KEK 高エネルギー加速器研究機構
物質構造科学研究所　放射光科学研究施設
PF Photon Factory

9th SESAME Users meeting and KEK School
14 (12–16) November, 2011@Jordan

Synchrotron-radiation photoemission spectroscopy:

Application to the high-throughput characterization of devices

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Photon Factory, KEK

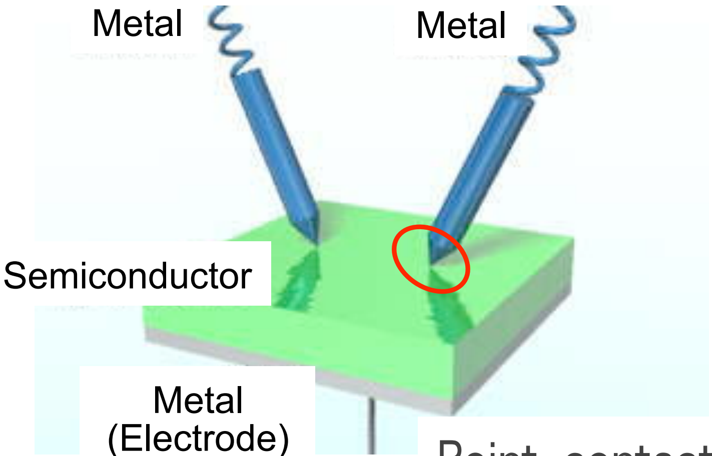
Outline of the lecture

1) Principle of photoemission and x-ray absorption spectroscopy
2) Evaluation of chemical bonding (valence) states by core-level shift
3) Determination of band diagram of Schottky junction and field effect transistor (FET) by photoemission spectroscopy.
4) Recent activities →Practical sessions

The interface is the device

Herbert Kroemer, Nobel Lecture in 2000.

1960

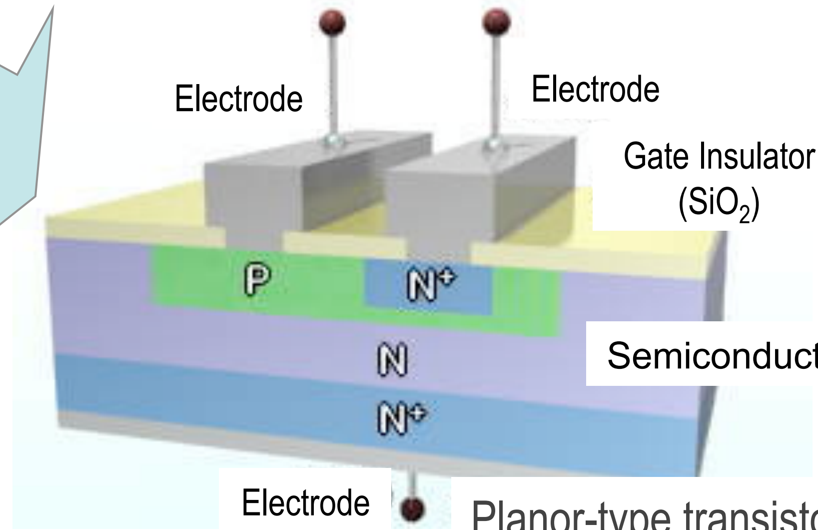


Point-contact transisto

MOS-FET

2000

(Metal-Oxide-Semiconductor Field Effect Transistor)

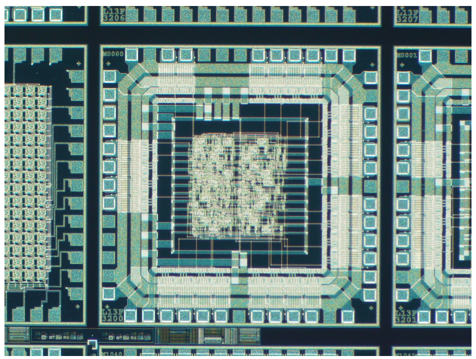


Planor-type transistor

Integration
on chip

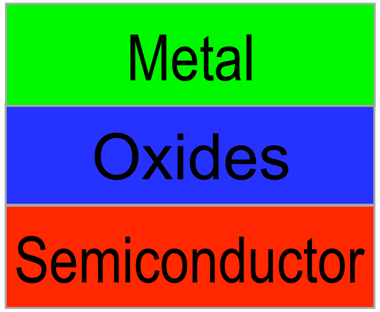
IC（Integrated Circuit）

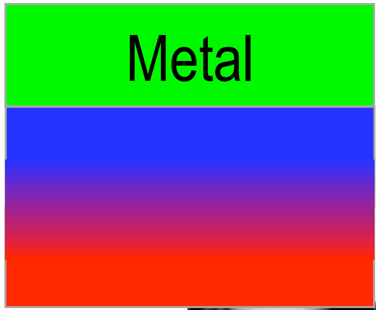
http://isotope.sist.chukyo-u.ac.jp/study/index.html



