
Structure model

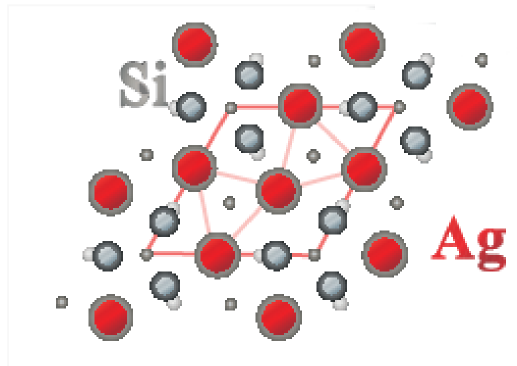
STM protrusions do not match the atom positions.

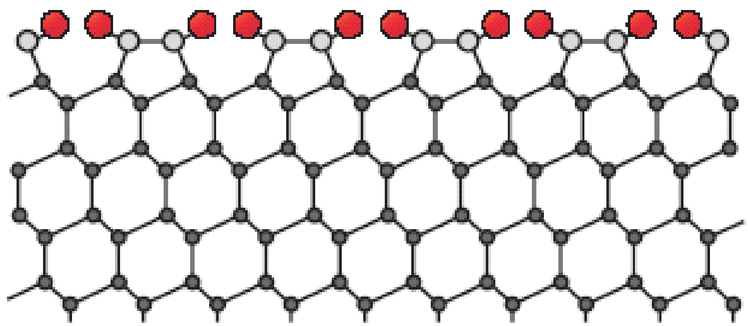
S. Watanabe *et al.*, Phys. Rev. B **44**, 8330 (1991).

Si(111)√3x√3-Ag

- Atomic Structure and CLS spectra







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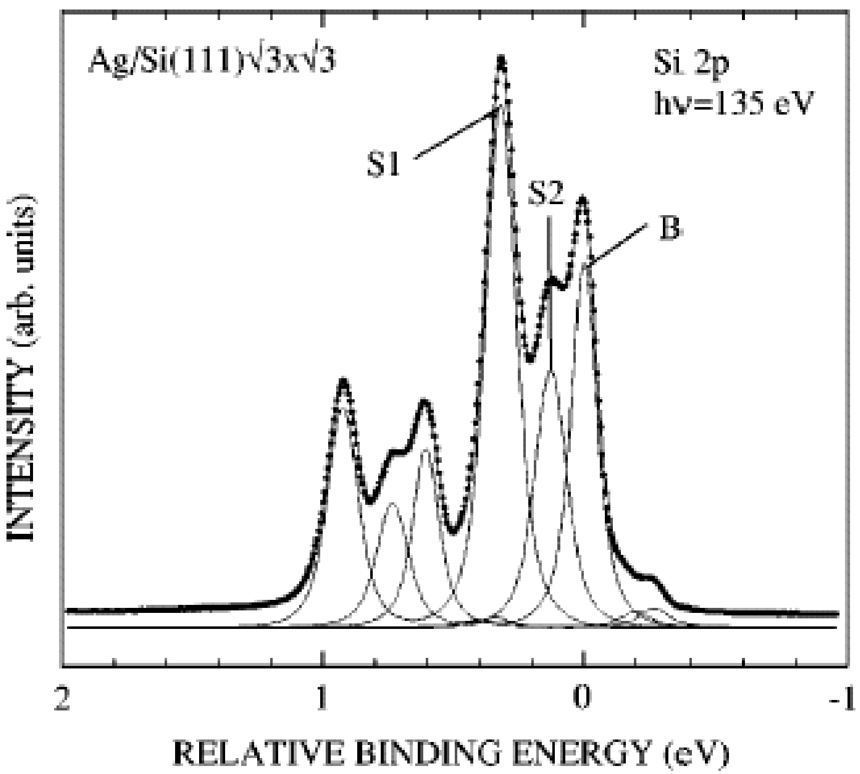
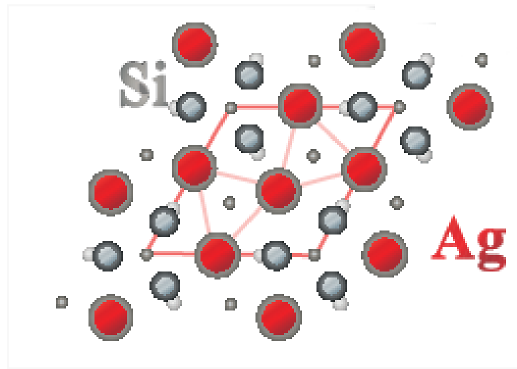
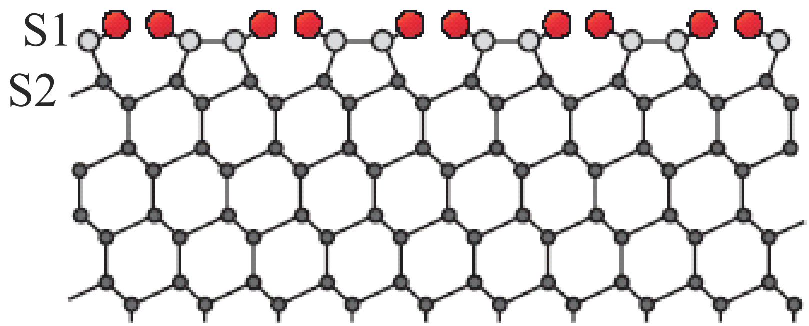
Si(111)√3x√3-Ag

- Atomic Structure and CLS spectra





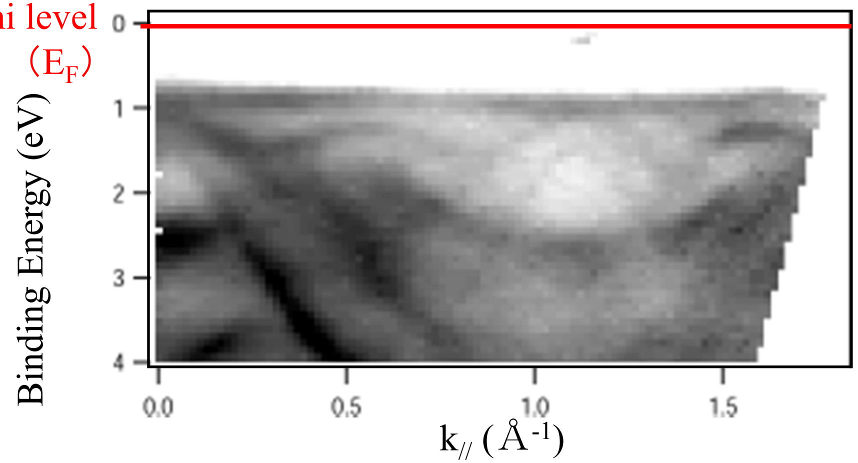


R.I.G Uhrberg *et al.*, Phys. Rev. B **65**, 081305(R) (2002).

Si(111)√3x√3-Ag

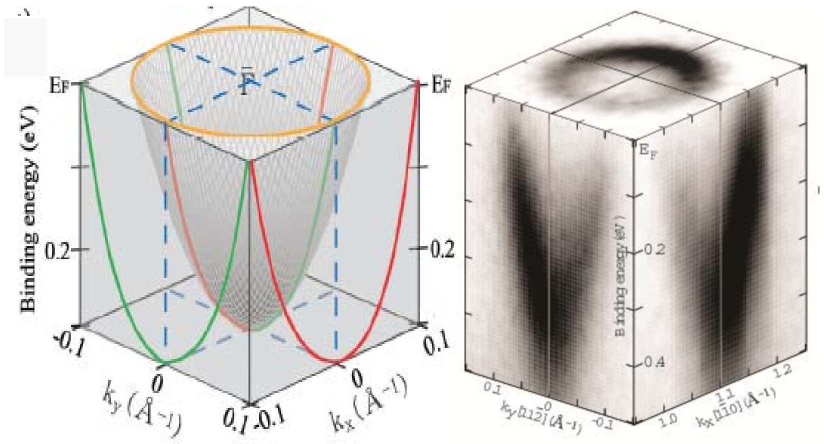
- Electronic Structure

Fermi level (E_F)



- Metallic surface-state band in the bulk band gap

Fermi surface

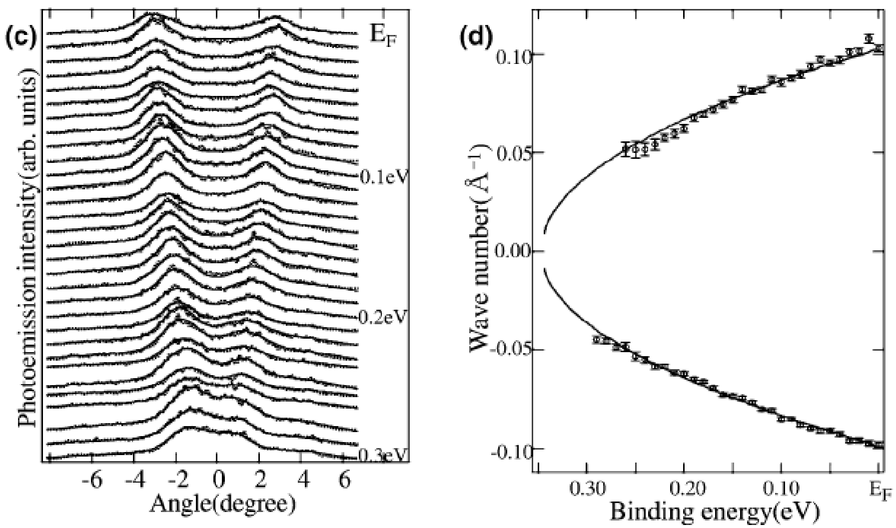


$E=\frac{\hbar^2 k^2}{2m^*}$ 2D Free-Electron-Like State

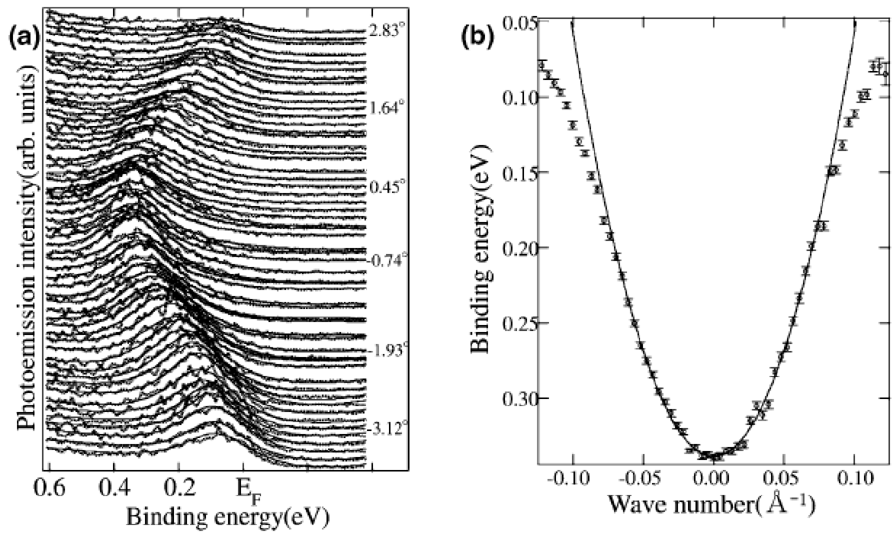
Si(111)√3x√3-Ag

- Electronic Structure

Angle-Distribution Curves (ADC)



Energy-Distribution Curves (EDC)



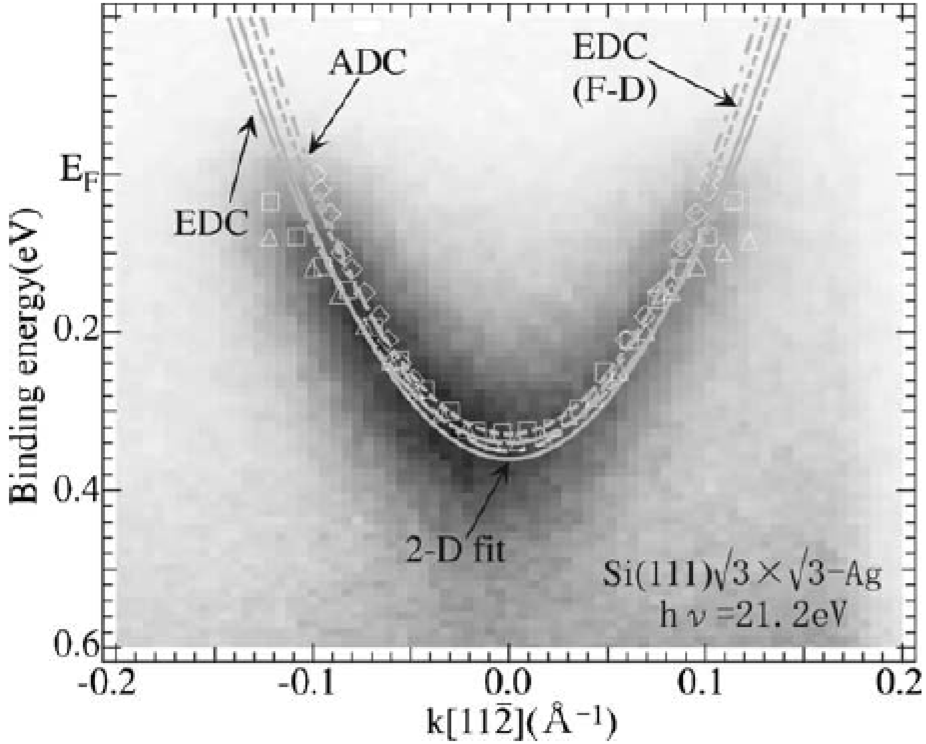
Si(111)√3x√3-Ag

- Electronic Structure

2D-fit

$$\chi^2 = \sum_i \left(\frac{E(k_i) - E_i}{w_i} \right)^2$$

$$E = \frac{\hbar^2 k^2}{2m^*} + E_0$$

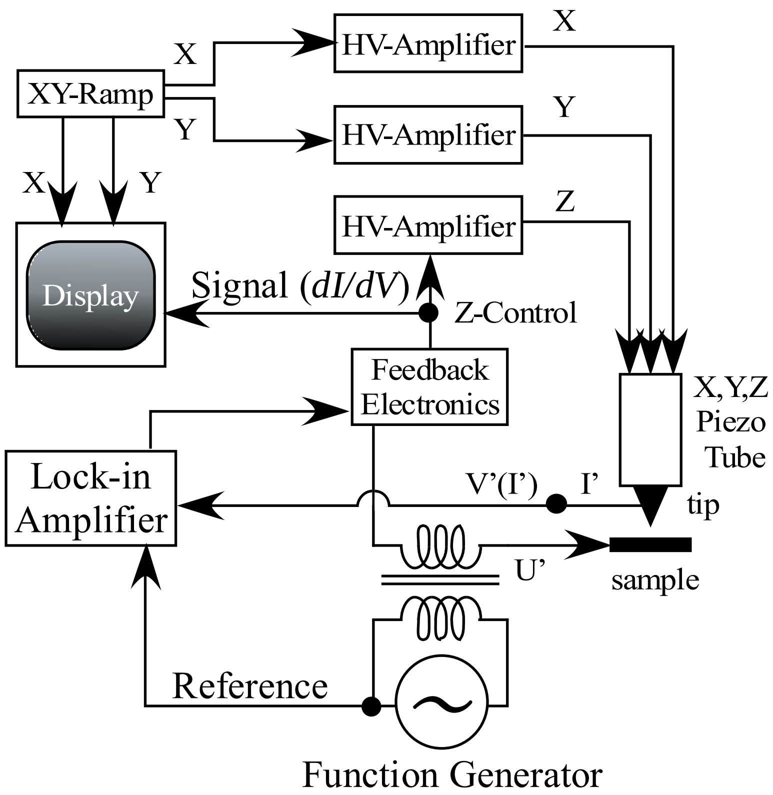


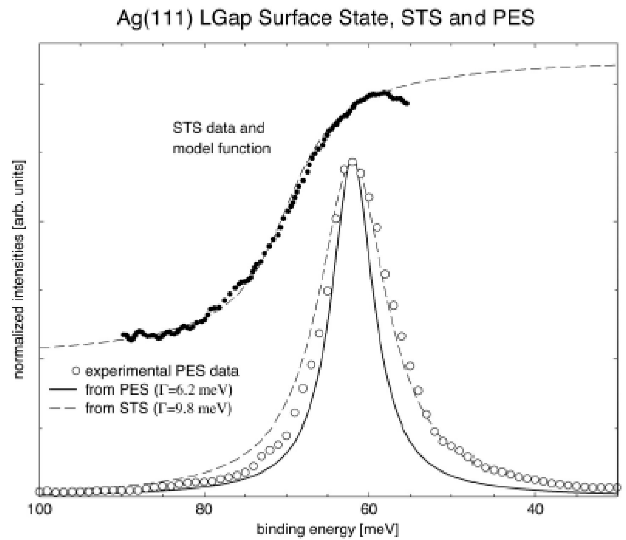
	m^*/m_e	E_0 (eV)	k_F (Å^{-1})
EDC	0.16 ± 0.02	0.32 ± 0.03	0.11 ± 0.01
ADC	0.10 ± 0.03	0.32 ± 0.03	0.10 ± 0.01
2-D	0.12 ± 0.02	0.33 ± 0.03	0.10 ± 0.01

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)

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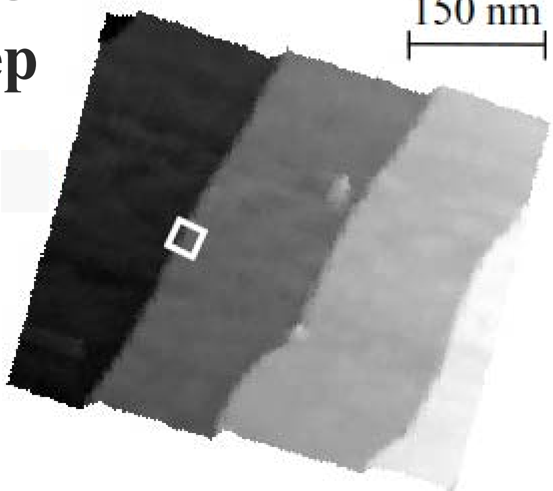
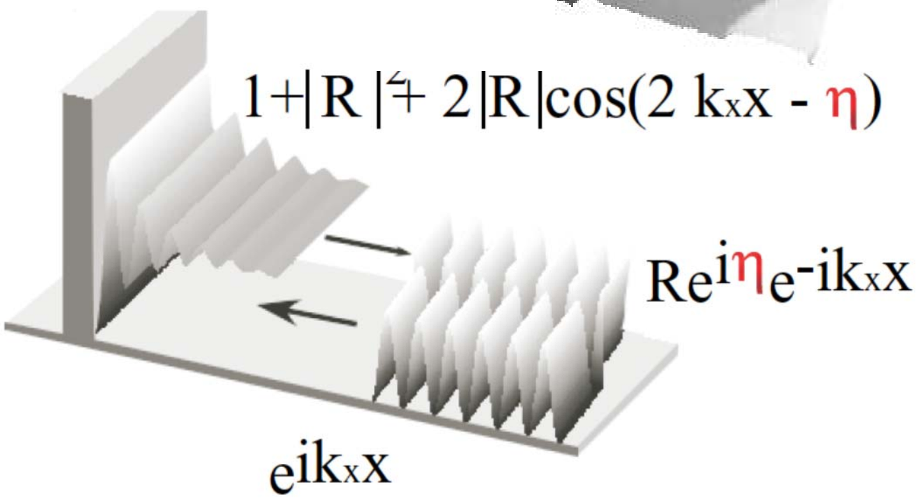
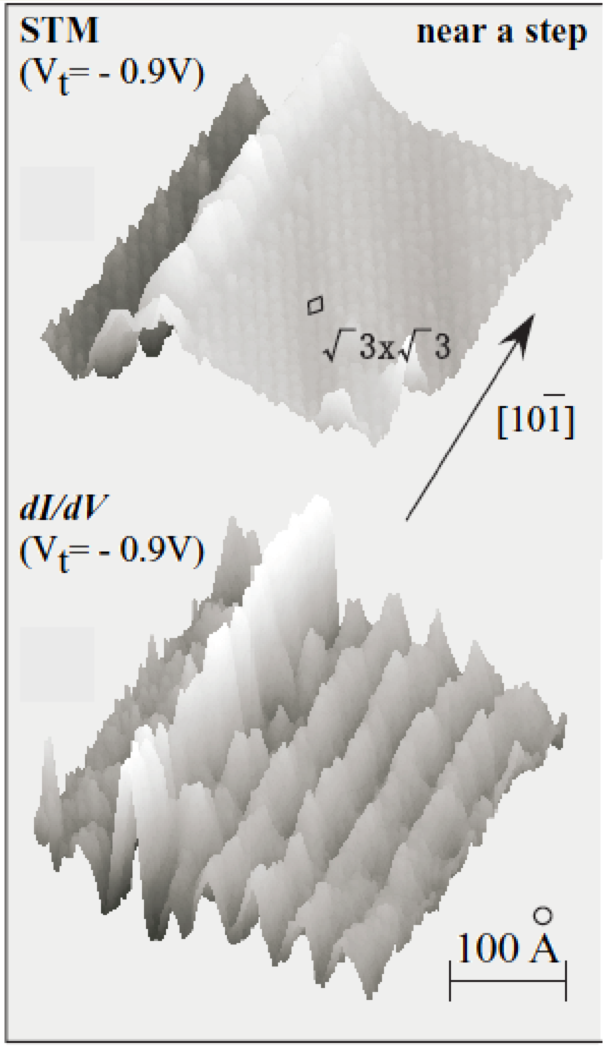
Si(111)√3x√3-Ag

- **Electron Standing wave at monatomic step**







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

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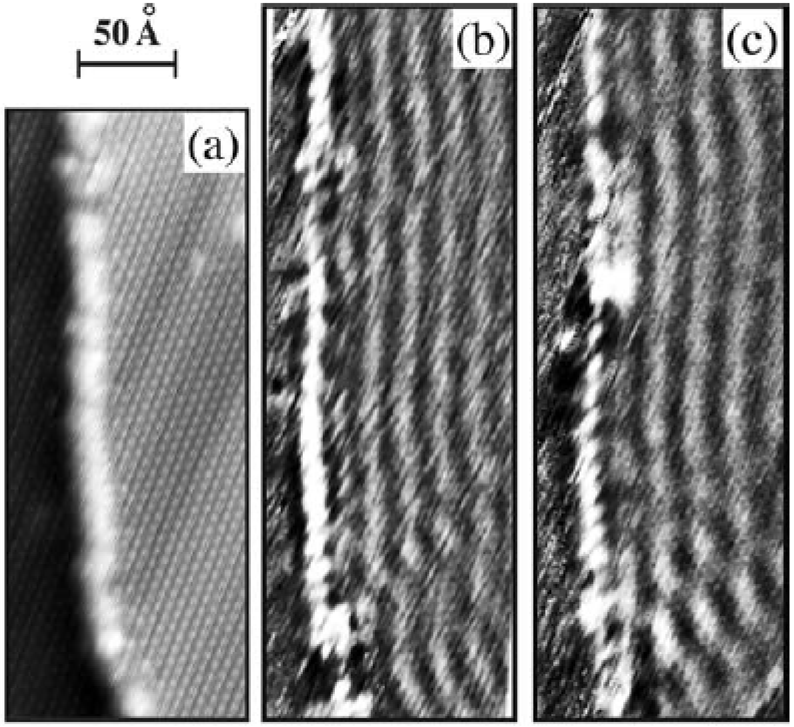
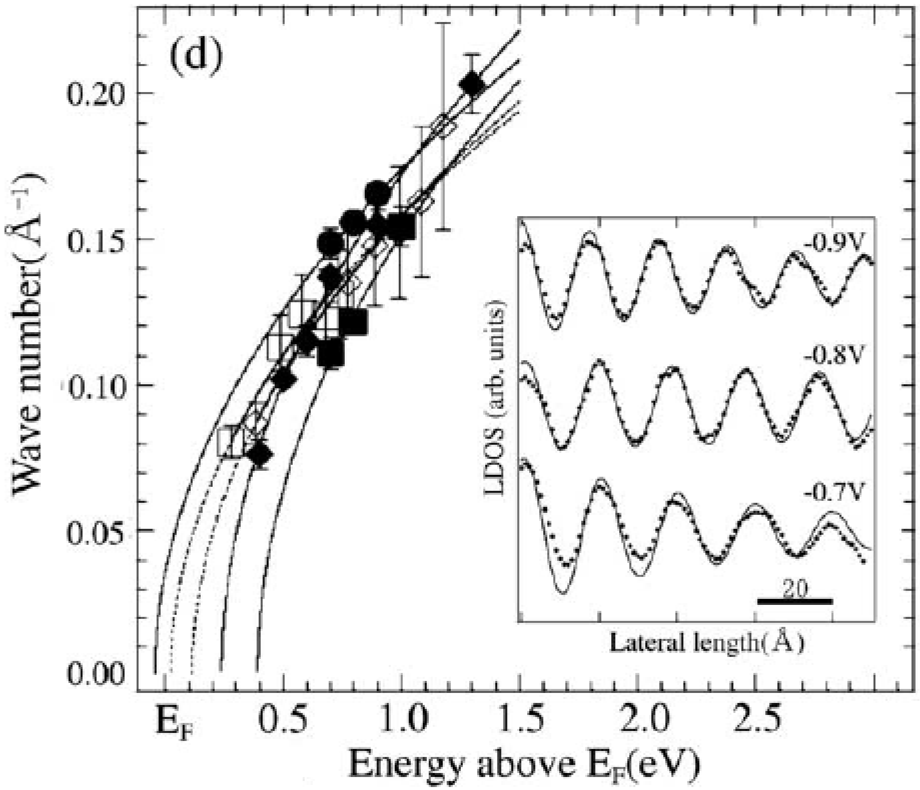
Si(111)√3x√3-Ag

- **Electron Standing wave**



STM (Vt: -0.7 V) **dI/dV (Vt: -0.9 V)** **dI/dV (Vt: -0.7 V)**



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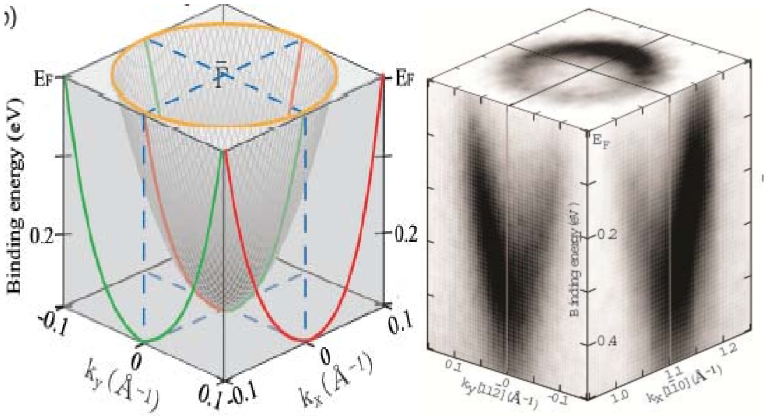
Si(111)√3x√3-Ag