The devices (MOS-FET) used in recent computer are scaled down to nm scale

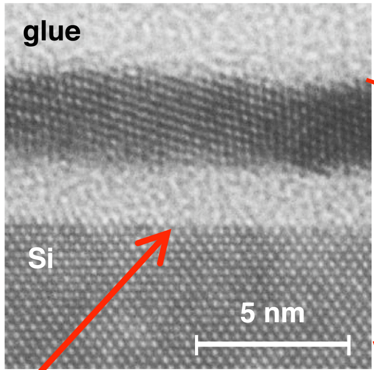
Si MOS-FET transistor

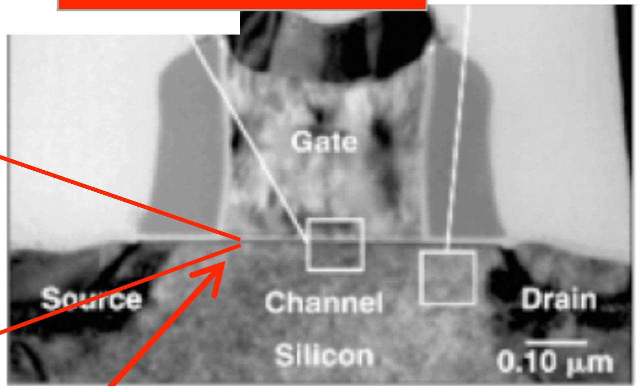


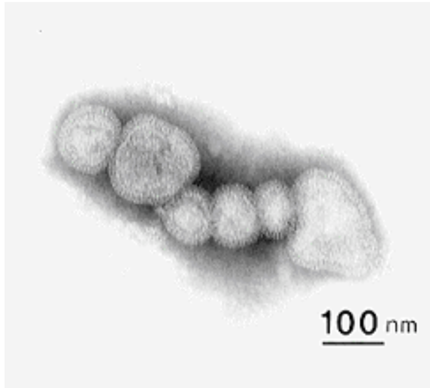


Chemical reaction occurs at the interface, and the physical properties of bulk material are modified at the interface.

Interface







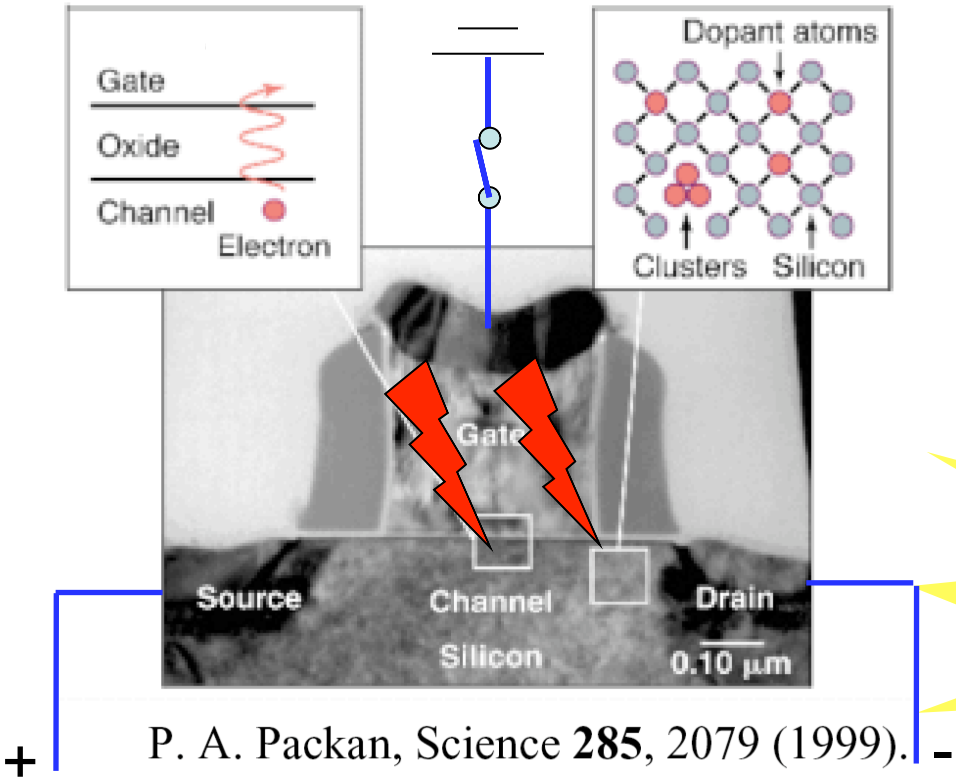
Influenza virus

Channel (the interface between Si and other materials)

For designing the high-performance devices, it is important to characterize the interfacial electronic structure (chemical states, band diagram, etc.) of devices in nm region.