- The 2-D Free electron metallic band



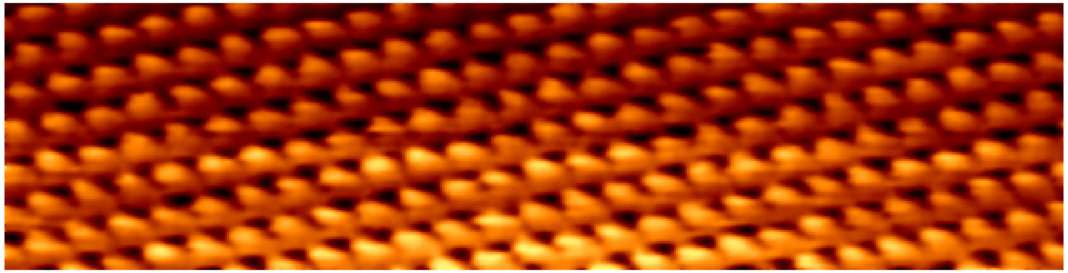
$$E = \frac{\hbar^2 k^2}{2m^*} + E_0$$

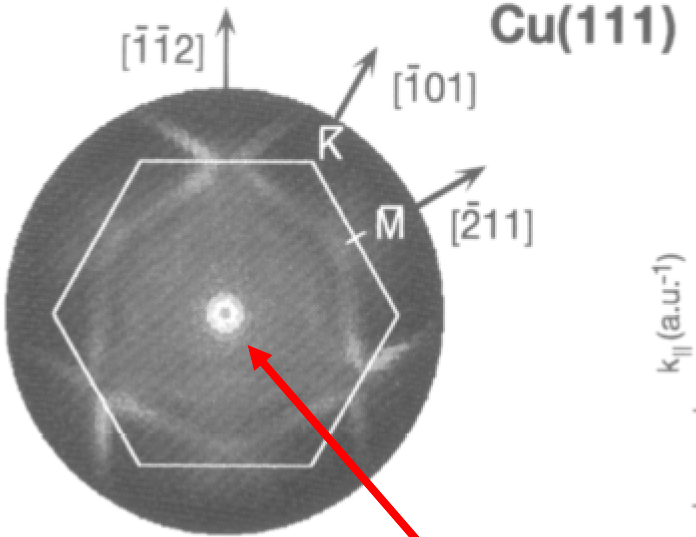
The values of m^*/m_e, E_0, k_F for analyses done by EDC, ADC, 2D fit, EDC corrected by the Fermi–Dirac distribution function, and STS

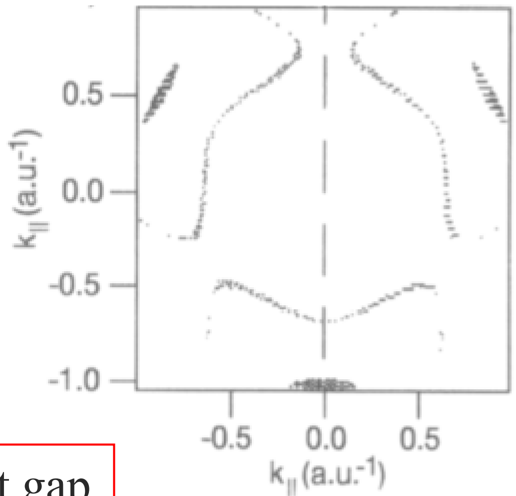
	m^*/m_e	E_0 (eV)	k_F (Å^{-1})
EDC	0.16 ± 0.02	0.32 ± 0.03	0.11 ± 0.01
ADC	0.10 ± 0.03	0.32 ± 0.03	0.10 ± 0.01
2-D	0.12 ± 0.02	0.33 ± 0.03	0.10 ± 0.01
EDC(FD)	0.15 ± 0.02	0.31 ± 0.03	0.11 ± 0.01
STS	0.13 ± 0.03		

Metal surface

Electronic structure

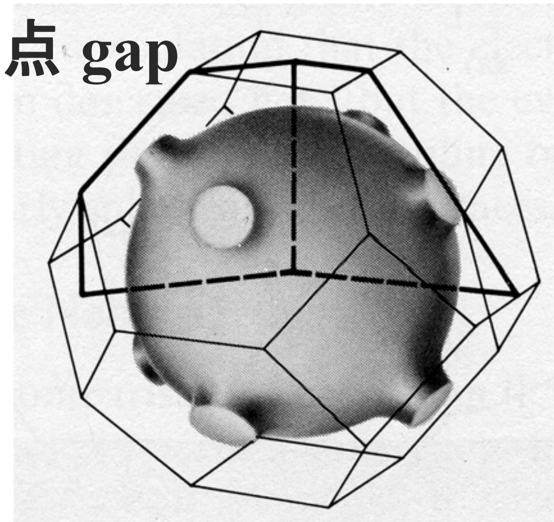




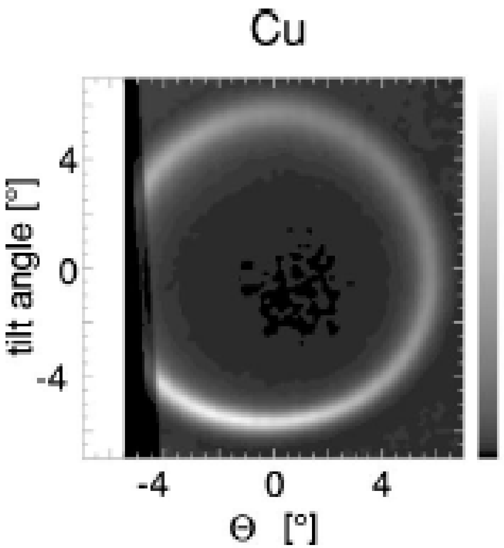


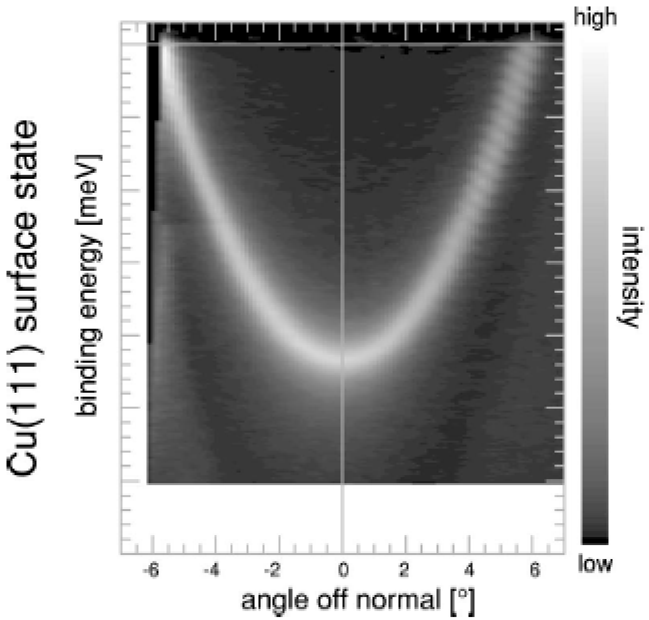
Cu(111)

L点 gap



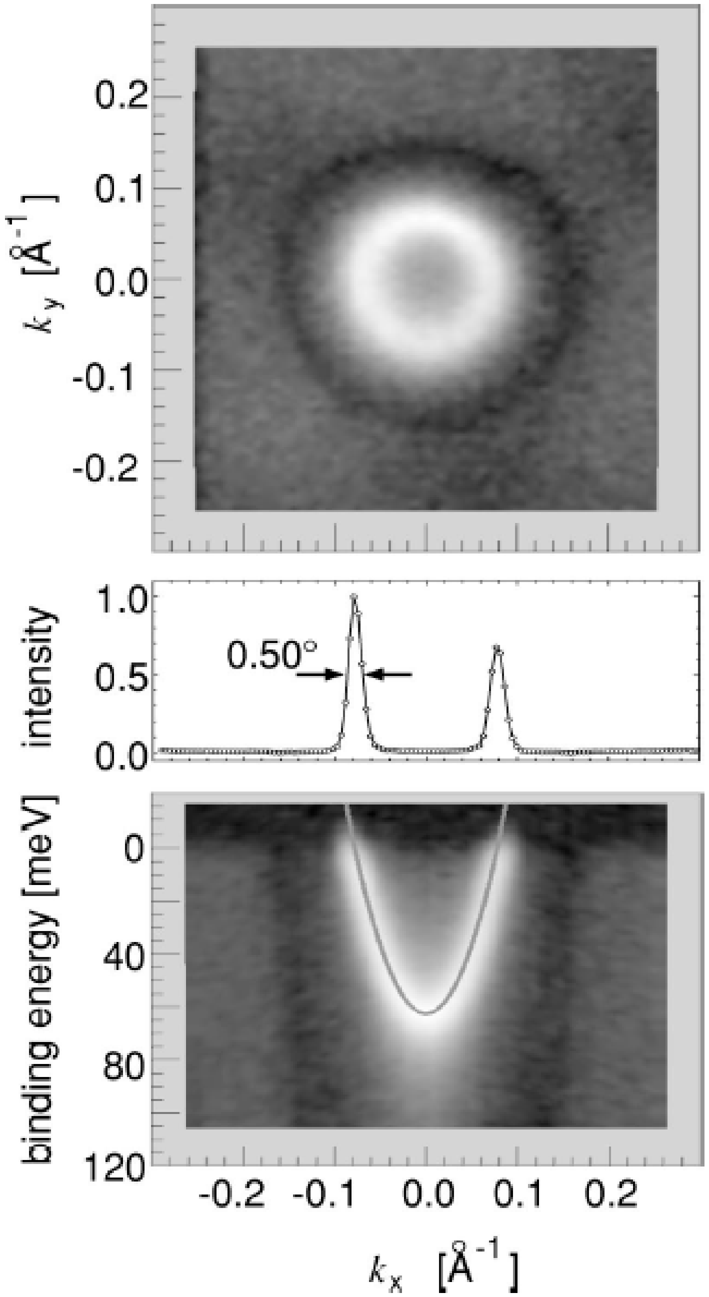
Surface state in L point gap

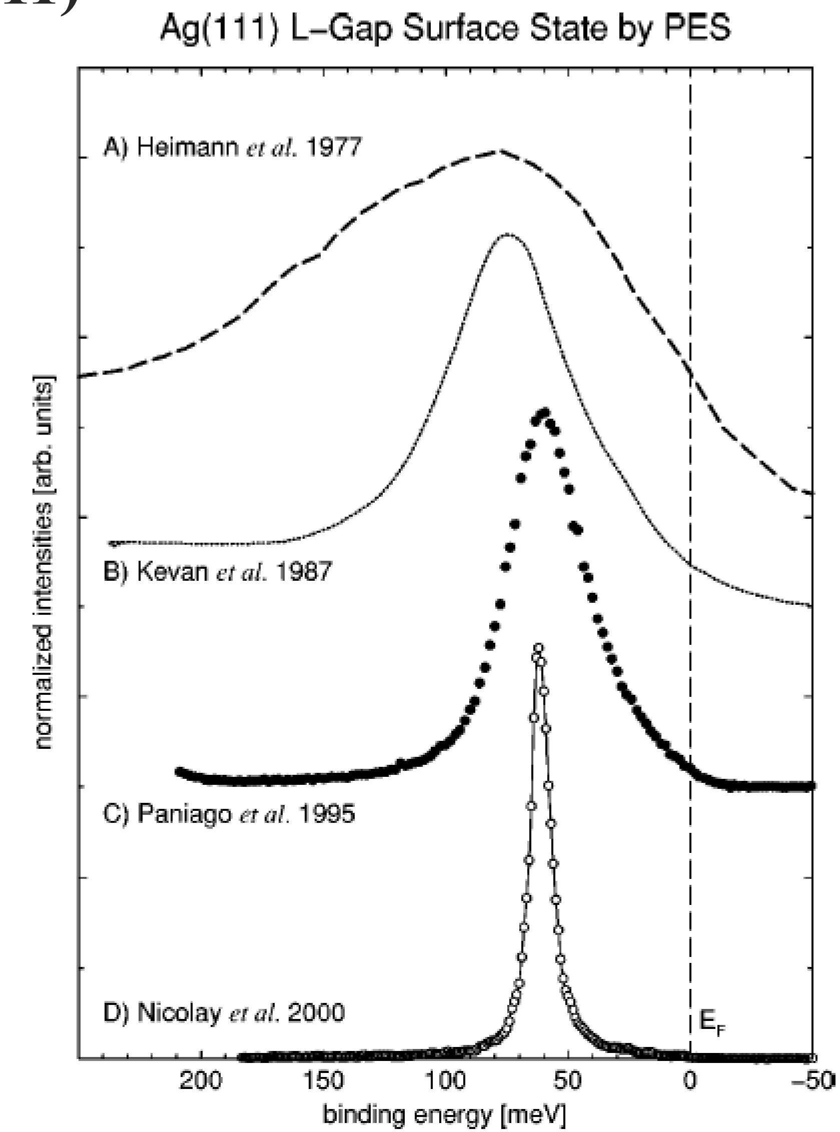




F. Reinert *et al.*,
Phys. Rev. B **63**, 115415 (2001).

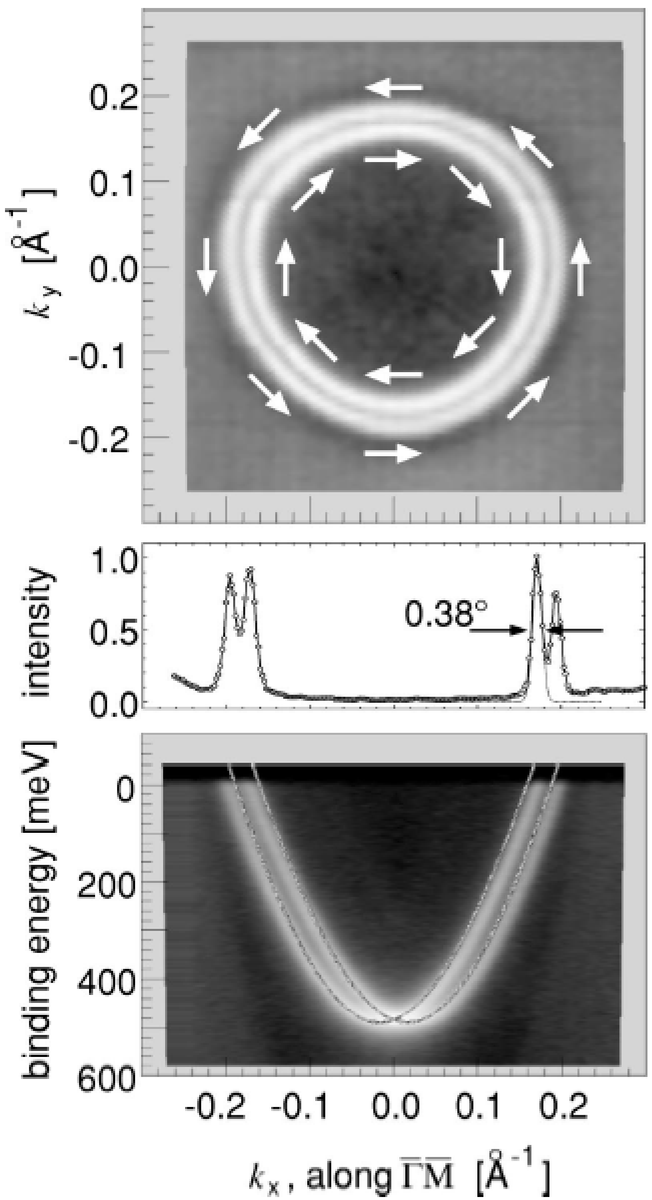
Ag(111)





F. Reinert *et al*., Phys. Rev. B **63**, 115415 (2001).
G. Nicolay *et al*., Phys. Rev. B **65**, 033407 (2001).

Au(111)



Appearance of the two surface-state bands

J. Henk *et al*., Phys. Rev. B **68**, 165416 (2003)

Surface Rashba effect

E. I. Rashba, Sov. Phys. Solid State 2, 1109(1960)

Kramers degeneracy : E(k,↑)=E(k,↓)

Time reversal symmetry: E(k,↑)=E(-k,↓)

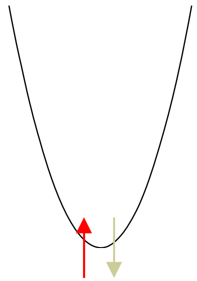
~~Space inversion symmetry: E(k,↑)=E(-k,↑)~~

Breakdown at a surface

Spin-split bands

$$-\frac{\hbar^2}{2m}\nabla^2\psi(\vec{r}) = E\psi(\vec{r})$$

$$E = \frac{\hbar^2 k^2}{2m}$$



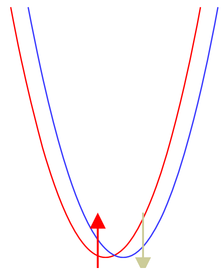
Spin-Orbit Coupling Hamiltonian

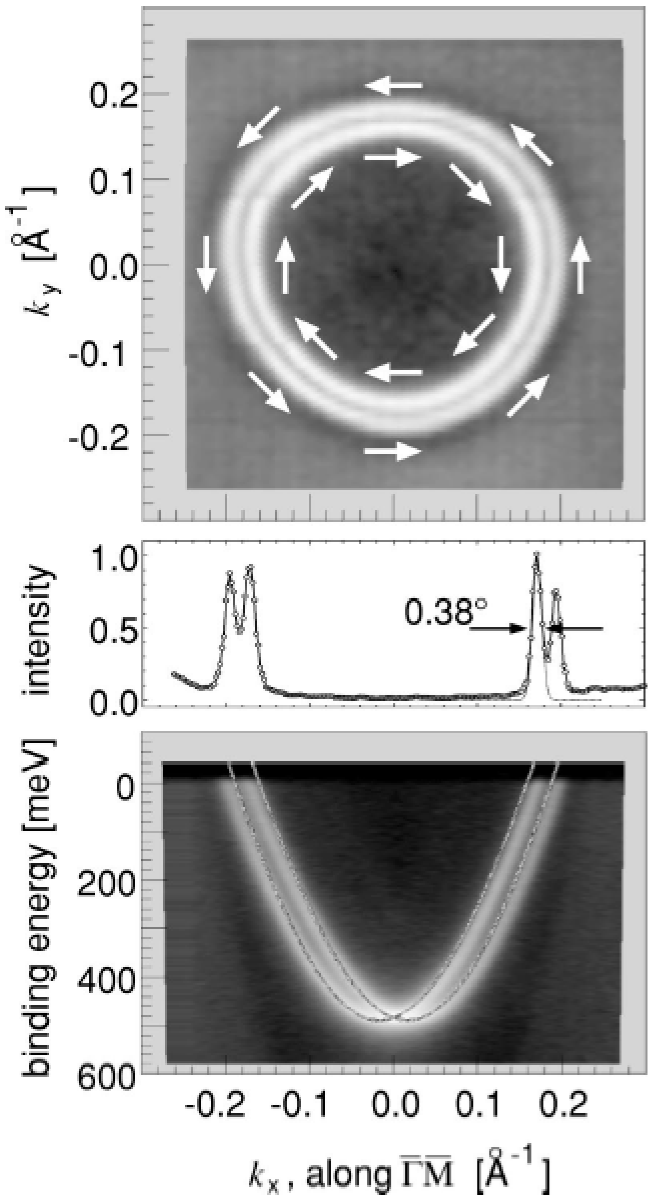
Pauli matrix

$$H_{SOC} = \frac{\hbar}{4m_e^2c^2}\vec{\sigma}\cdot(\nabla V \times \vec{p})(\propto \vec{s}\cdot\vec{L})$$

Electric field (0,0,E_z)

$$E = \frac{\hbar^2 k^2}{2m} \pm \alpha\hbar k$$





J. Henk *et al*., Phys. Rev. B **68**, 165416 (2003)

Au(111)

Spin-orbit splitting

$$H_{SOC} = \frac{\mu_B}{2c^2}(\mathbf{v} \times \boldsymbol{\mathcal{E}}) \cdot \boldsymbol{\sigma},$$

$$E^{\uparrow,\downarrow}(k) = E_0 + \frac{\hbar^2 k^2}{2m^*} \pm \alpha k = E_0' + \frac{\hbar^2 (k \pm k_0)^2}{2m^*},$$

↓

Spin-slit surface-state band

↓

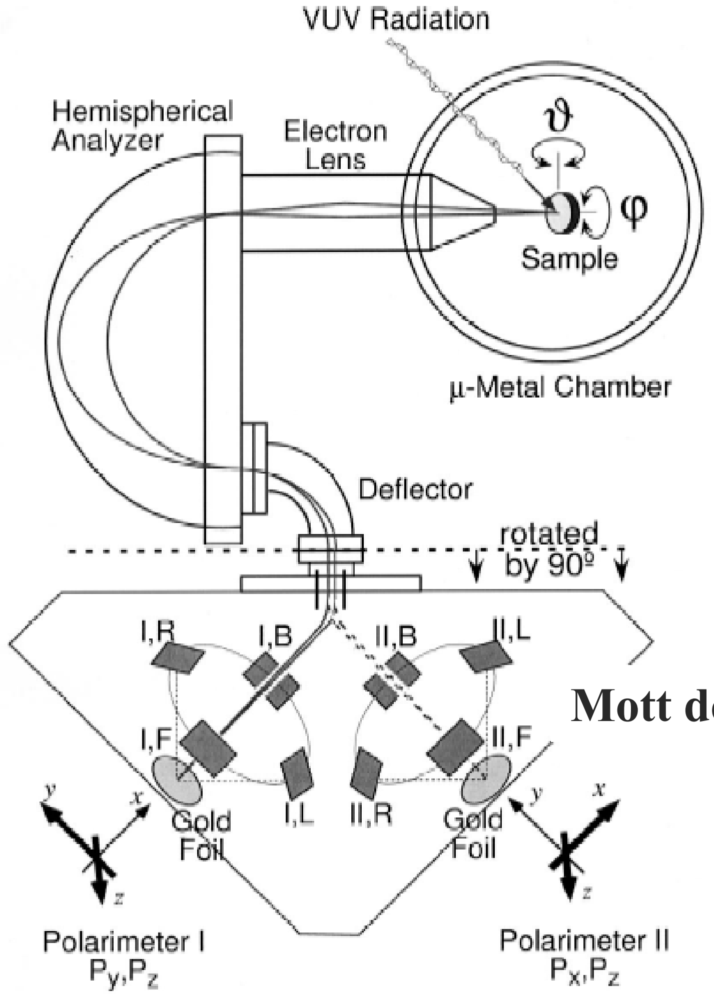
Spin-resolved photoemission spectroscopy

Fermi surface mapping with spin-resolved photoemission spectroscopy

H. Moritz *et al*., J. Elec. Spec. Rel. Phenom. **124**, 263 (2002).

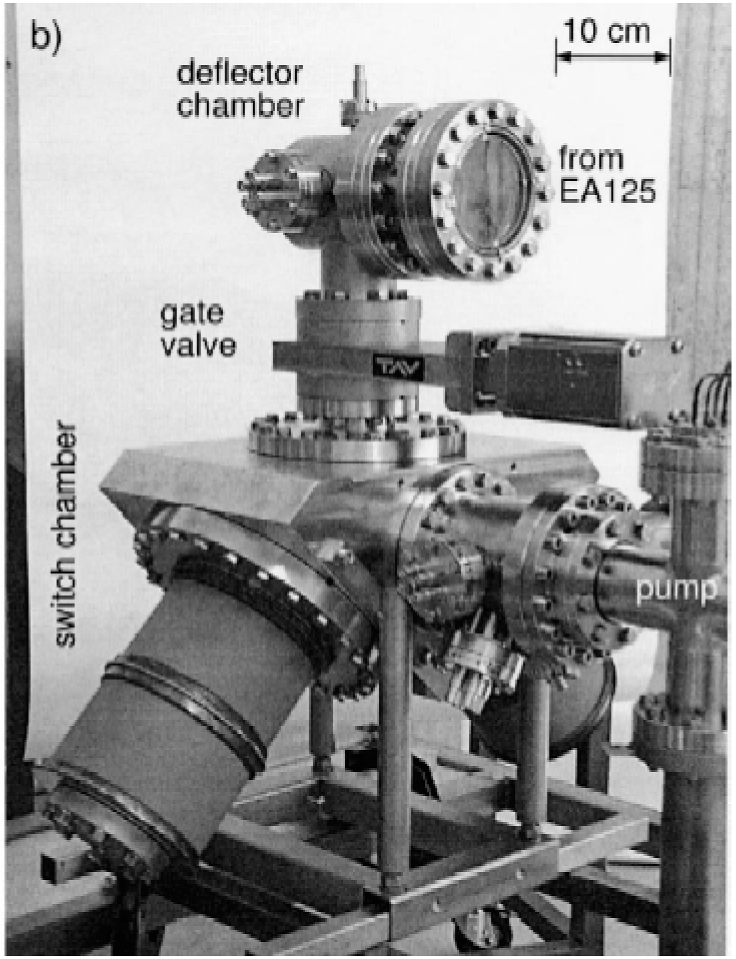
kx,ky,kz,σx,σy,σz are determined with synchrotron radiation

<u>COmplete PHotoEmission Experiment (COPHEE)</u>

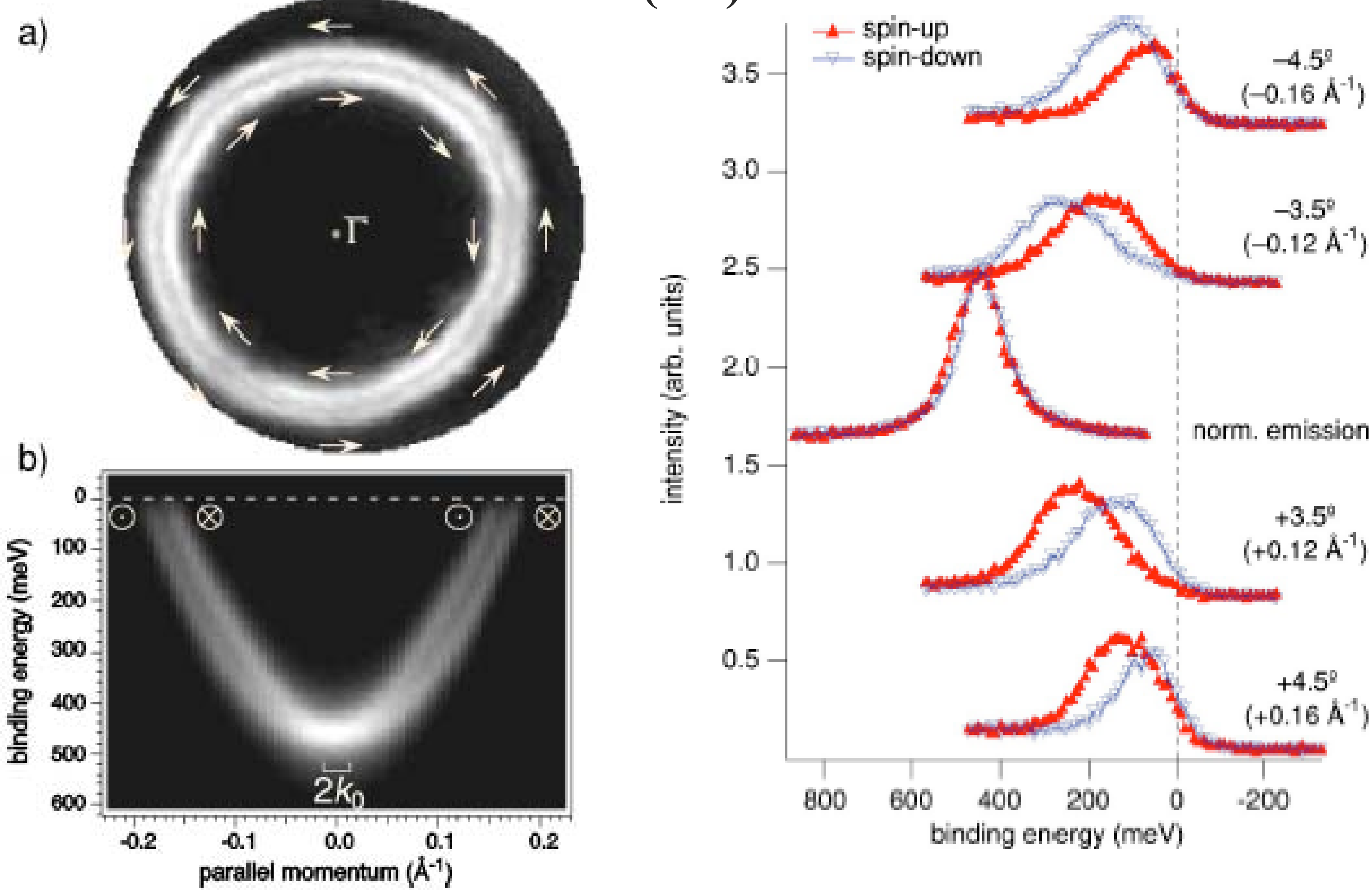


Mott detector

Fig. 4. Schematic view of COPHEE, the COmplete PHotoEmission Experiment. Electrons photoemitted from a sample by UV radiation are energy- and angle-selected by an electrostatic analyzer and detected in two orthogonal Mott polarimeters. In an electrostatic beam deflection system the spin direction is conserved and polarimeter I measures the polarization components P_y and P_z, while polarimeter II measures P_x and P_z. The beam is switched between the two to allow quasi-simultaneous data collection. The labels of the detectors are used in Eq. (10) in the text. The polarimeter system is shown rotated by 90° for graphical clarity.

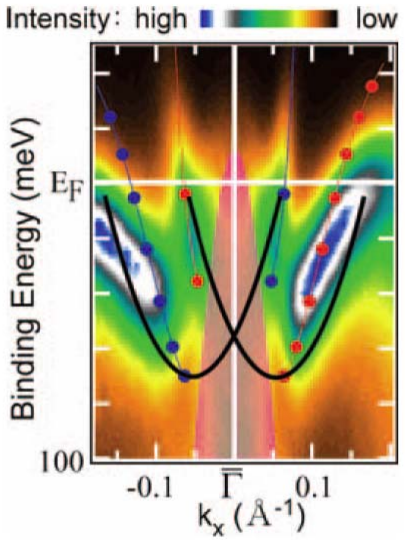


Au(111)



M. Hoesch *et al*., Phys. Rev. B **69**, 241401(R) (2004)

Surface Rashba effect



A band diagram of the Bi(111) surface states taken at photon energy of 21.2 eV.[11, 12] Dispersion curves of the theoretical calculation results and the simple Rashba model are overlapped on the figure.

Table 1. Rashba parameters for various crystal surfaces[18]: Atomic number (Z), the Rashba constant ($|\alpha_R|$), the Rashba momentum(k_R), the Rashba energy(E_R).

Surface	Z	$\lvert\alpha_R\rvert$(eVÅ)	k_R(Å^{-1})	E_R(meV)	Ref.
Ag(111)	47	0.03	0.004	$<$0.2	13, 14)
Au(111)	79	0.33	0.012	2.1	14, 15)
Bi(111)	83	0.56	0.05	14	16)
$\sqrt{3}\times\sqrt{3}$-Pb/Ag(111)	82/47	1.42	0.03	21	17)
$\sqrt{3}\times\sqrt{3}$-Bi/Ag(111)	83/47	3.05	0.13	200	18)

Metal films

Electronic structure

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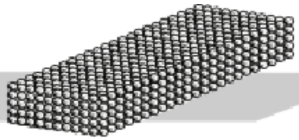
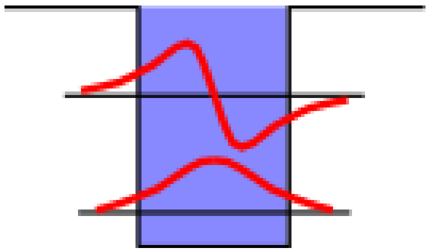
- Quantum Film



Quantum Size effect, Quantum Confinement Effect

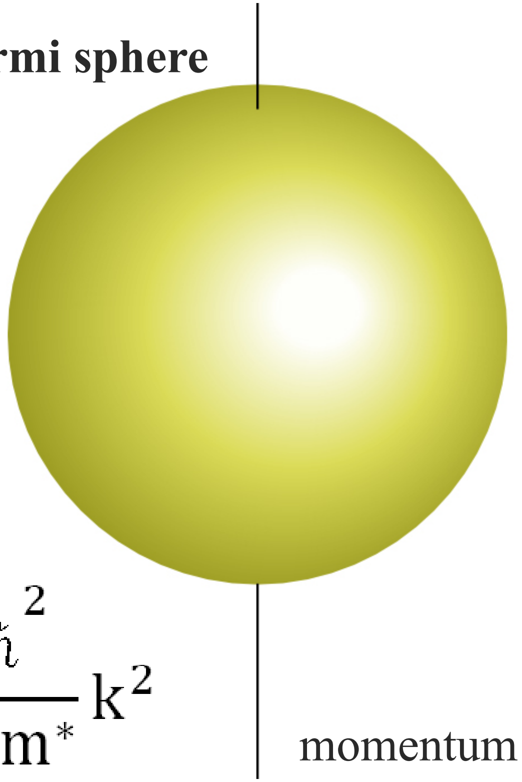


A problem of particles (electrons) in a box

Energetically quantized electronic states
Quantum Well States (**QWS**)

Free electron model

Fermi sphere



$$E = \frac{\hbar^2}{2m^*} k^2$$

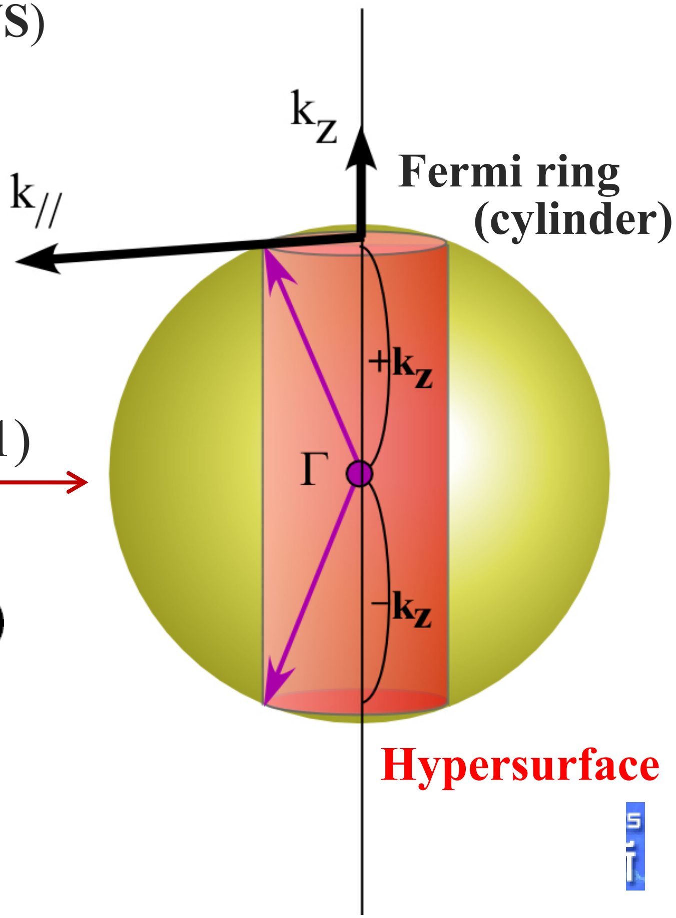
momentum space

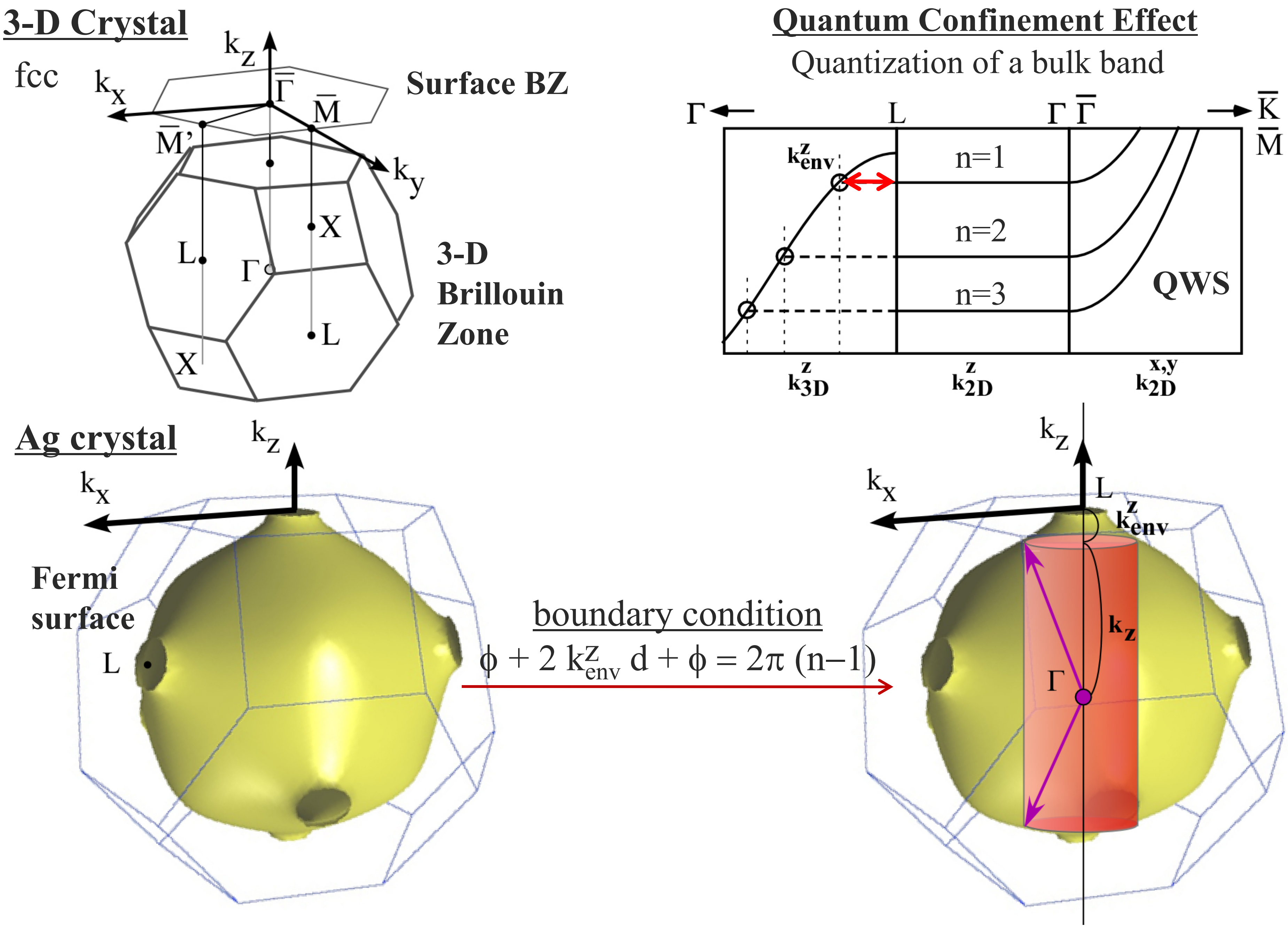
boundary condition

$$\phi + 2\,k_z\,d + \phi = 2\pi\,(n-1)$$

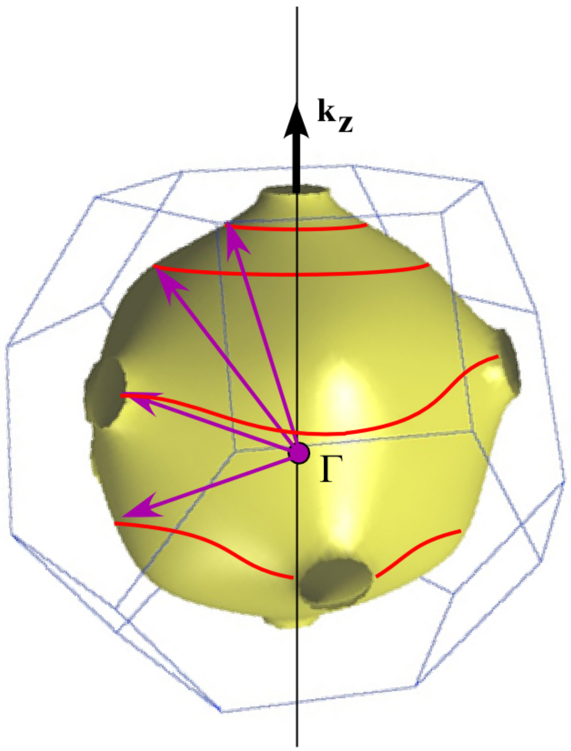
$$E = \frac{\hbar^2}{2m^*}(k_z^2 + k_{//}^2)$$

discrete



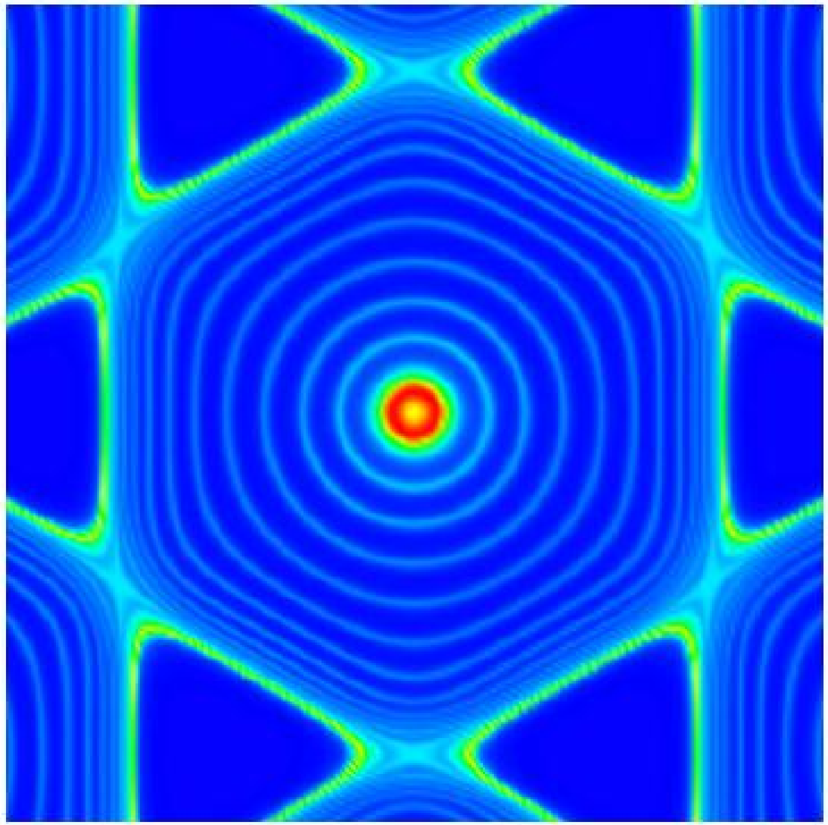

3-D Crystal
fcc
k_z
k_x
$\bar{\Gamma}$
Surface BZ
$\bar{M}$
$\bar{M}$'
k_y
X
L
Γ
L
X
3-D
Brillouin
Zone
Quantum Confinement Effect
Quantization of a bulk band
Γ
L
Γ $\bar{\Gamma}$
$\bar{K}$
$\bar{M}$
k^z_{env}
n=1
n=2
n=3
QWS
k^z_{3D}
k^z_{2D}
$k^{x,y}_{2D}$
Ag crystal
k_z
k_x
Fermi
surface
L
boundary condition
$\phi + 2\, k^z_{env}\, d + \phi = 2\pi\, (n-1)$
k_z
k_x
L
k^z_{env}
k_z
Γ

Uktrathin Ag(111) film (quantum film)



Fermi surface of Ag(111) slab calculation

(15 ML-Ag(111) free-standing slab)



6-fold symmetry

Summation of the wave functions of + kz and -kz

weight: spectral intensity

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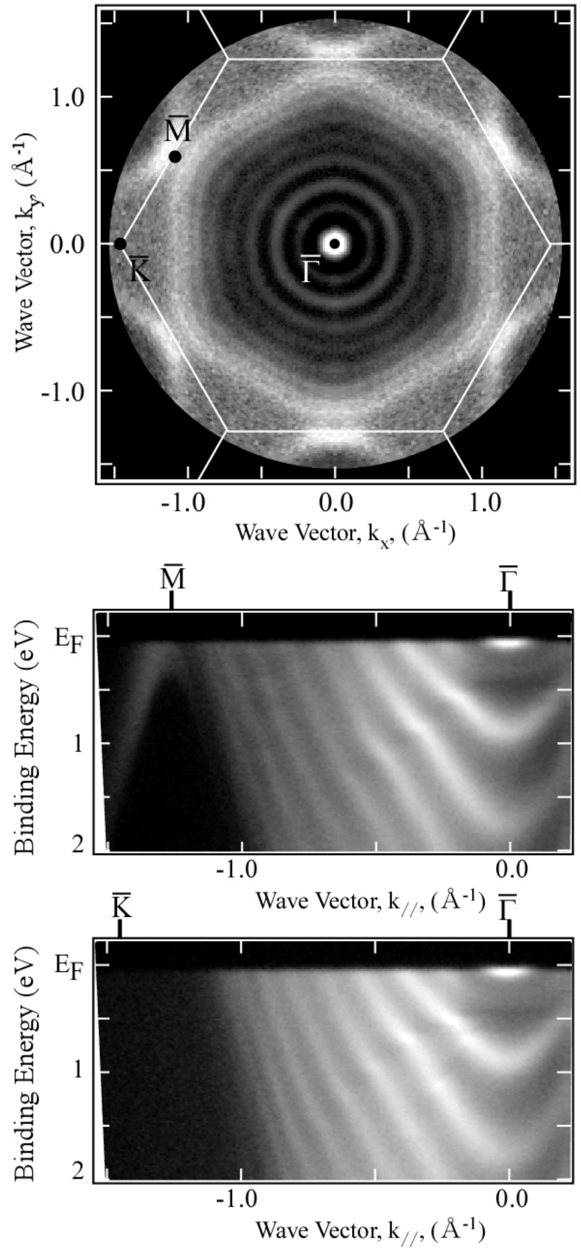
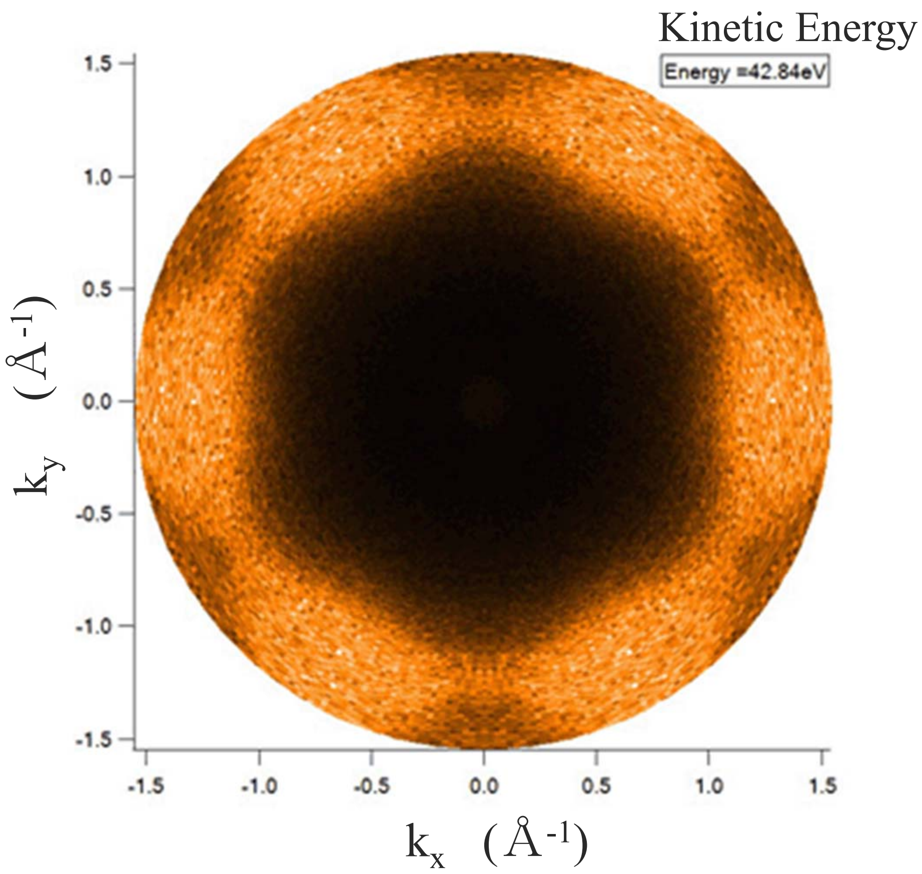
Epitaxial 15ML-Ag(111) film on Si(111)





In addition to band features expected,
new features, kinks, hexagons at $\bar{\Gamma}$, are observed.

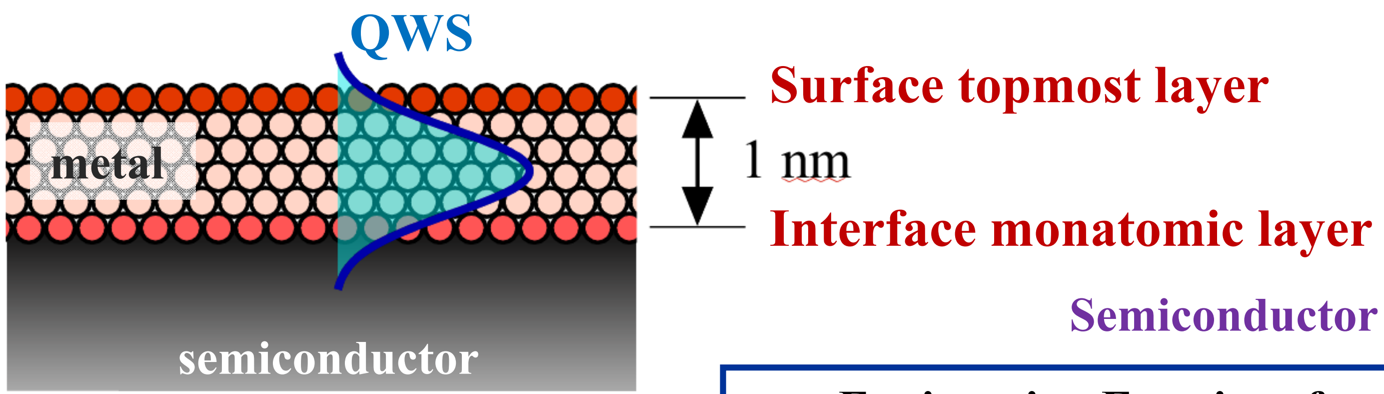
Our interests

<u>**Quantum Size effect, Quantum Confinement Effect**</u>

Thickness : <u>Semiconductor</u>
de Broglie wave, ~ 100 nm
<u>Metal</u>
Fermi wavelength, **~ 1nm**

Large ratio of a surface (interface) monatomic layer to film atomic layers: > 1 / 10

Ultrathin film (2-D growth)



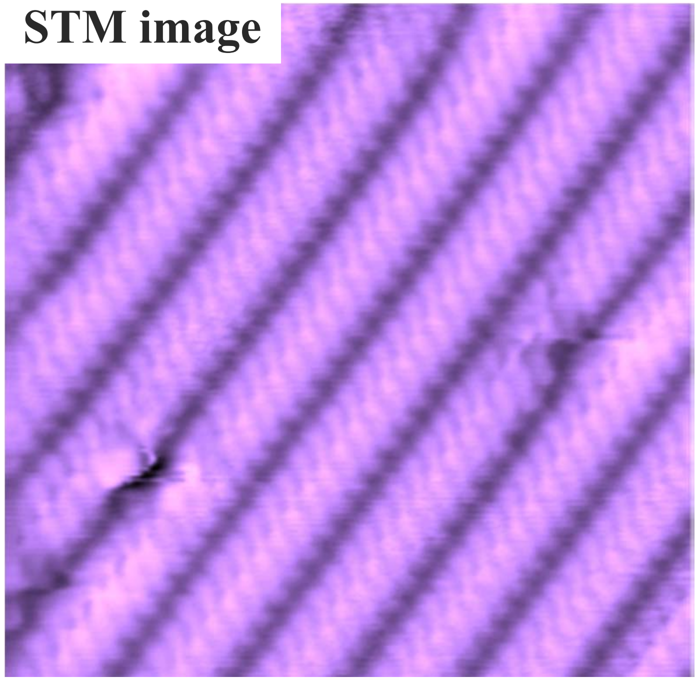
Semiconductor Surface Science

Engineering Fermi surface topology
Electronic topological transition
by an interface monatomic layer

Choice in Semiconductor Surface Science

A periodic array of atomic wires:

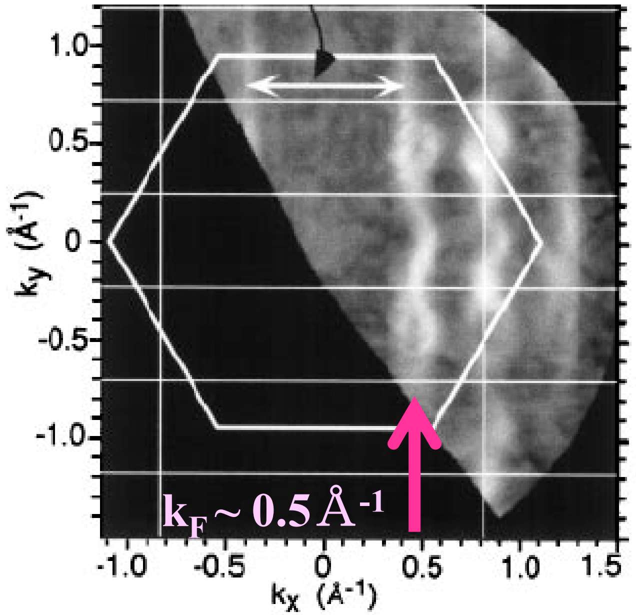
STM image

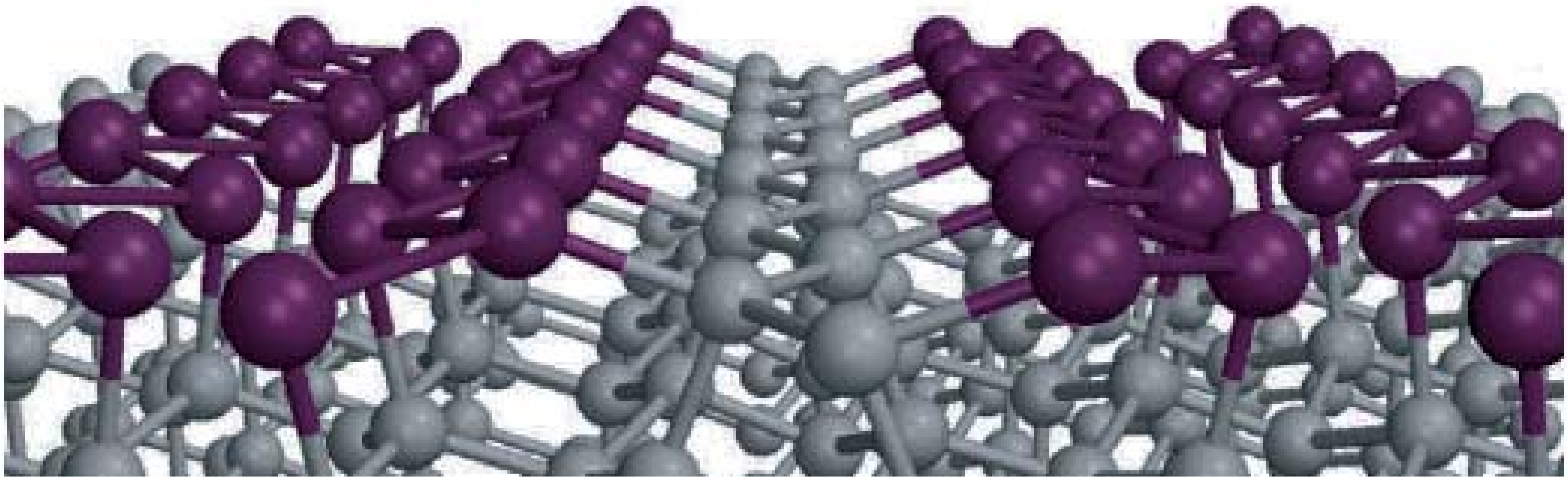


Si(111)4x1-In

$a_{int} = 1.3$ nm

Photoemission Fermi surface

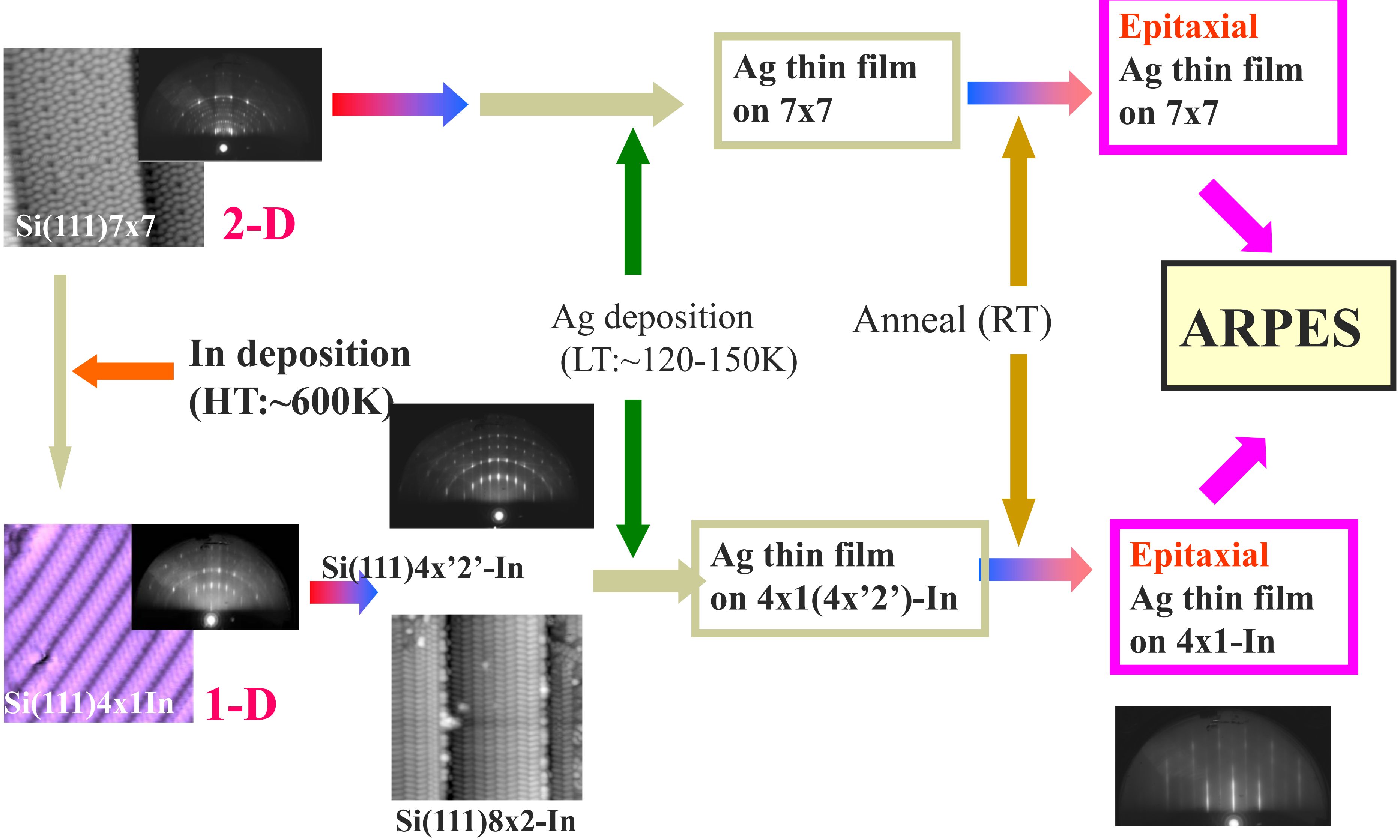




Experiments

Exchange of interface layer between film and substrate

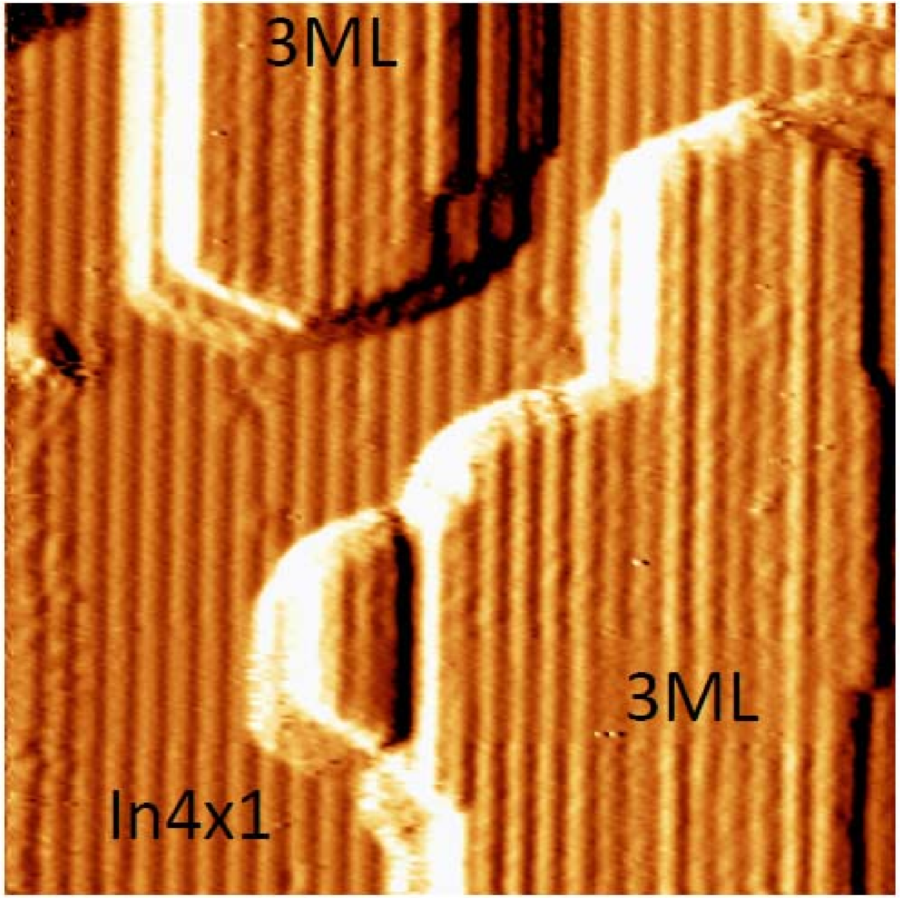
Substrate: vicinal Si(111) (1.8° -off)

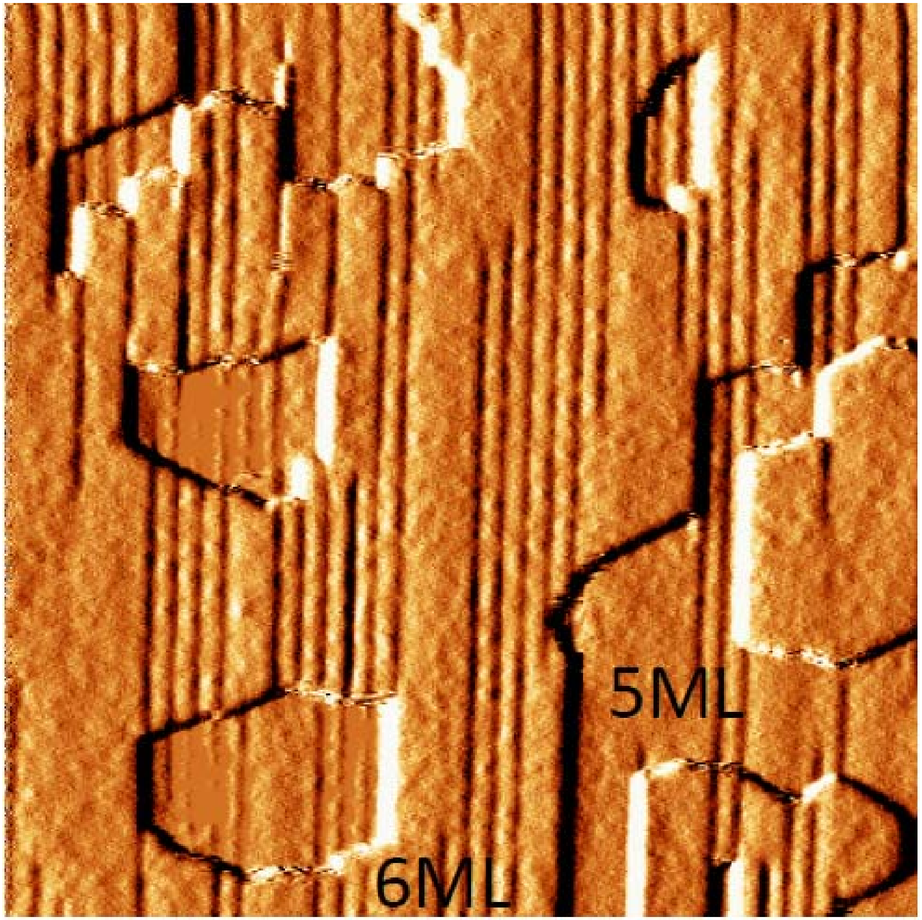


Results & Discussions

STM: Ag film / Si (111)4x1-In

T. Uchihashi *et al*., Phys. Rev. Lett. **96,** 136104 (2006)



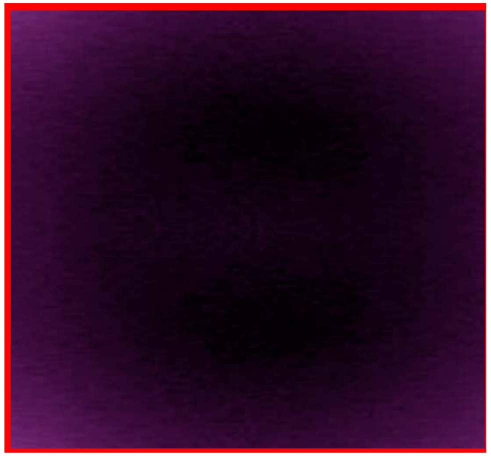


Results & Discussions

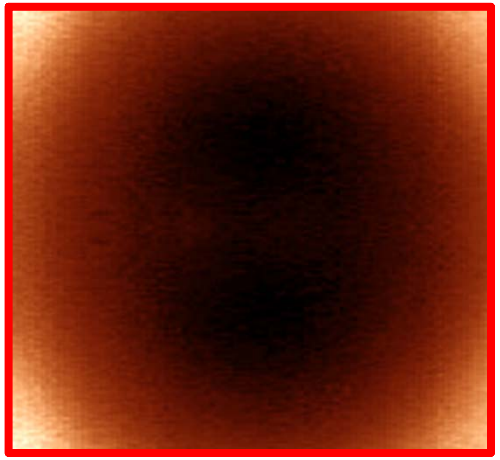
BL3.2 VUV Elettra, Italy

hv=50eV room temperature

Ag film (~1nm) / Si (111)4x1-In



Ag film (~1nm) / Si (111)7x7



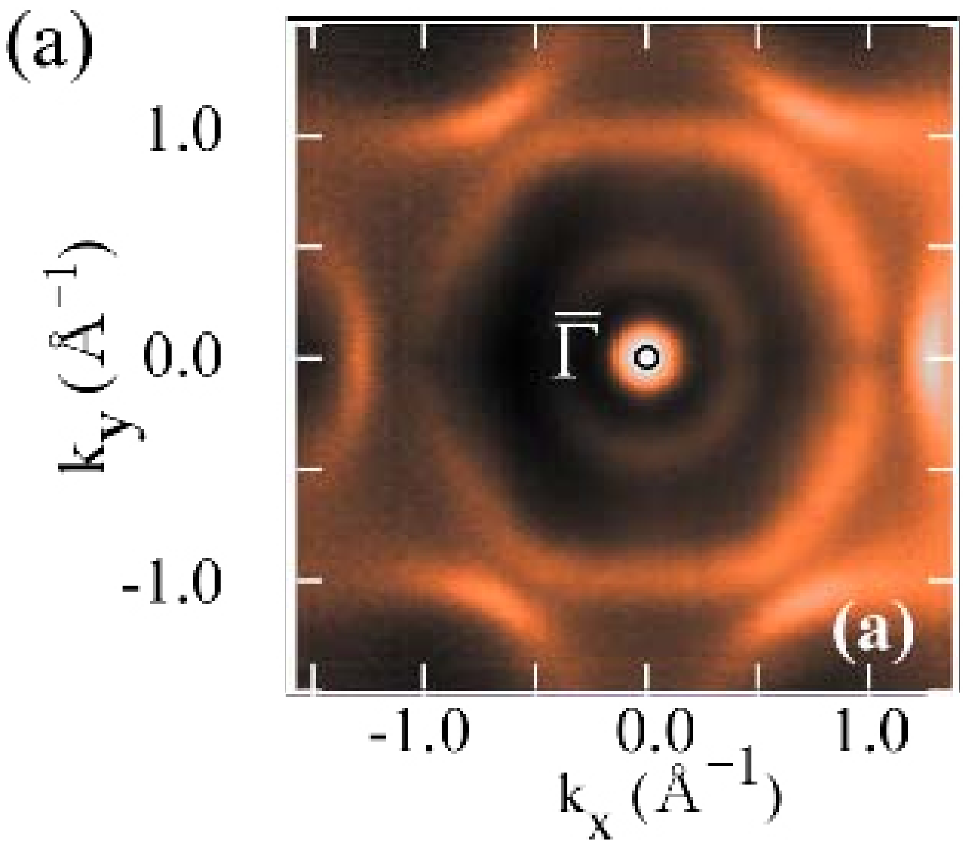
1.0 $Å^{-1}$

1.0 $Å^{-1}$

Results & Discussions

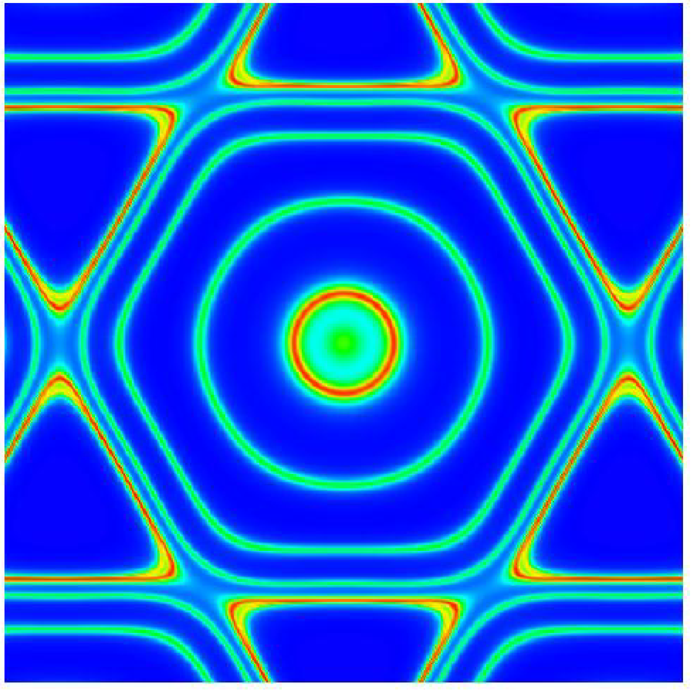
ARPES: Ag film (~1nm) / Si (111)7x7

Photoemission Fermi surface



Calculation

(6 ML-Ag(111) free-standing slab)



weight:
spectral intensity

$$\phi_{vac} + 2k_z d + \phi_{sub} = 2\pi n \quad \Longleftrightarrow \quad 2k_z d + 2\phi_a = 2\pi n$$

Different $k_z(E)$ or $E(k_z)$

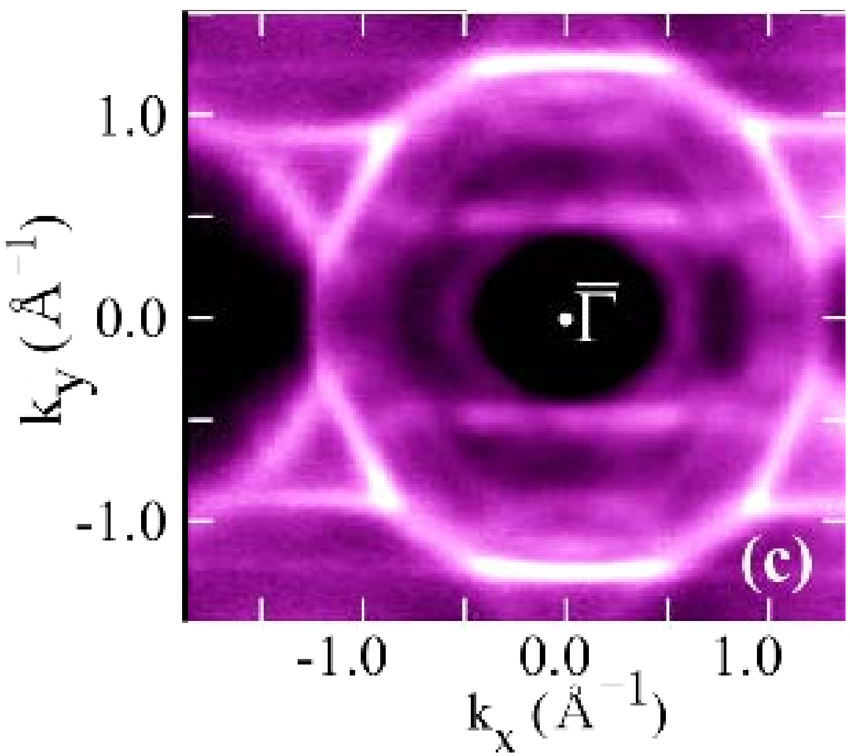
Results & Discussions

ARPES: Ag film (~1nm) / Si (111)4x1-In

hv=50eV

room temperature

Photoemission Fermi surface



Solid Surface

Playgrounds for low-dimensional physics

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THE INSTITUTE FOR SOLID STATE PHYSICS 東京大学 物性研究所

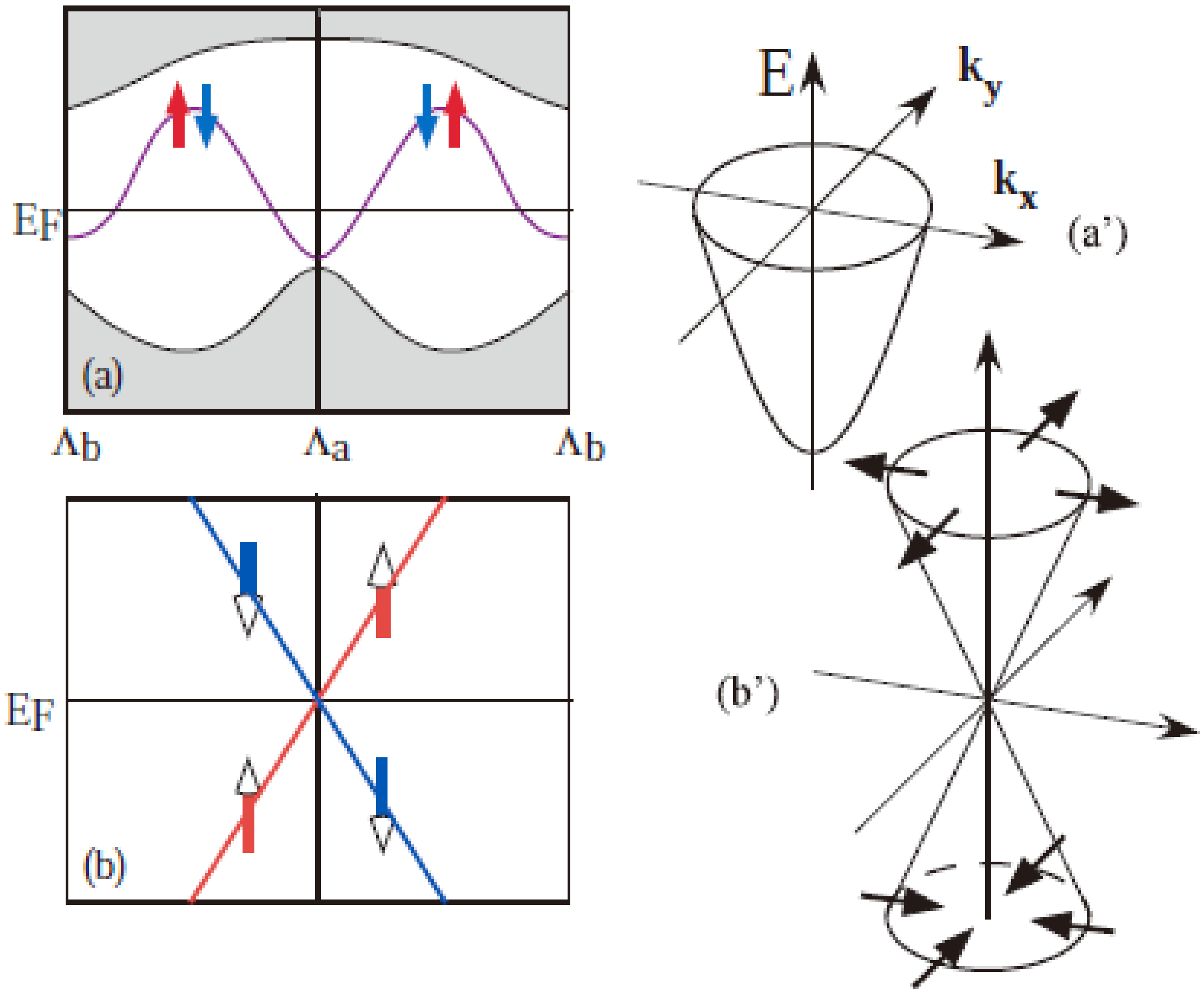
Surface electronic structures

Schroedinger electron

$$\frac{\mathbf{p}^2}{2m}\Psi = E\Psi$$

Dirac-Wely electron

$$(c\alpha \cdot \mathbf{p})\Psi = E\Psi$$



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Surface electronic structures

Spin-orbit interaction

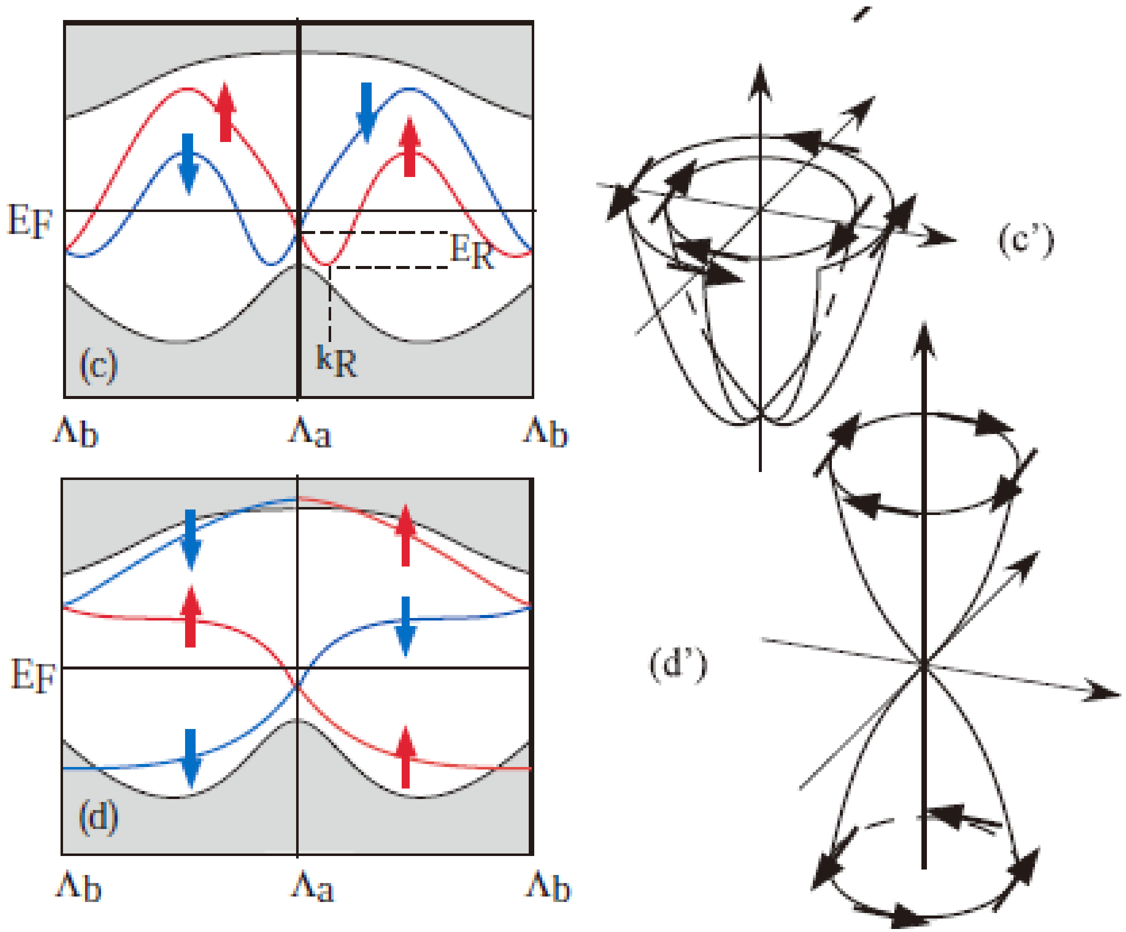
Dirac equation: $[\frac{\mathbf{p}^2}{2m} - \frac{e\hbar\sigma\cdot\mathbf{p}\times\xi}{4m^2c^2} + \frac{e\hbar}{2m}\sigma\cdot\mathbf{B} - \frac{e\hbar^2}{8m^2c^2}\nabla\cdot\xi]\Psi = E\Psi$

Surface Rashba effect

$$E^{\uparrow,\downarrow}(k) = \frac{\hbar^2k^2}{2m} \pm \frac{\hbar^2}{2m^2c^2}(\frac{\partial V}{\partial z})k$$

$$= \frac{\hbar^2k^2}{2m} \pm \frac{\hbar^2}{m}k_Rk = \frac{\hbar^2k^2}{2m} \pm \alpha_Rk$$

Quantum Spin Hall Phase



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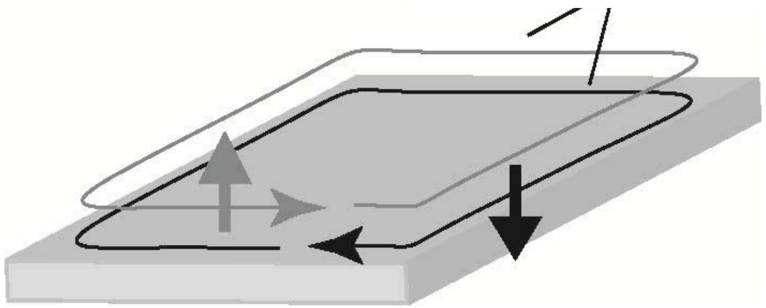
Quantum spin Hall phase (topological insulator)

Kane,Mele, PRL(2005), Bernevig, Zhang, PRL (2005)

- bulk = gapped (insulator)
- gapless edge states -- carry spin current, topologically protected
  robust against nonmagnetic impurities
- spin analogue of the quantum Hall effect "new state of matter"
- no field required

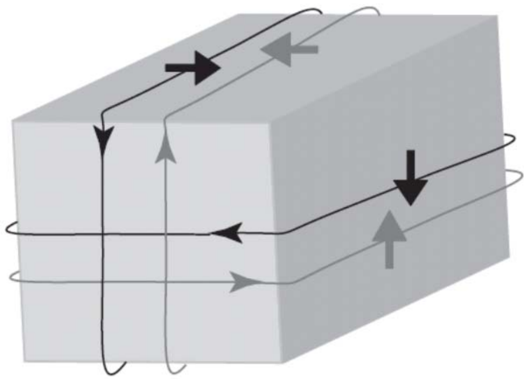
Spin current
(Kramers pair
of gapless edge states)

2D



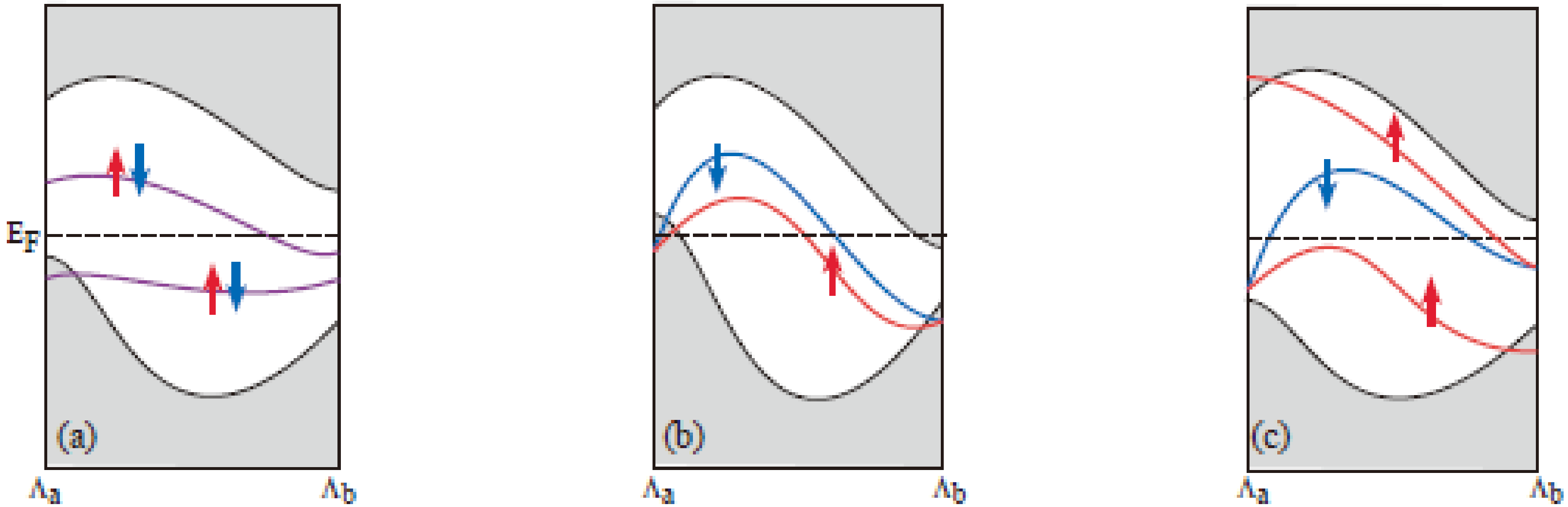
1D-edge states

3D



2D-edge states
surface states

Surface electronic structures



Typical surface states
within the bulk band gap
(ex. Si, Ge)

- Schockley states
- Tamm states

- spin-degenerate

Z_2 invariants: zero

Surface states
of (semi)metal crystals
with strong spin-orbit interaction
(ex. Bi, Au)

-Rashba effect

- spin-split

Z_2 invariants: zero

Edge-states
of topological insulators
(ex. $Bi_{0.9}Sb_{0.1}$)

-Odd number of
Fermi level crossings

- spin-split

Z_2 invariants: nonzero

Topological band theory

Z_2 topology in band structure

Parity: $\delta_i = \pm 1$

$\delta_i = \prod_{m=1}^{N} \xi_{2m}(\Gamma_i)$ With inversion symmetry

Parity eigenvalue
+1: symmetric
-1: asymmetric

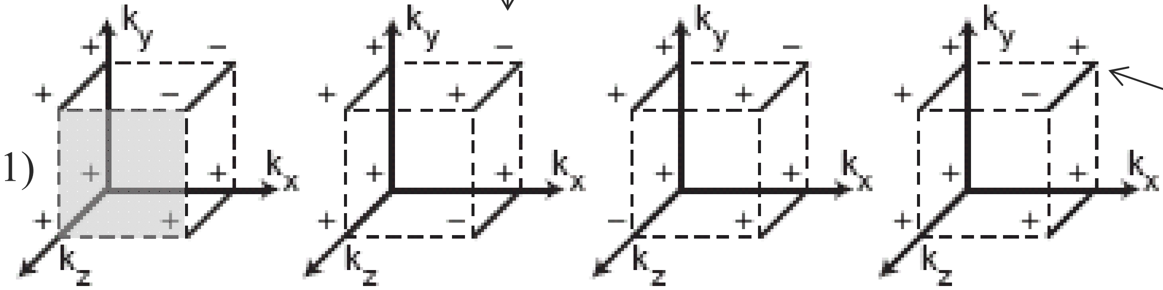
$\delta_i = \frac{\sqrt{\det[w(\Gamma_i)]}}{\mathrm{Pf}[w(\Gamma_i)]}$ No inversion symmetry

$w_{mn}(\vec{k}) = \langle u_{-k,m} | \Theta | u_{k,n} \rangle$

Time-reversal operator

1/8 of the 3D-Brillouin Zone (BZ)

(001)



time-reversal invariant, satisfying $-\Gamma_i = \Gamma_i + \boldsymbol{G}$

$$(-1)^{\nu_0} = \prod_{i=1}^{8} \delta_i.$$

expressed as the product over all eight points

Z_2 topological numbers: products of the parity eigenvalues

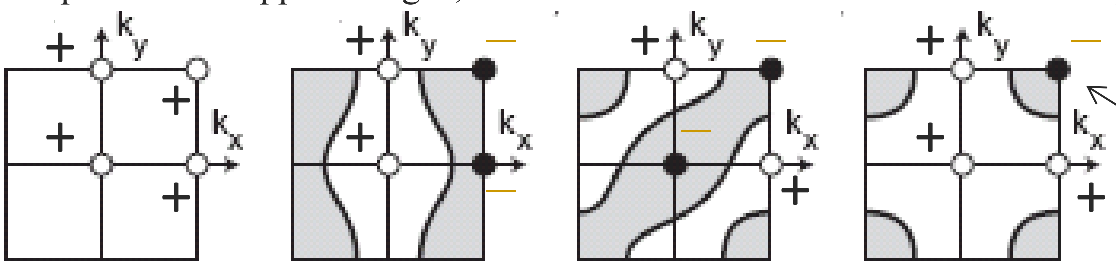
0; (001) 0; (011) 0; (111) 1; (111)

$$(-1)^{\nu_k} = \prod_{n_k=1;\, n_{j\neq k}=0,1} \delta_{i=(n_1 n_2 n_3)}.$$

given by products of four δ's for which Γ_i reside in the same plane

(001) 2D-BZ
with Fermi arcs of surface states enclosing the specific Λ points

If the two k-points have opposite signs, the Fermi surface crosses between the two points.



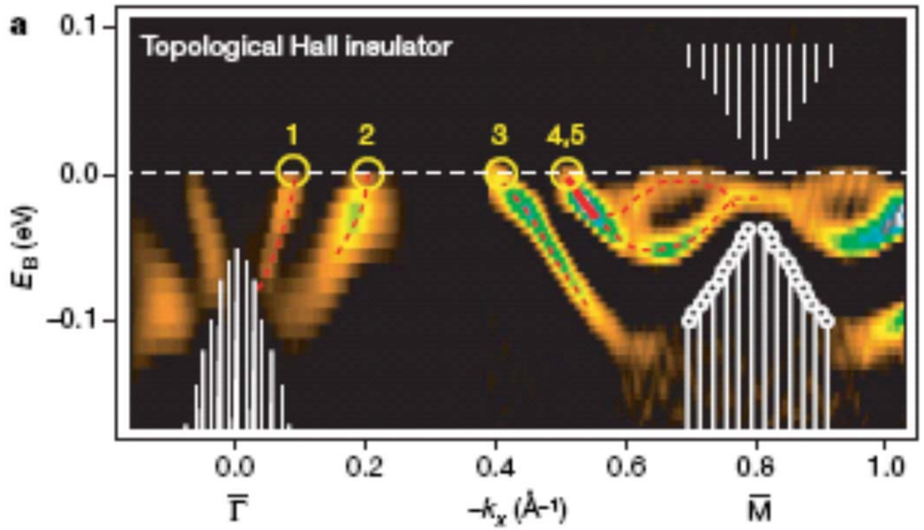
time-reversal invariant momenta, Λ

The $Bi_{1-x}Sb_x$ case

Experiment ARPES

theory: Fu et al., Phys. Rev. Lett. ('07)
exp.: Hsieh et al., Nature ('08)

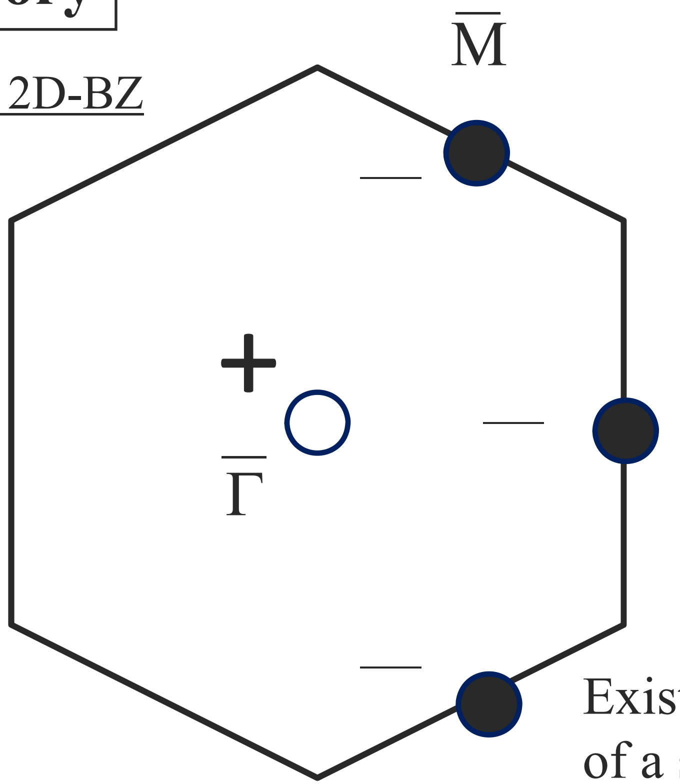
$Bi_{0.9}Sb_{0.1}$



Odd number (five) of Fermi points between Γ̄ and M̄.

Theory

(111) 2D-BZ

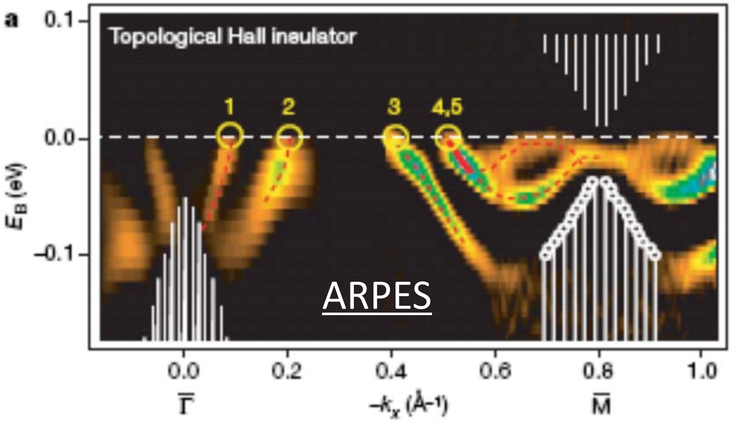


Agreement

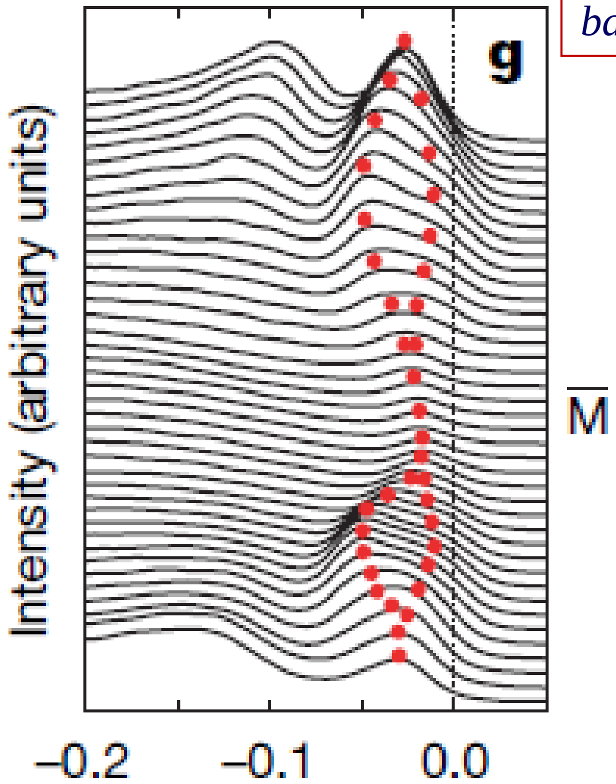
Existence of Fermi crossing of a spin-nondegenerate band between Γ̄ and M̄.

Motivation

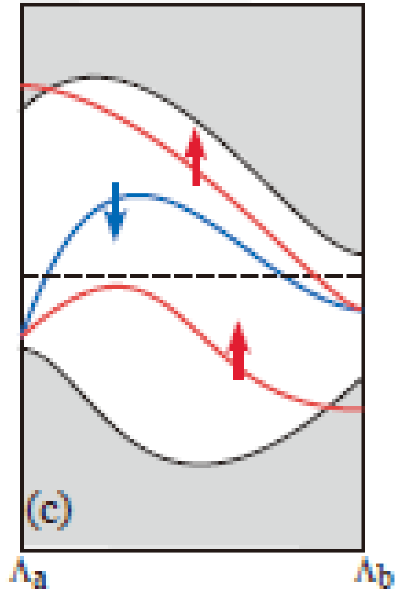
$Bi_{0.9}Sb_{0.1}$



theory: Fu et al., Phys. Rev. Lett. ('07)
exp.: Hsieh et al., Nature ('08)



Elaborate band structure?



Spin-polarized band structure?

Spin- and angle(momentum)-resolved photoemission spectroscopy

How do we determine momentum of electrons?

Electron spectrometers from VG, Scienta, Omicron, Specs….

How do we determine their spin coordinates?

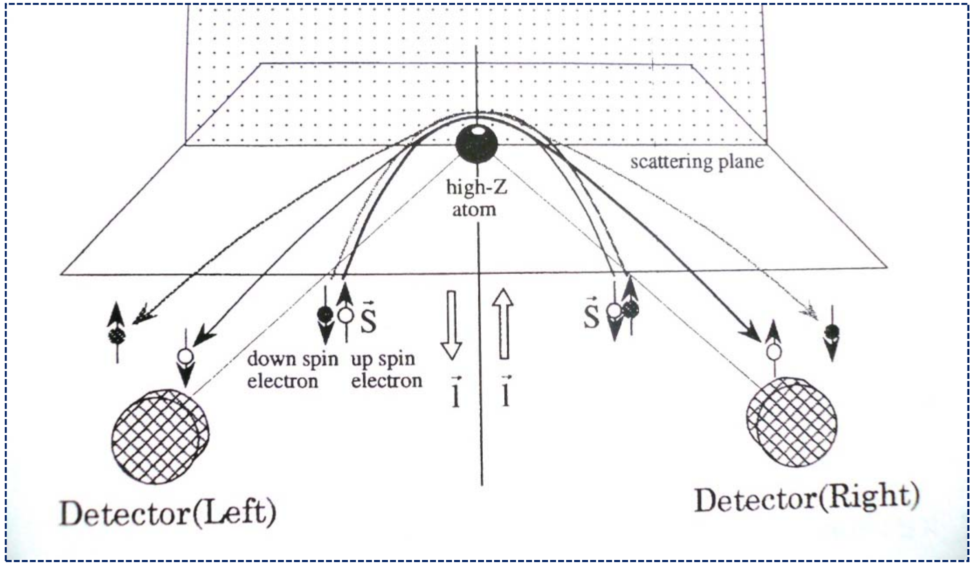
Spin detector , Spin polarimeter

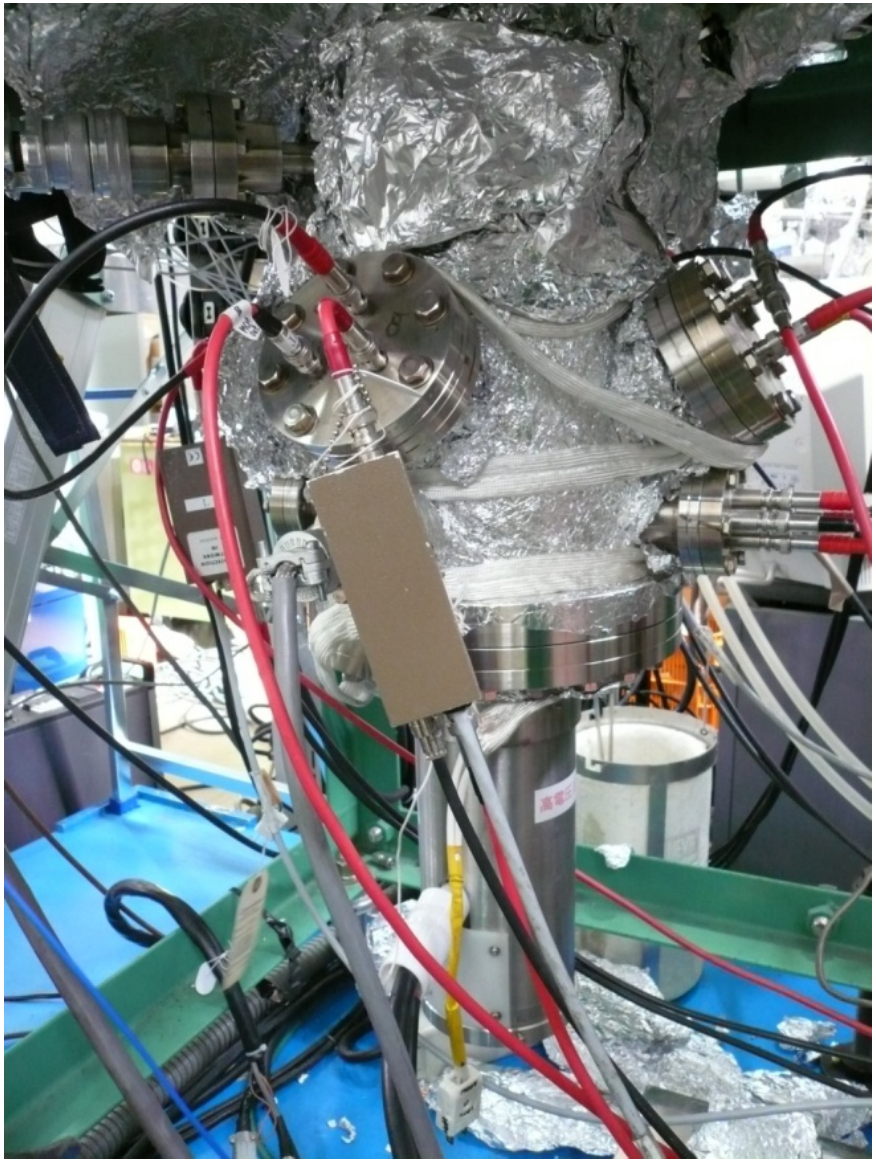
Spin-detector (Mott detector)

25 kV-Compact Mott detector

by A. Kakizaki *et al.*

S. Qiao, *et al.*, Rev. Sci. Instrum., **68**, 4390 (1997).

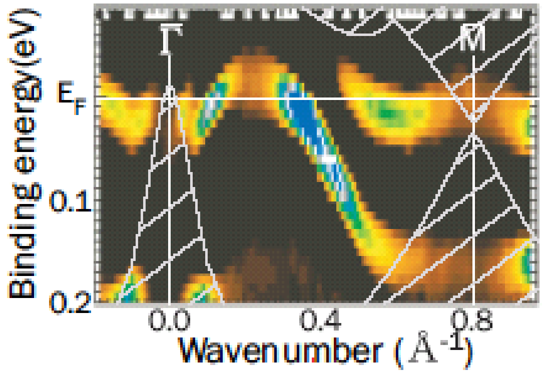


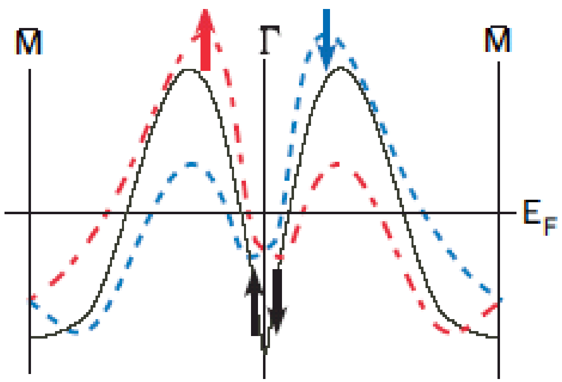


- 25 keV electrons
- spin-orbit interaction
- Au target

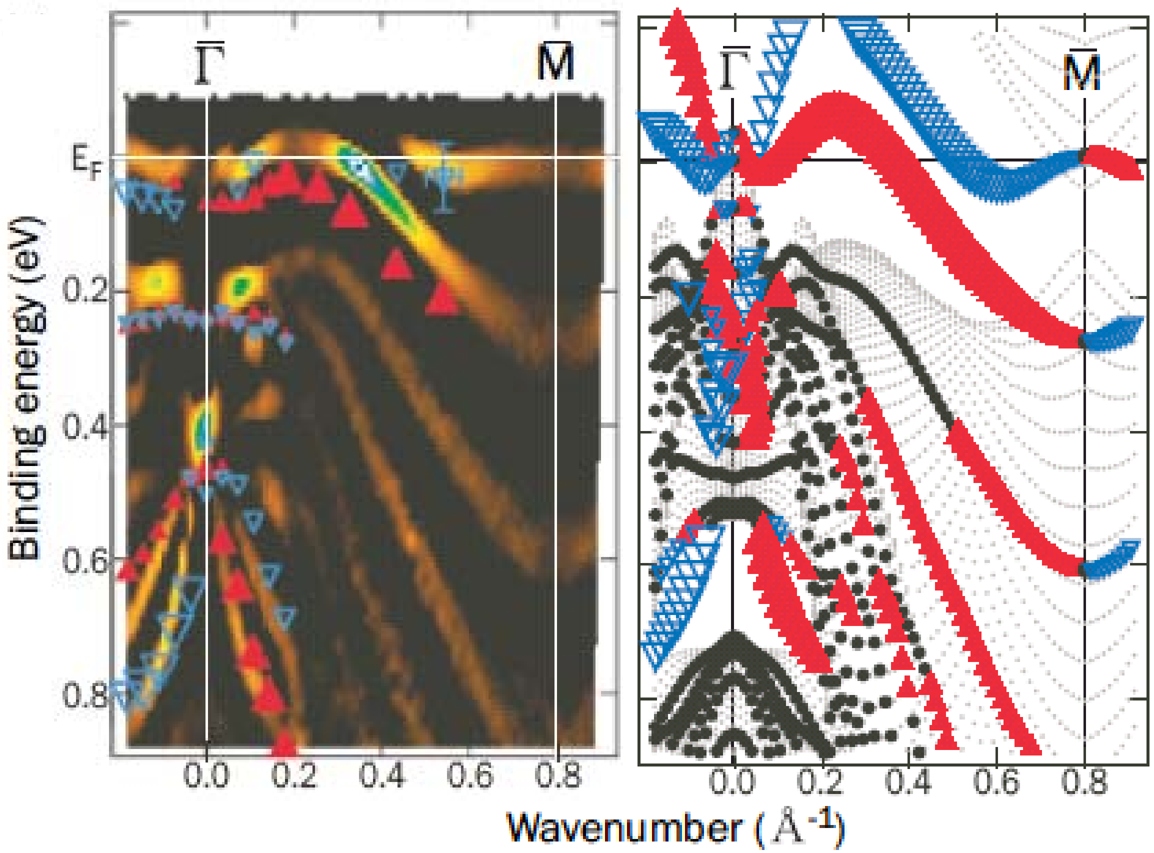
Spin-detector (Mott detector)

Spin-resolved band mapping of Bi crystal film with a 25 kV-Compact Mott detector





Rashba effect
of the surface state

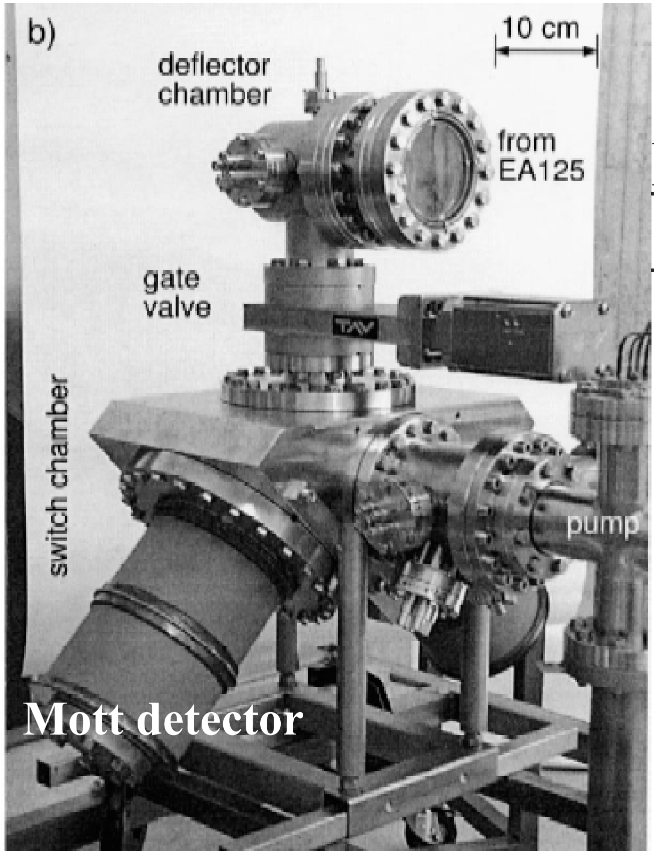


T.Hirahara *et al.*, Phys. Rev. B **76**,153305 (2007).

Spin-detector (Mott detector)

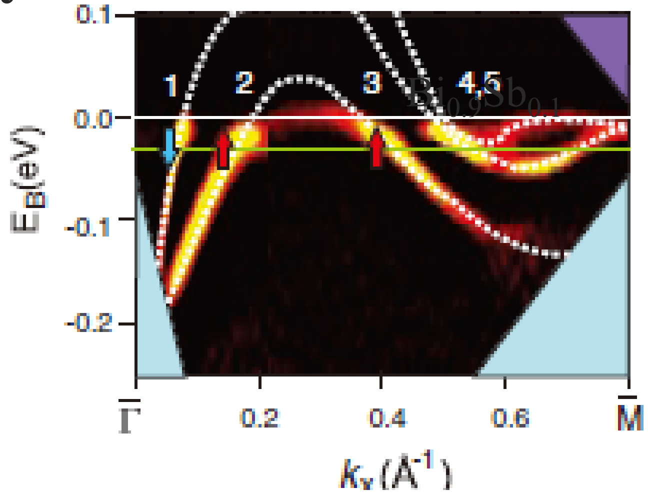
Spin-resolved band mapping of $Bi_{1-x}Sb_x$ crystal with a Compact Mott detector

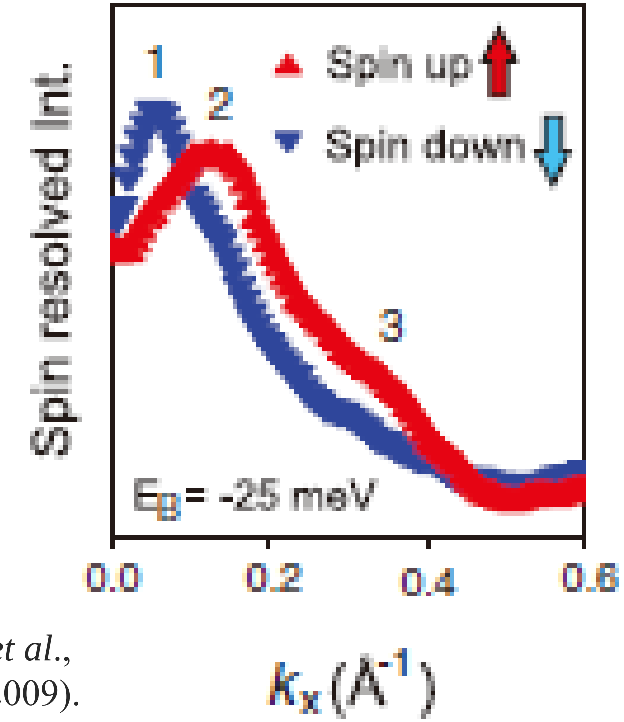
COmplete PHotoEmission Experiment (COPHEE)



Low
spin efficiency

ΔE=
100~200meV





H. Moritz *et al.*,
J. Elec. Spec. Rel. Phenom. **124**, 263 (2002).

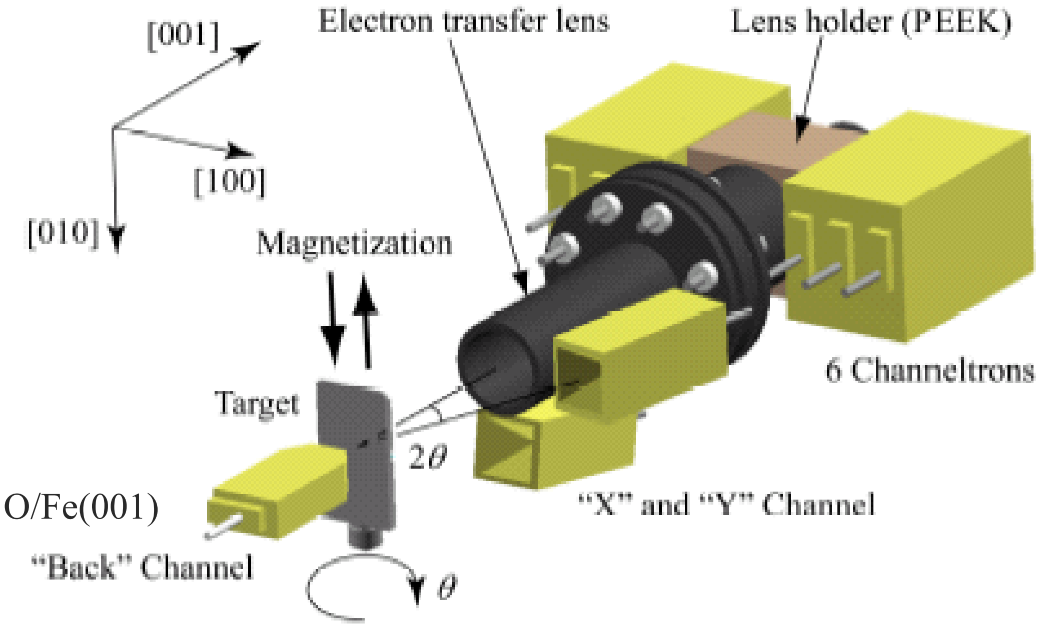
Hsieh *et al.*,
Science **323,** 919 (2009).

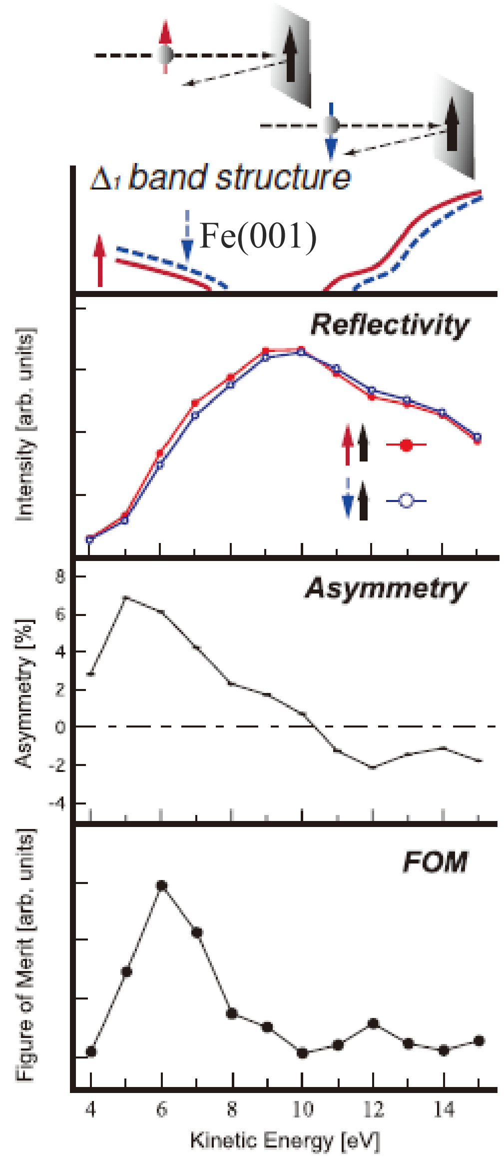
Spin-detector (VLEED detector)

Very Low- Energy Electron Diffraction (VLEED) detector

by T. Okuda *et al.*

T. Okuda, Y. Takeichi, Yuuki Maeda, A. Harasawa, I. Matsuda, T. Kinoshita, and A. Kakizaki, Rev. Sci. Instrum. **79,** 123117 (2008).

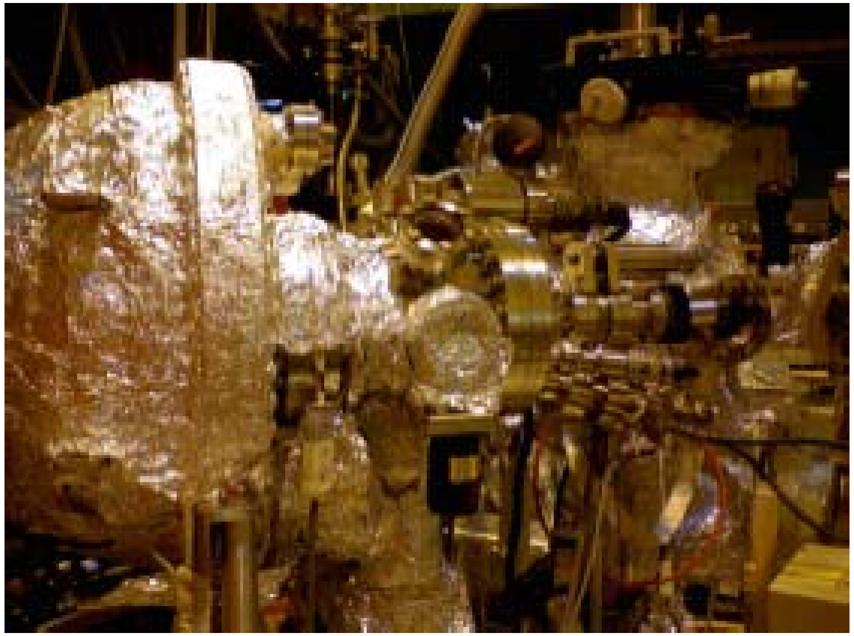


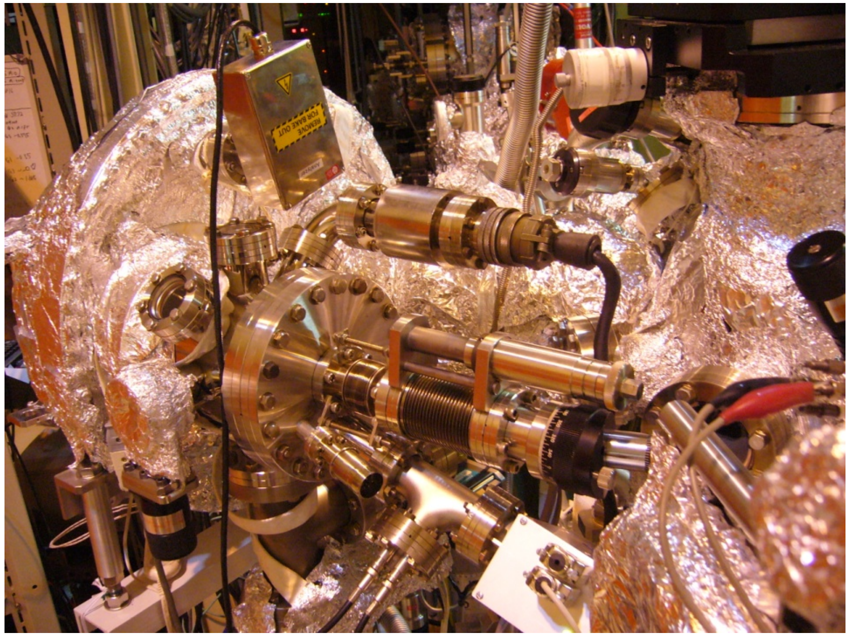


- 6 eV electrons
- exchange interaction
- Fe, O/Fe target

Spin-detector (VLEED detector)

SPECS-PHOIBOS150+VLEED detector





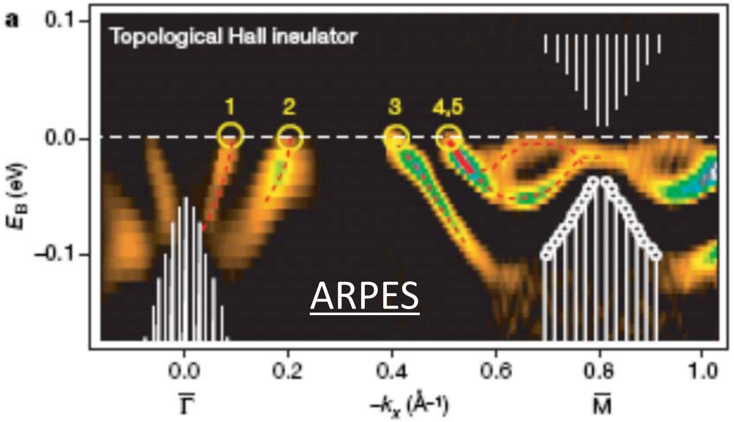
High-efficient spin detection (100 times better than the Mott detector)

→ A combination with high-resolution analyzer

$\varepsilon = (1.0 \pm 0.2) \times 10^{-2}$, $\Delta E < 30$ meV

Motivation

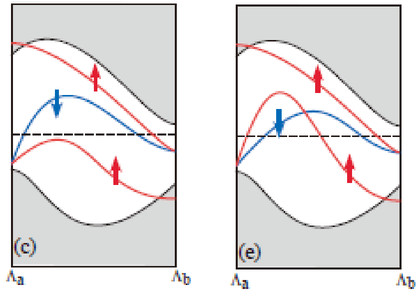
$Bi_{0.9}Sb_{0.1}$



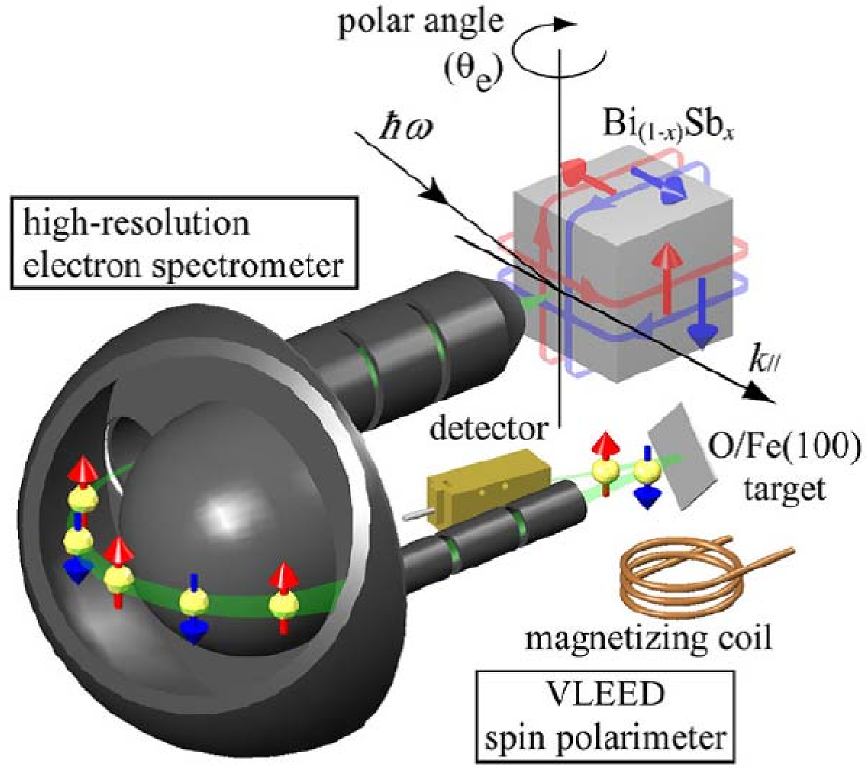
theory: Fu et al., Phys. Rev. Lett. ('07)
exp.: Hsieh et al., Nature ('08)

Odd number (five) of Fermi points between $\bar{\Gamma}$ and $\bar{M}$.

Spin-polarized band structure?



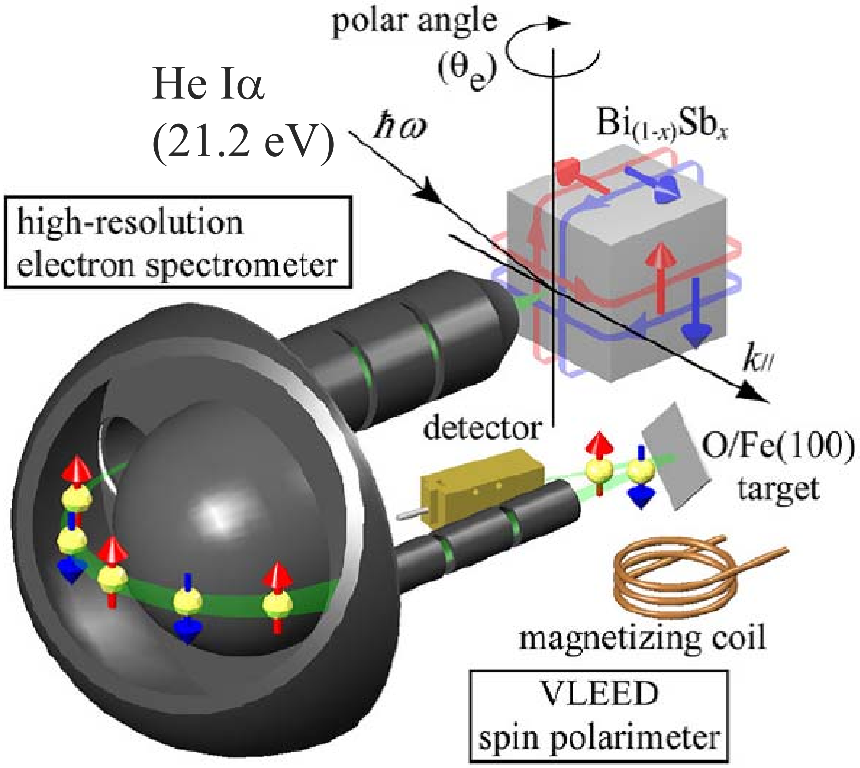
high-resolution spin-resolved
photoemission spectroscopy

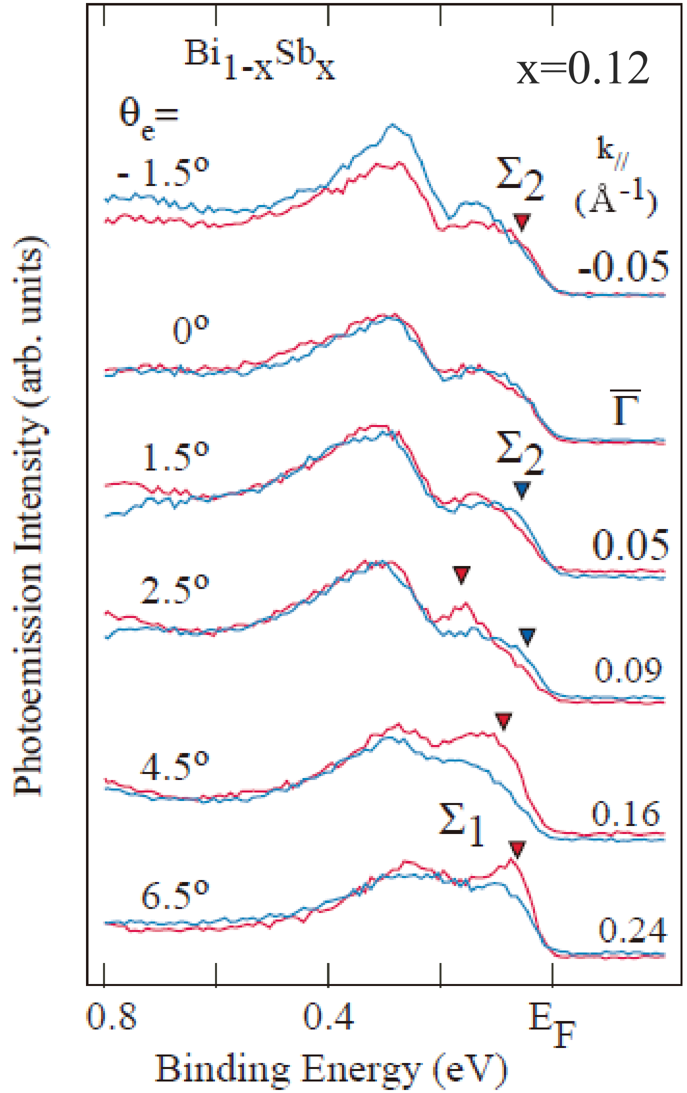


Results and Discussion

high-resolution spin-resolved photoemission spectroscopy

Measurement condition





ΔE =50 meV, $\Delta\theta = \pm 1°$

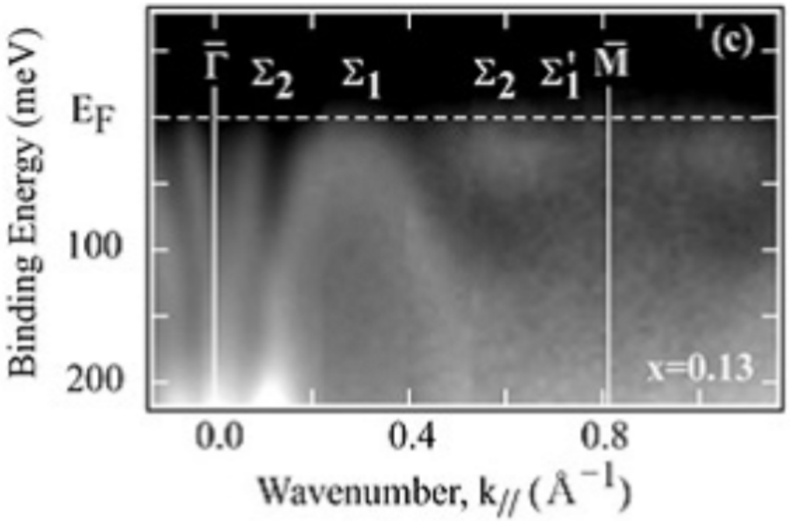
T~130 K

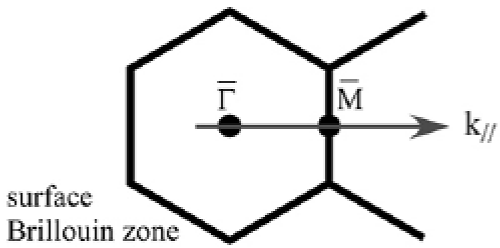
Seff = 0.*32* ± *0.04*,
determined by the polarization
of secondary electrons from Fe(001).

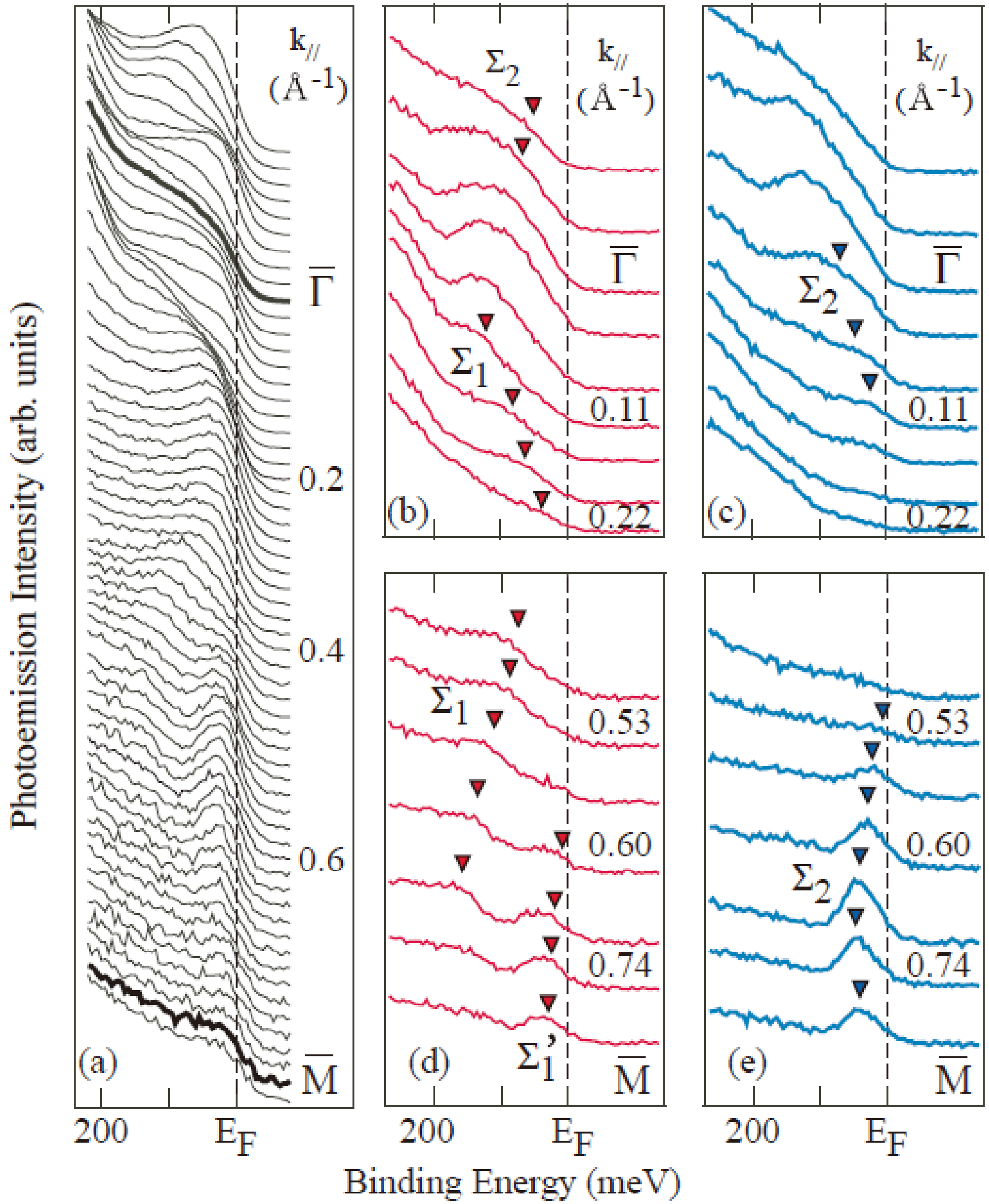
Results and Discussion

$Bi_{1-x}Sb_x$

x=0.12,0.13

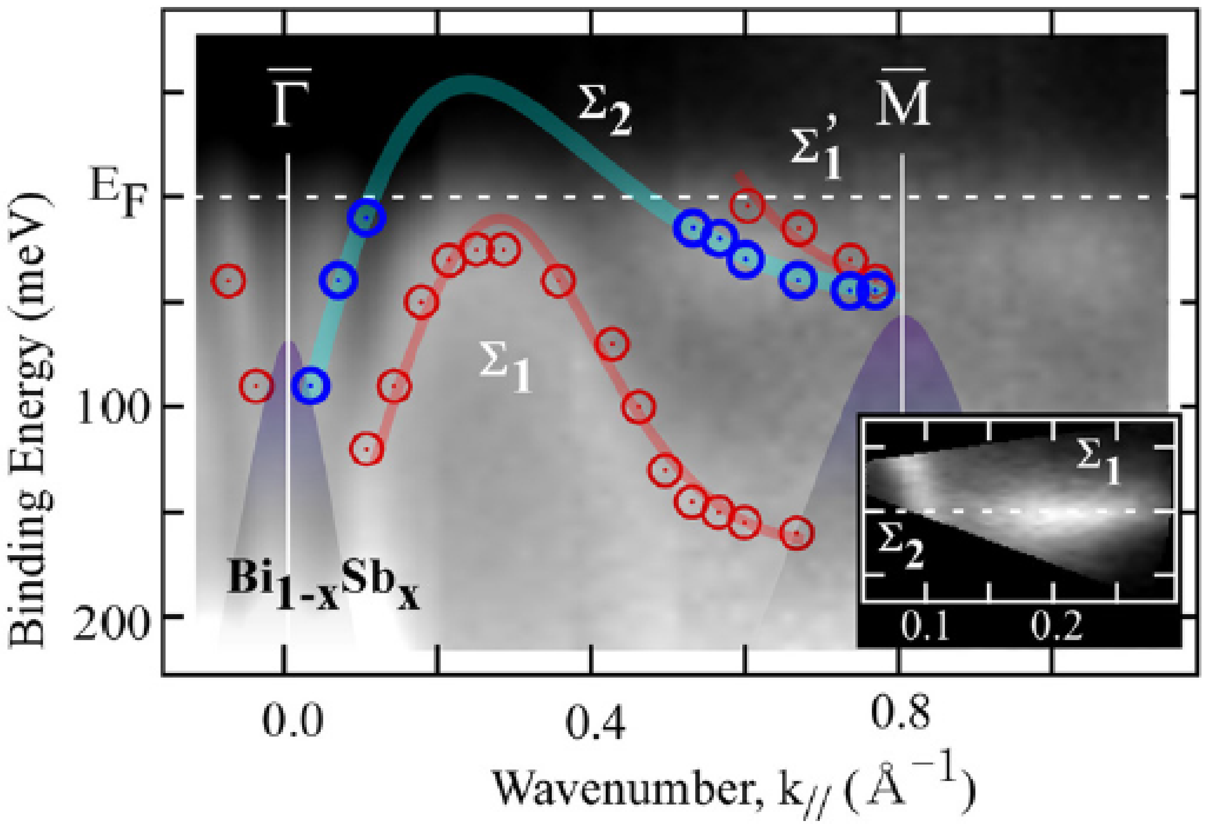


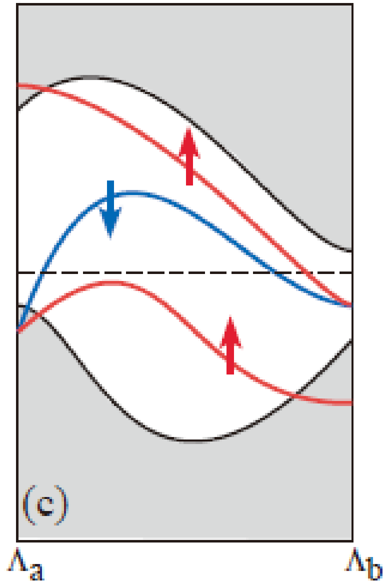




Results and Discussion

Spin-resolved band plots
on spin-integrated grayscale band diagram





Edge-states
of topological insulators
(ex. $Bi_{\sim 0.9}Sb_{\sim 0.1}$)

-Odd number of
Fermi level crossings

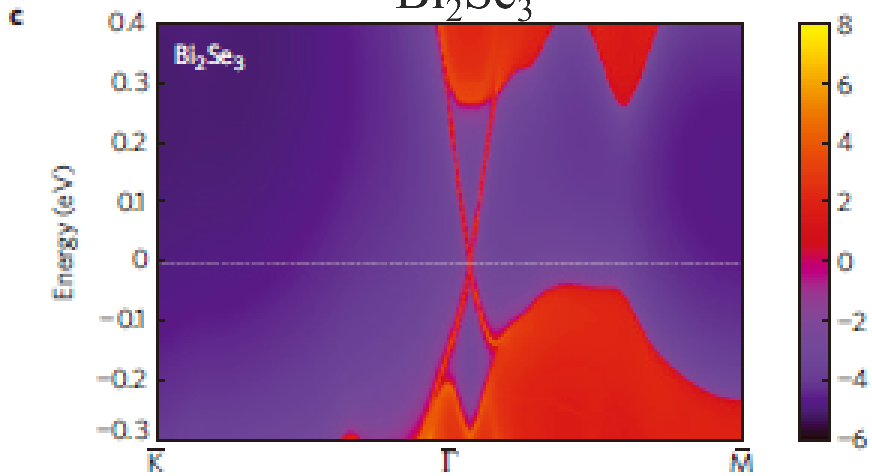
- spin-split

- **Z_2 invariants: nonzero**

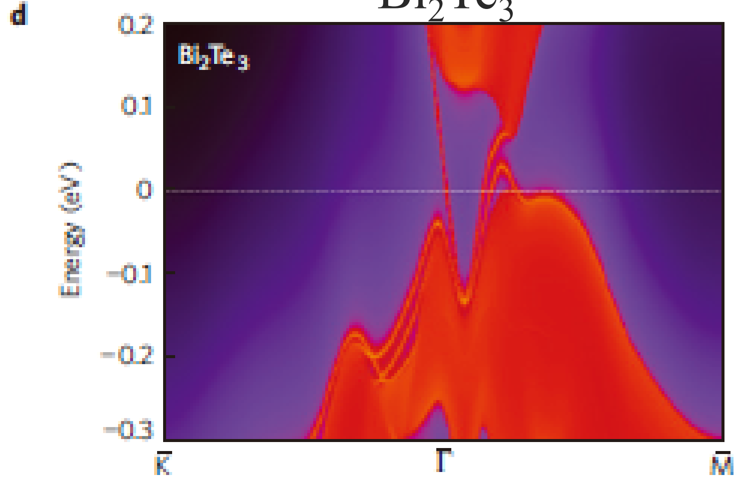
○The second generation samples

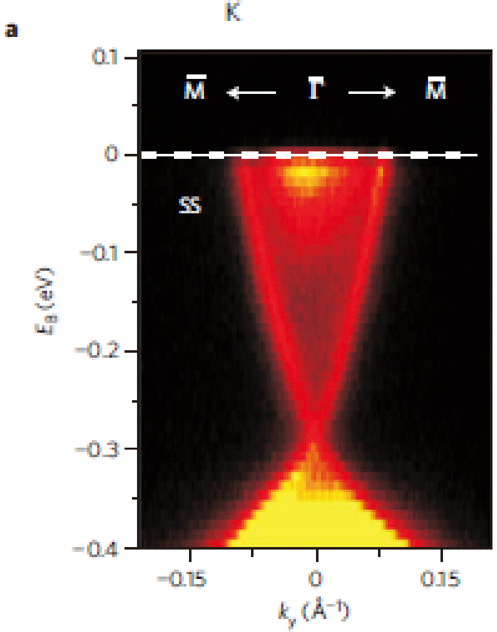
H.Zhang *et al.*, Nature Phys. 5 438 (2009).

Bi_2Se_3

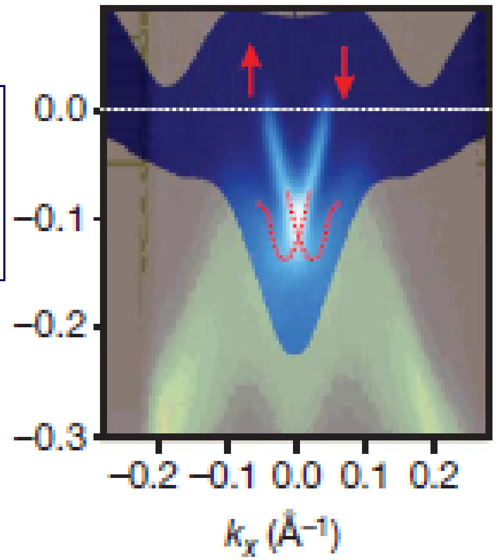


Bi_2Te_3





Well-defined stoichiometry
Single-band (One Kramers pair)
Wide bulk band gap (300 meV, 3600 K)



Y. Xia *et al.*, Nature Phys. **5** 398 (2009).

D. Hsieh *et al.*, Nature **460** 1101 (2009).

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…)**

- Solid surfaces are important playgrounds for studying low-dimensional physics.

  Photoemission spectroscopies with synchrotron radiation are the important experimental tools.

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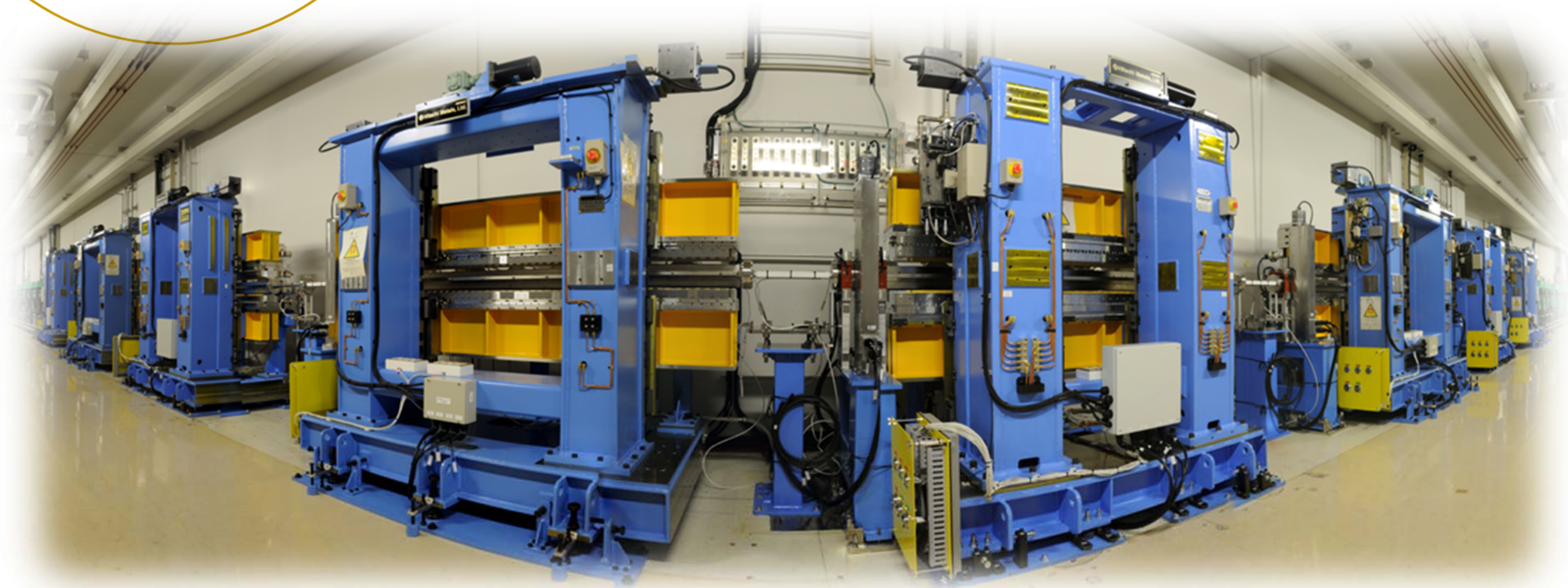
Frontier Spectroscopy experiments at SPring-8 BL07LSU:

with time-resolution and at nano-space



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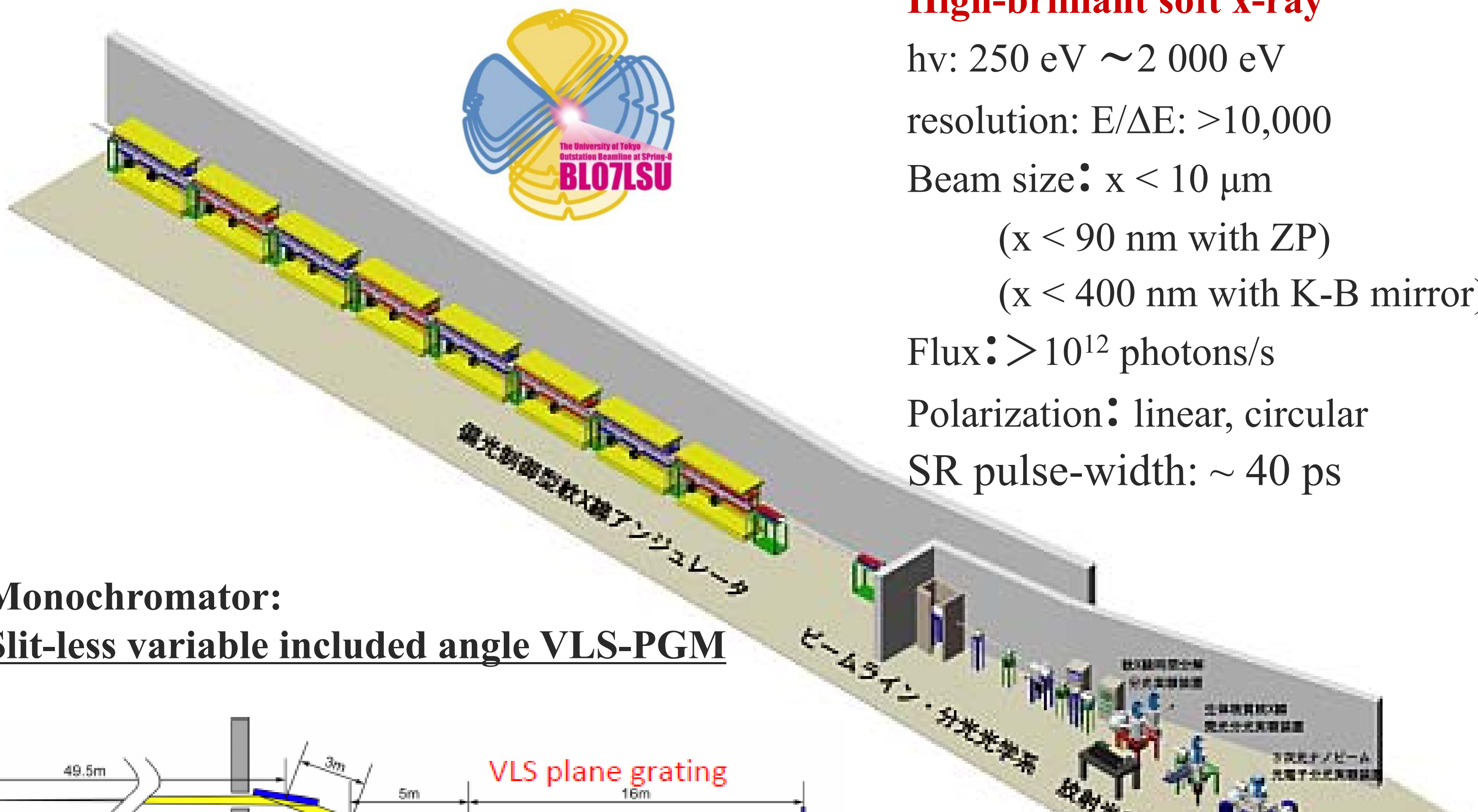
SPring-8 BL07LSU



Specification

High-brilliant soft x-ray

hv: 250 eV ～2 000 eV

resolution: E/ΔE: >10,000

Beam size: x < 10 μm

(x < 90 nm with ZP)

(x < 400 nm with K-B mirror)

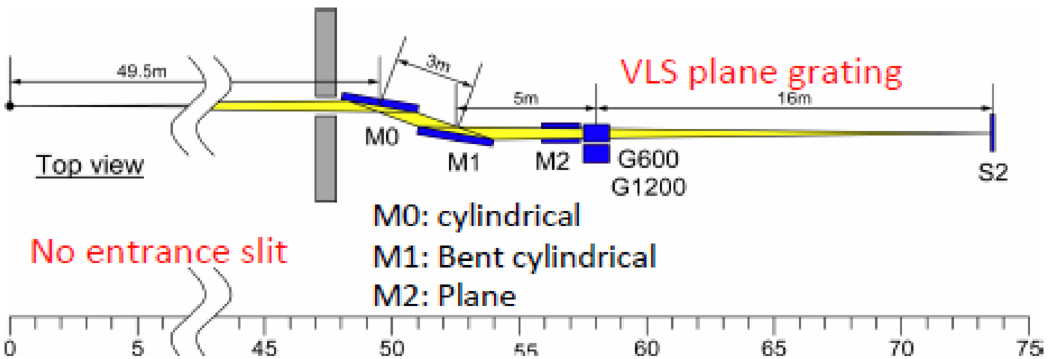
Flux: > 10^{12} photons/s

Polarization: linear, circular

SR pulse-width: ~ 40 ps

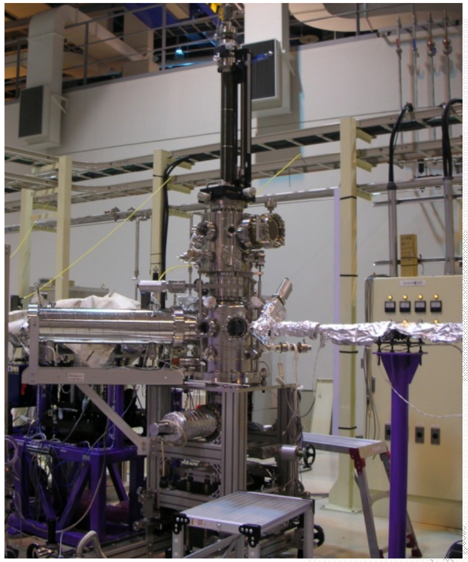
Monochromator:

Slit-less variable included angle VLS-PGM



SPring-8　BL07LSU

Four spectroscopy end-stations

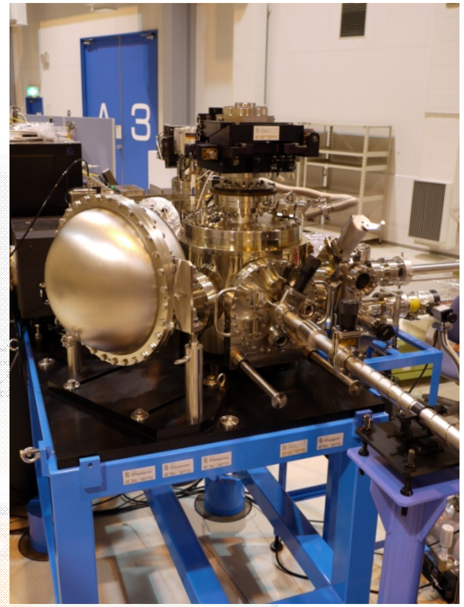


Time-Resolved soft X-ray spectroscopy station
TR-SX spectroscopy

Time-resolved angle-resolved photoemission spectroscopy with a 2D-ARTOF spectrometer and fs-pulse lasers

3D-scanning photoelectron microscope
3D nano-ESCA

Spatial resolution: 50 nm (x,y)
Depth profile： 0.1 nm (z)



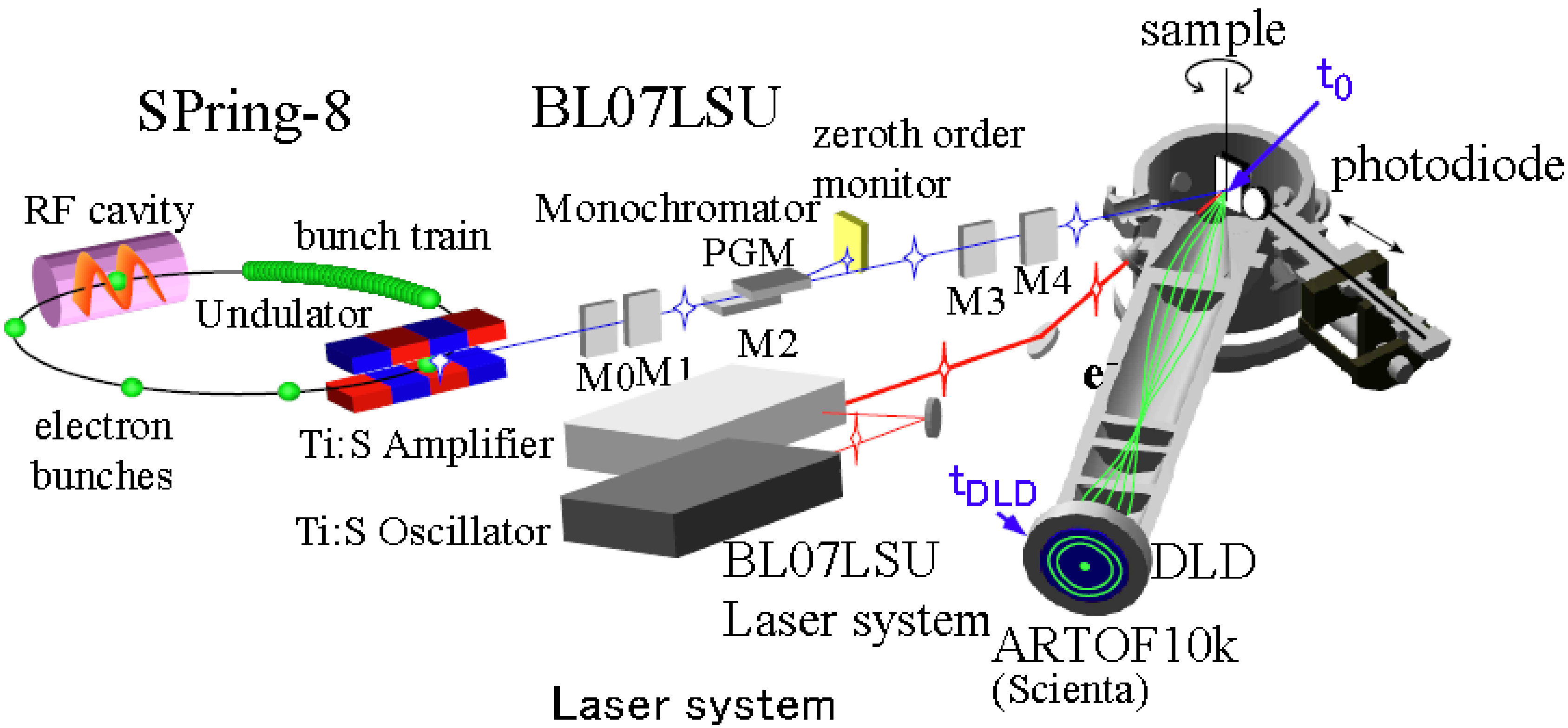
Ultra high-resolution soft X-ray emission spectroscopy
HORNET

Ultimate resolution
Measurement of solid, liquid, gas

Free-Port station

Open for experimental system of users

Time-Resolved soft X-ray spectroscopy station
TR-SX spectroscopy



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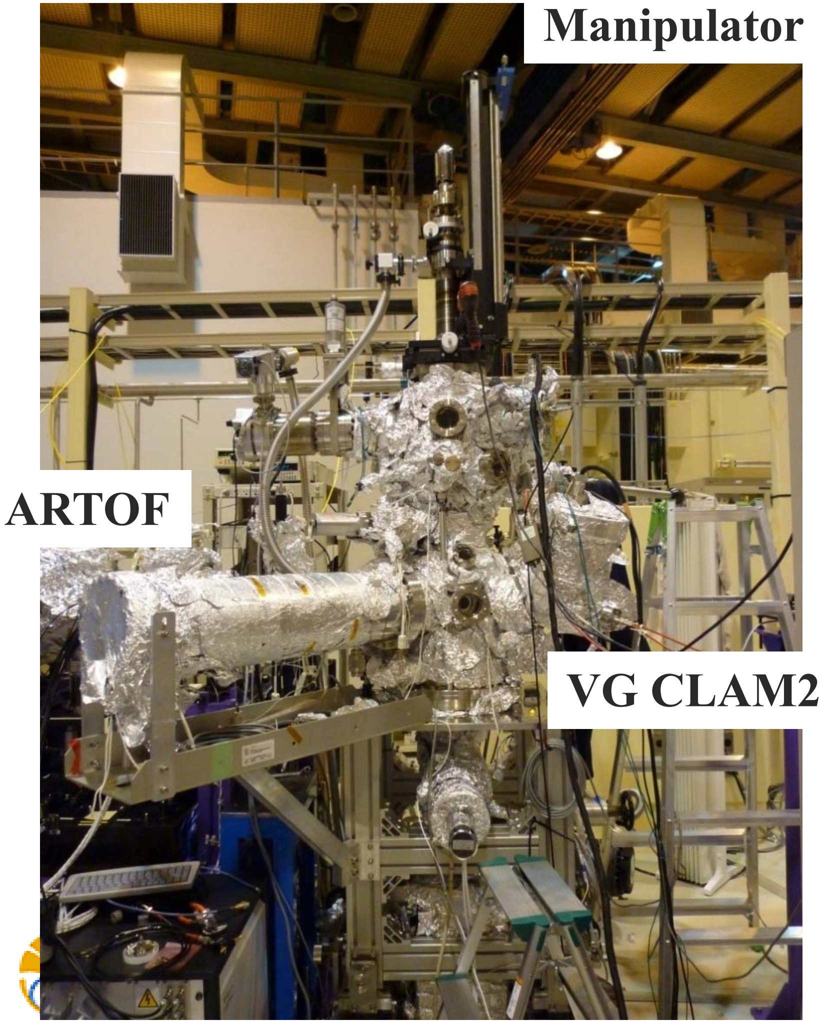
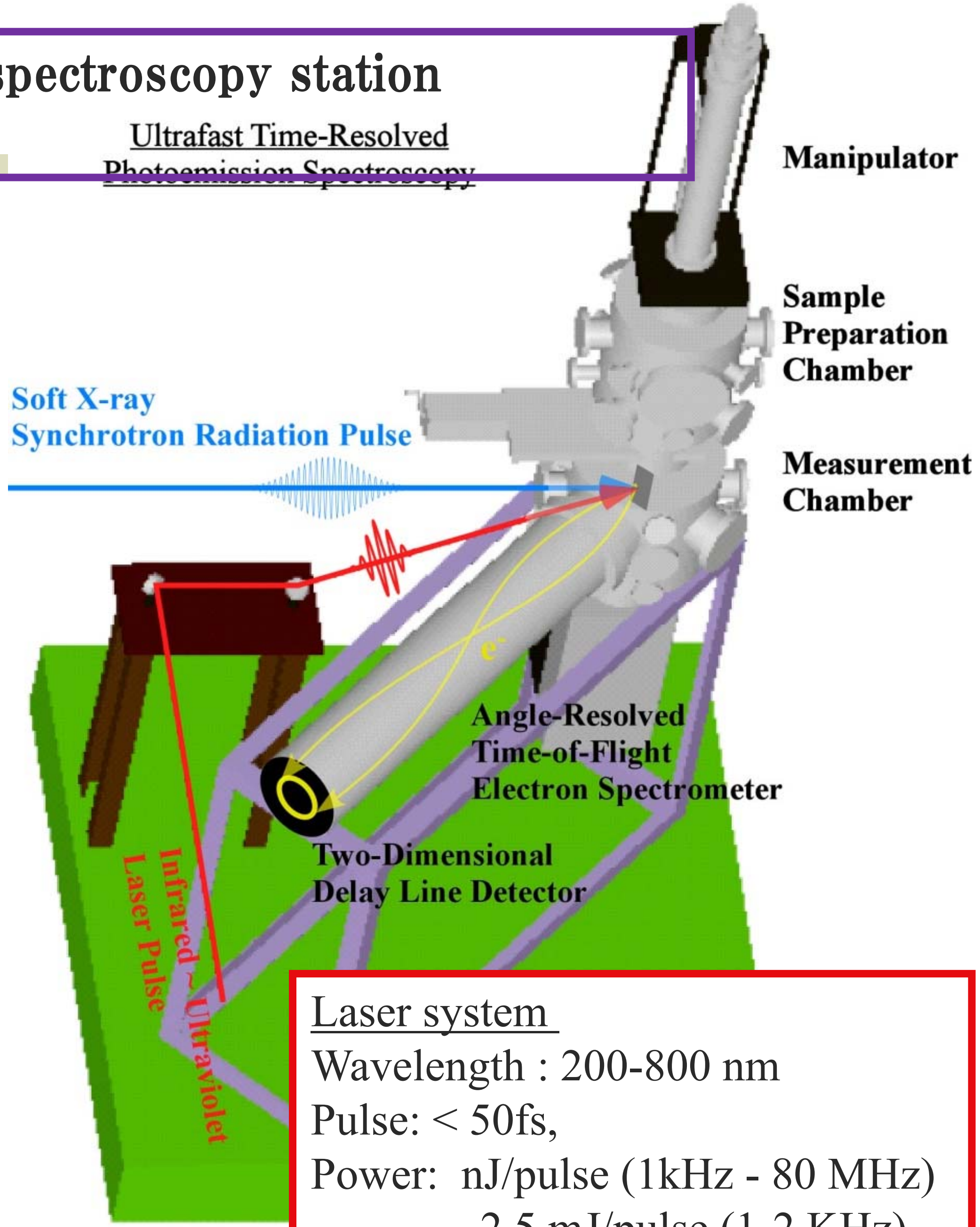
Time-Resolved soft X-ray spectroscopy station
TR-SX spectroscopy

The measurement system



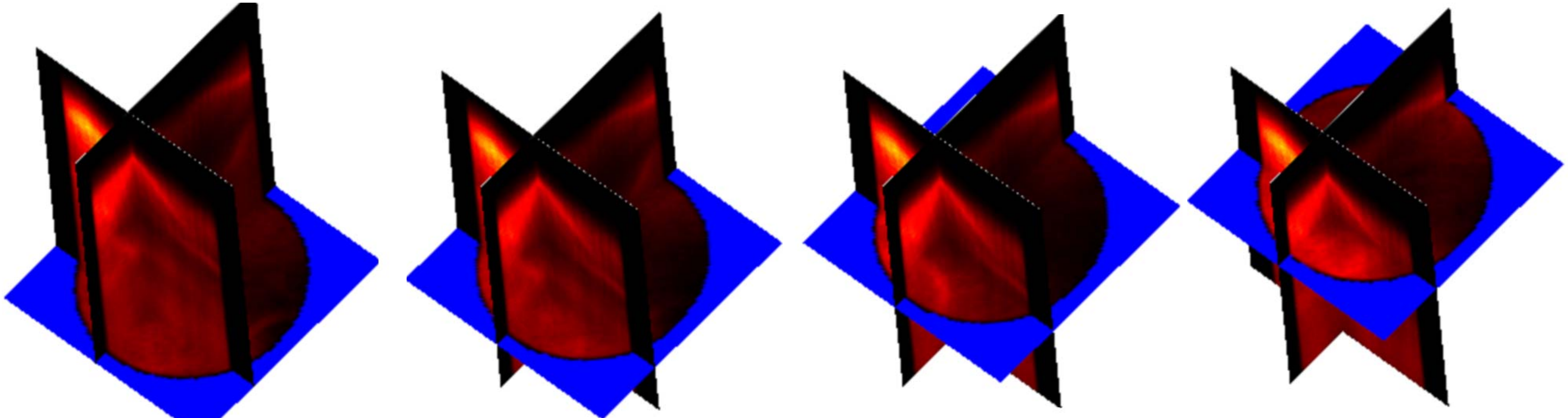


Laser system
Wavelength : 200-800 nm
Pulse: < 50fs,
Power: nJ/pulse (1kHz - 80 MHz)
2.5 mJ/pulse (1-2 KHz)

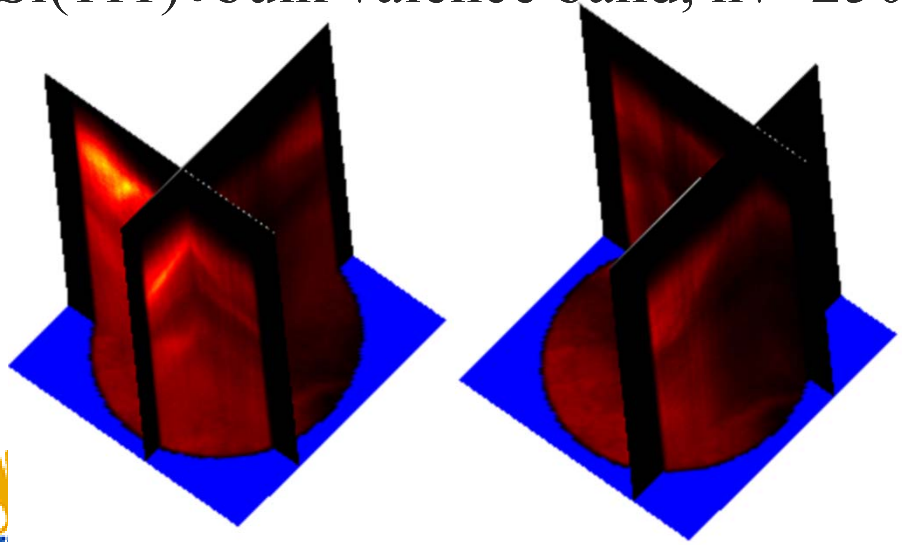
Time-Resolved soft X-ray spectroscopy station
TR-SX spectroscopy

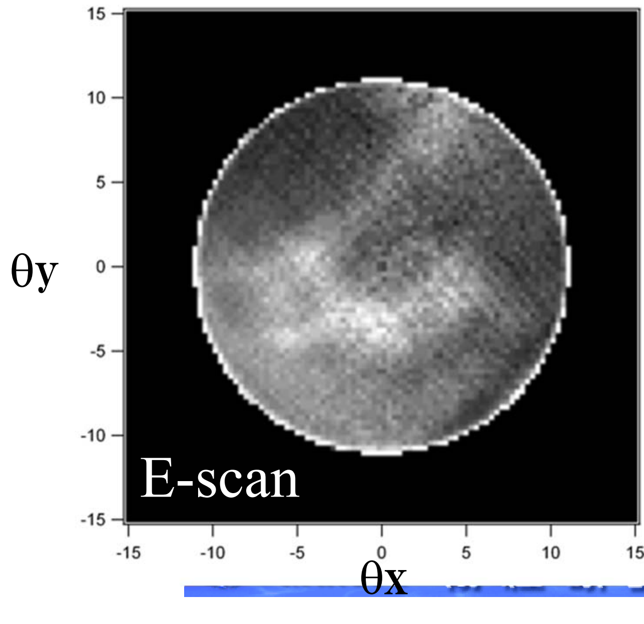
θx 、 θy range=+/- 12.5°
（θx 、 θy、 Max. range= +/- 15° ）
Energy range＝17.5eV

○ 2-D angle-resolved mapping **without** the sample rotation



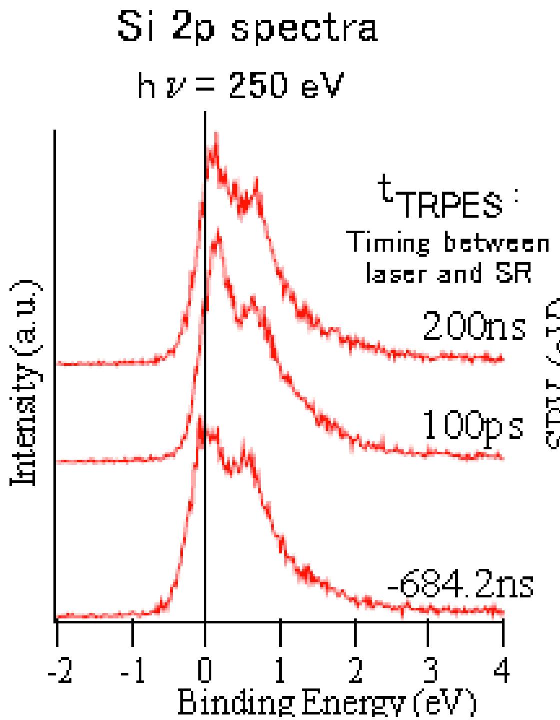
Si(111)：bulk valence band, hv=250 eV

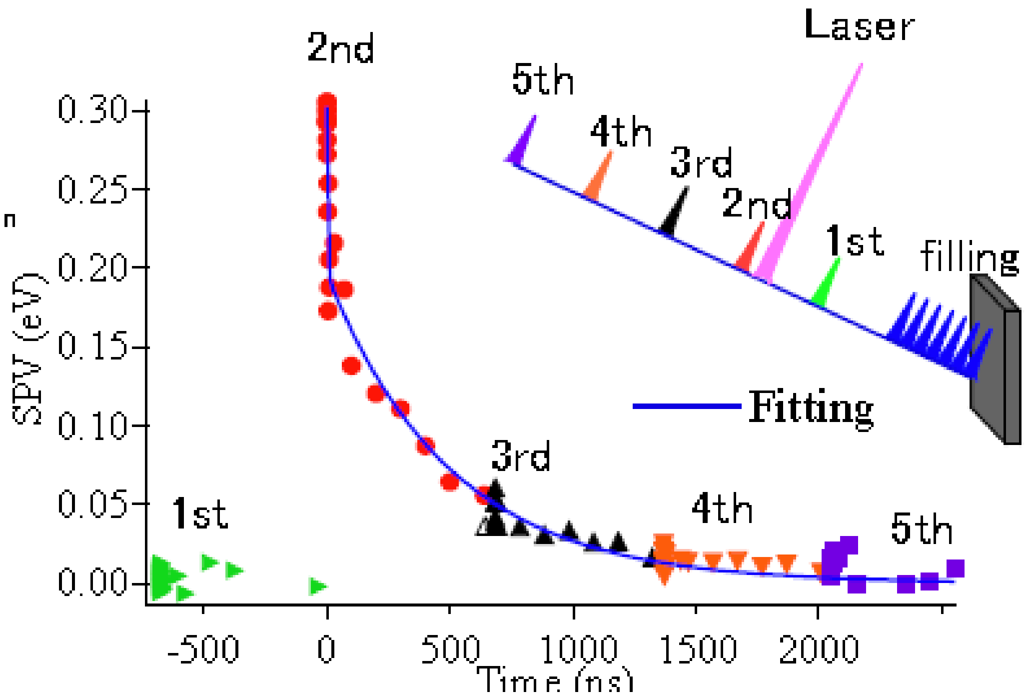




Time-Resolved soft X-ray spectroscopy station
TR-SX spectroscopy

Pump(laser)-Probe(synchrotron radiation) time-resolved photoemission experiments on relaxation after the surface photovoltage effect of Si(111)7x7





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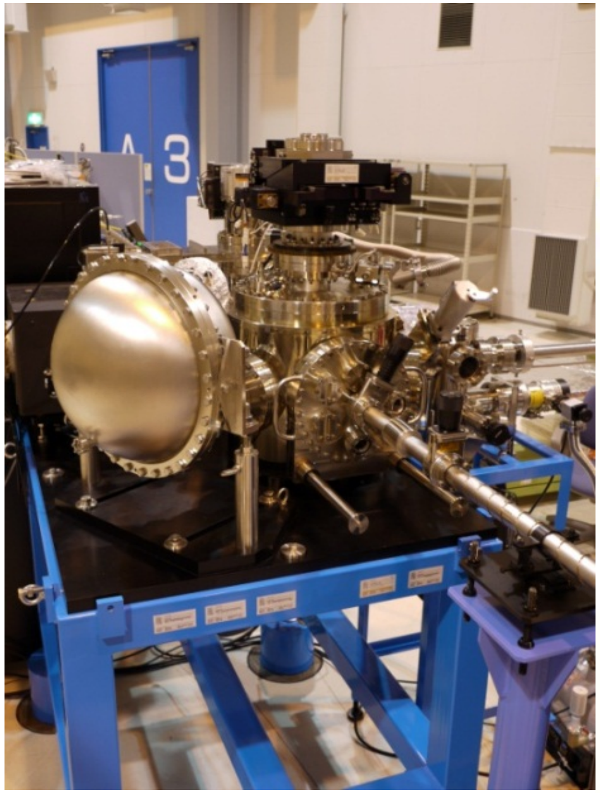
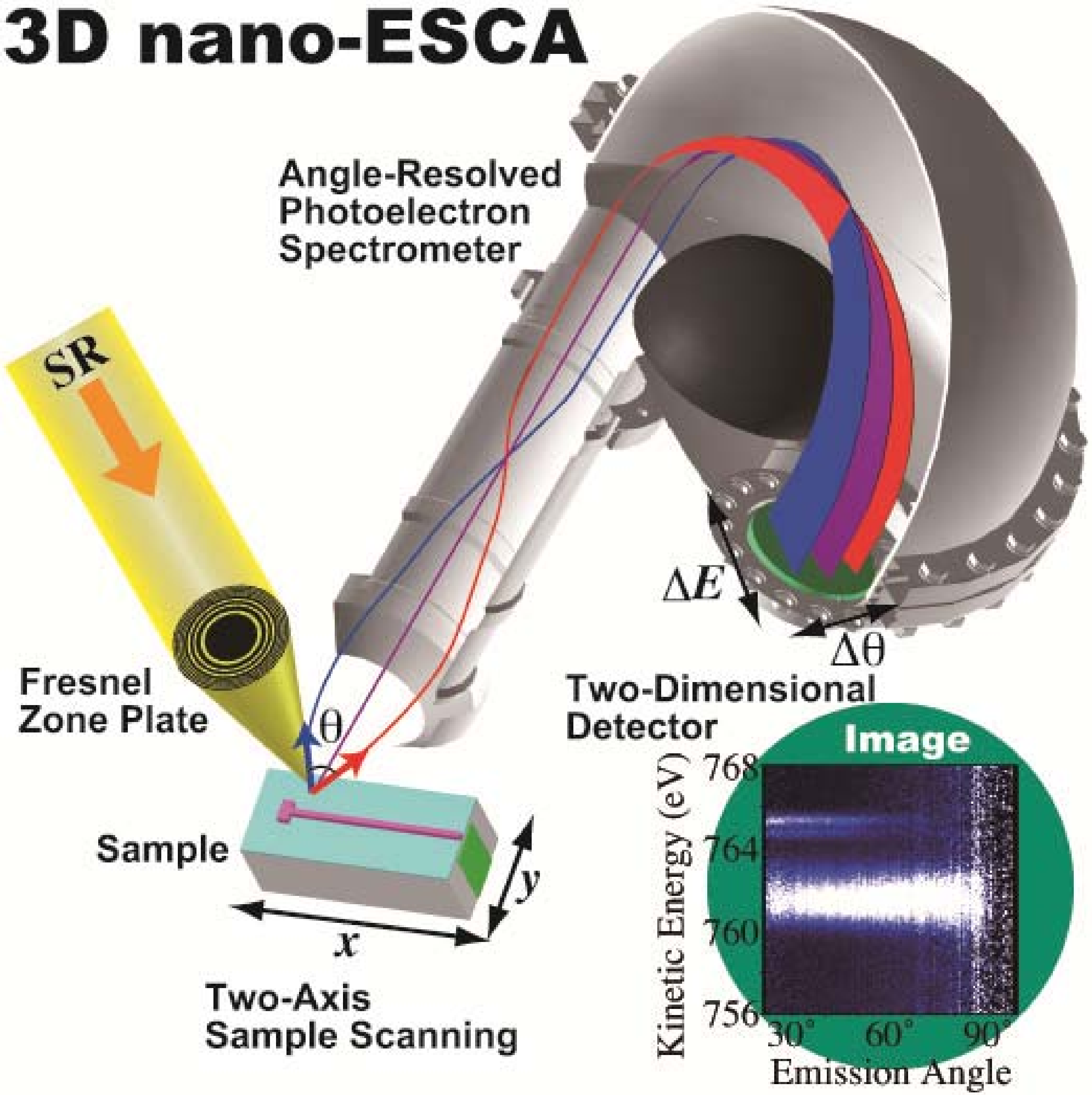
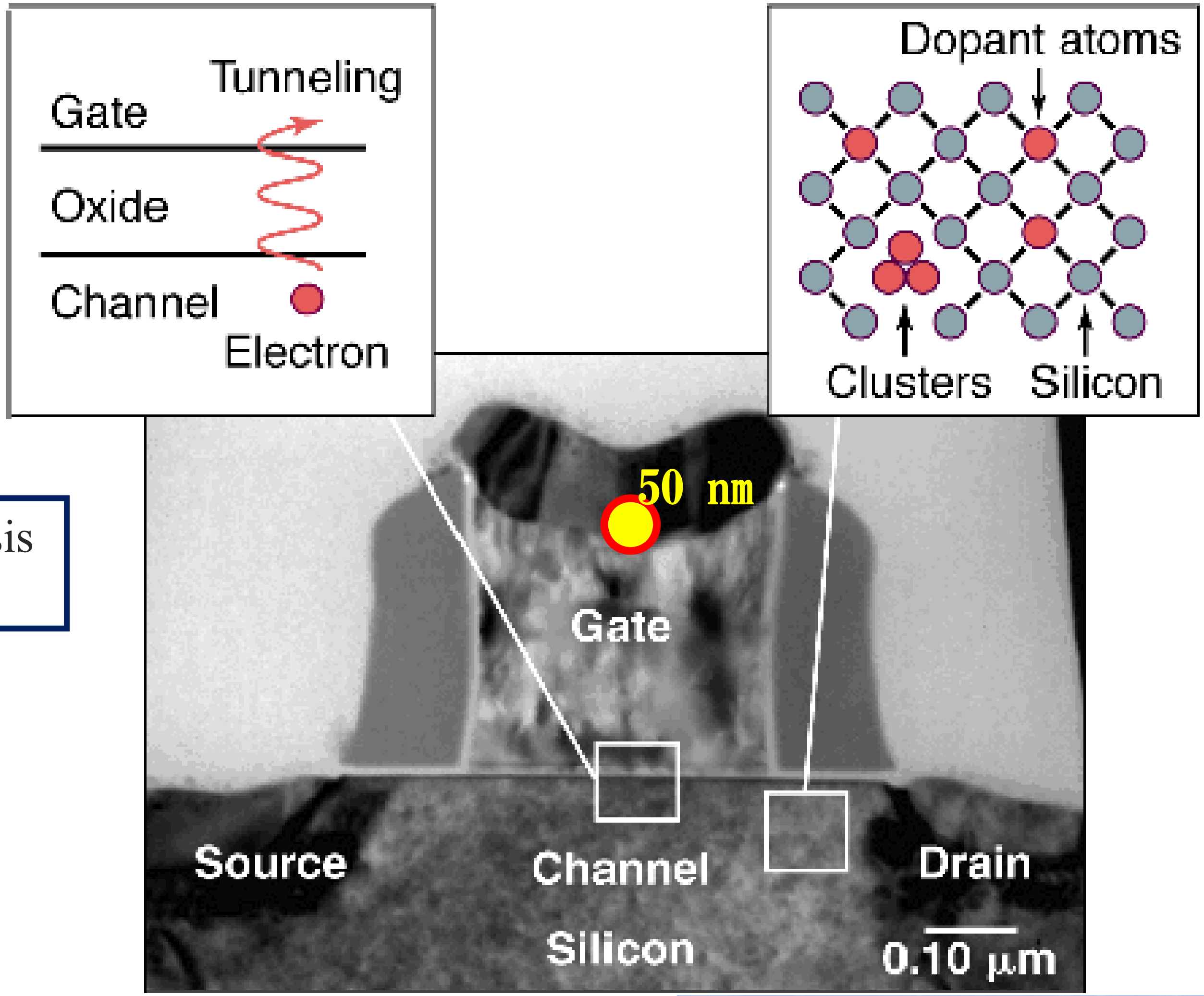
3D-scanning photoelectron microscope



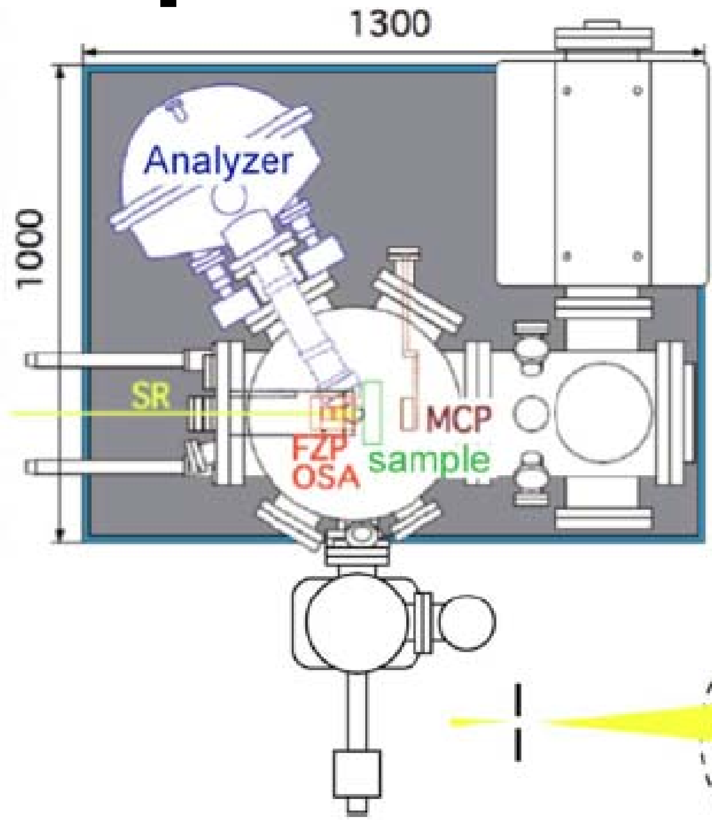


3D-scanning photoelectron microscope
3D nano-ESCA

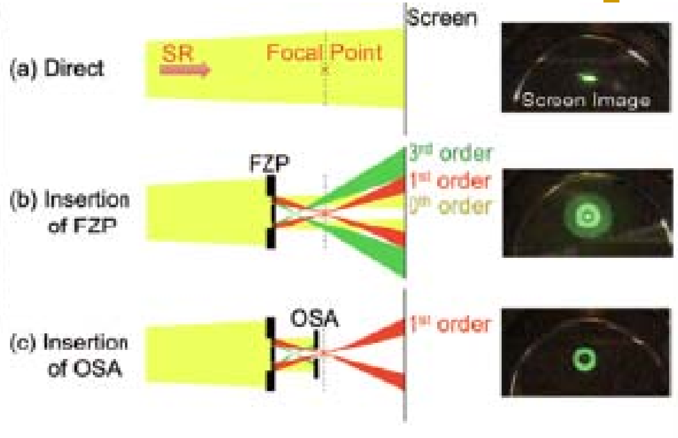
Element and chemical analysis in nano-region

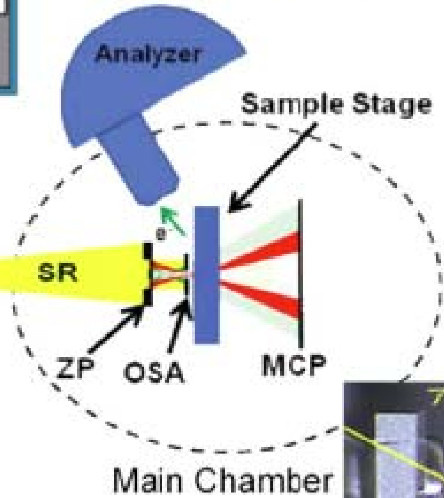


3D-scanning photoelectron microscope
3D nano-ESCA

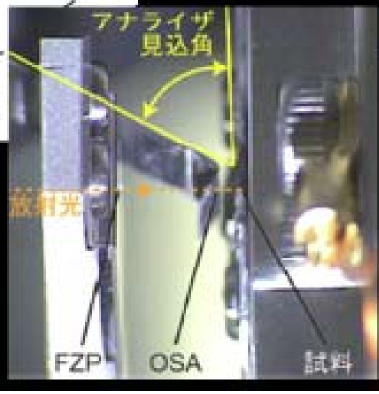


FZP (SEM image from NTT AT)



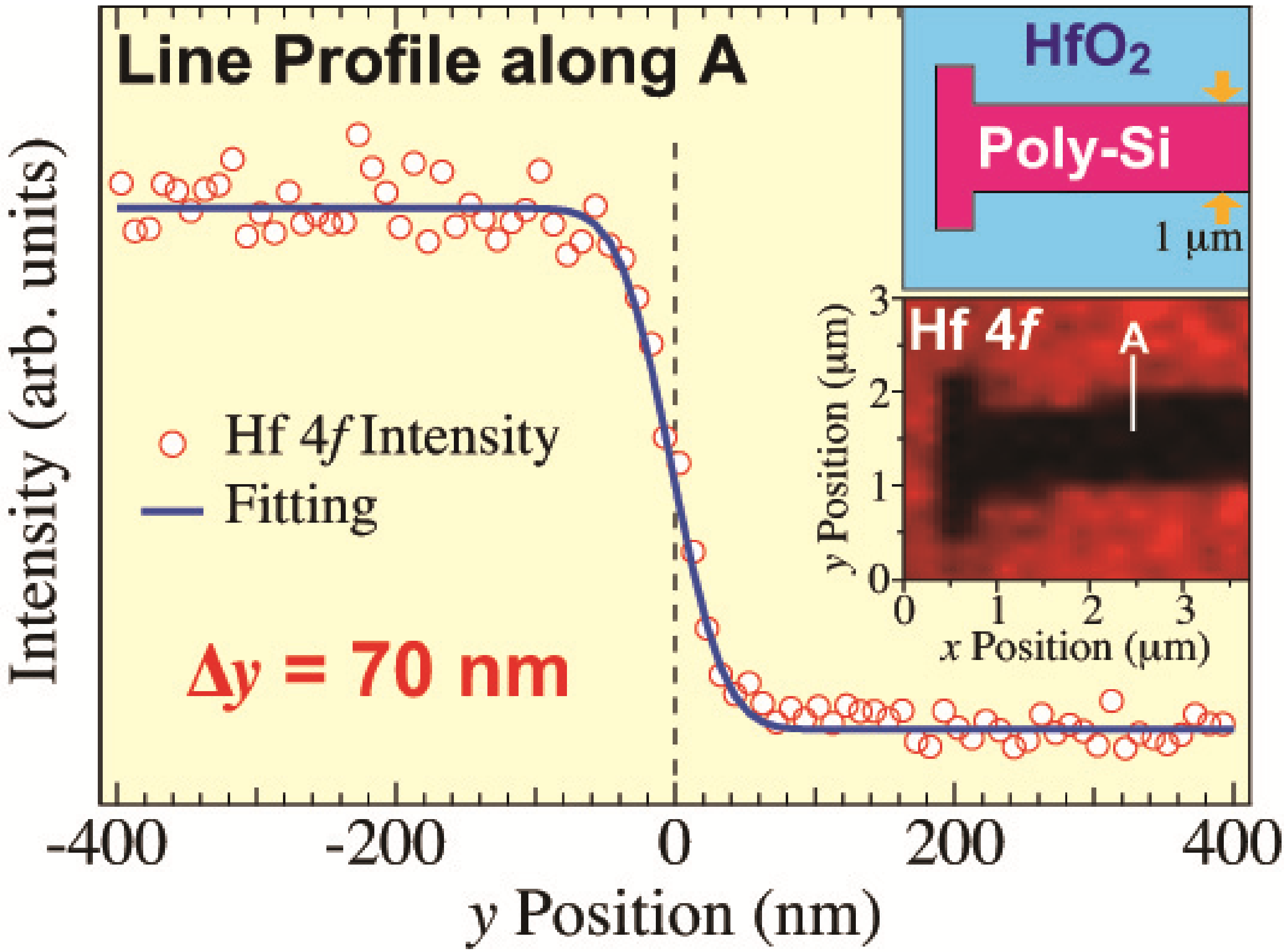


SPEM
+
depth profiling by Angle Resolved technique with MEM analysis



High-resolution angle-resolved electron spectrometer (VG-Scienta R3000)

3D-scanning photoelectron microscope
3D nano-ESCA



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Thank you for your kind attentions.

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