Why is your computer becoming so hot?

MOS transistor



P. A. Packan, Science **285**, 2079 (1999).

Silicide

MSi_2 : Metal

Silicate

MSiO_4 : Insulator $(MO2)_x(SiO2)_{1-x}$

Leak current

•Due to silicide metal formation at the interface

•Due to the crystallization of gate insulator (amorphous)

For designing the high-performance devices, it is important to characterize the interfacial electronic structure (chemical states, band diagram, etc.) of devices

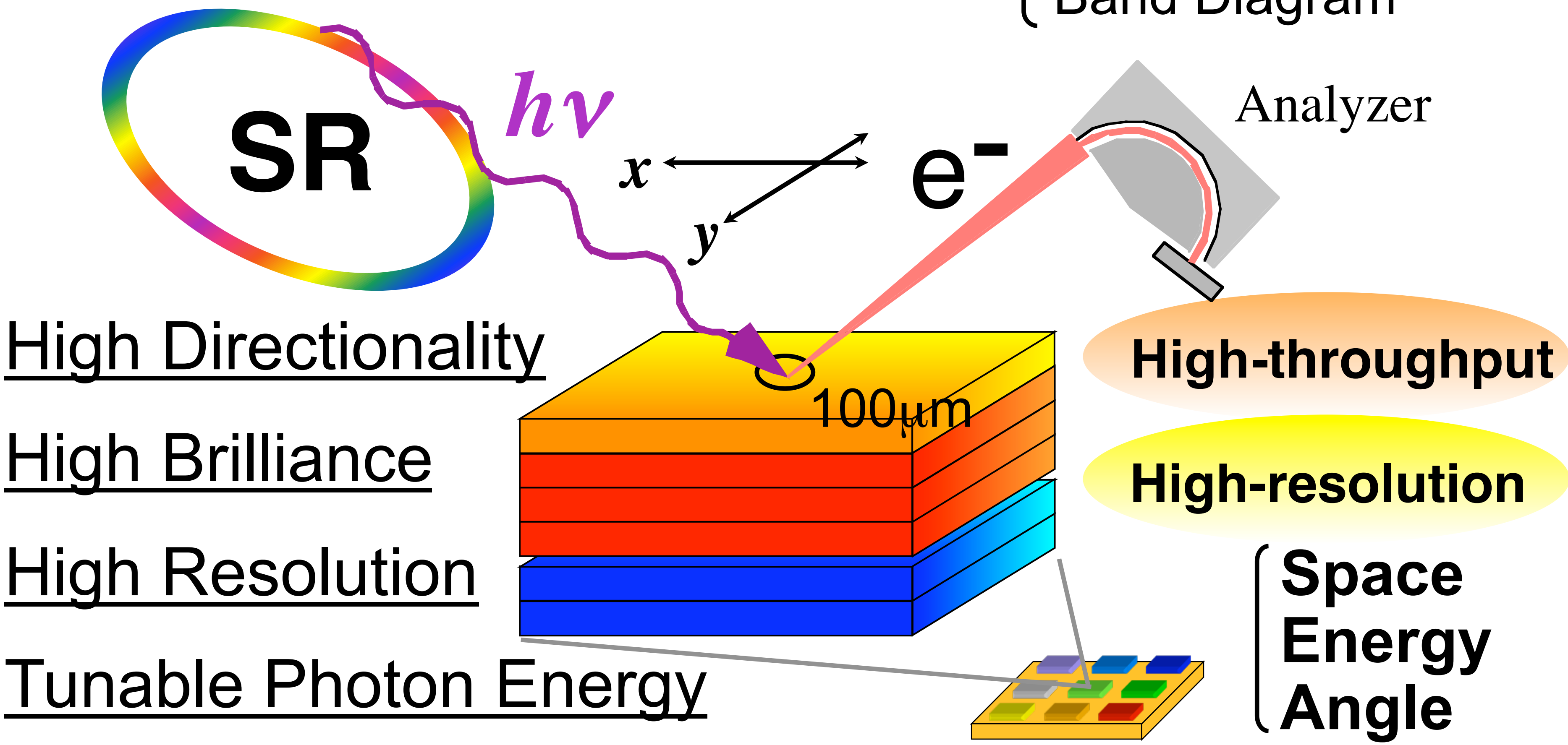
Photoemission characterization using SR light

Advantage of SR-PES

☆Non-destructive

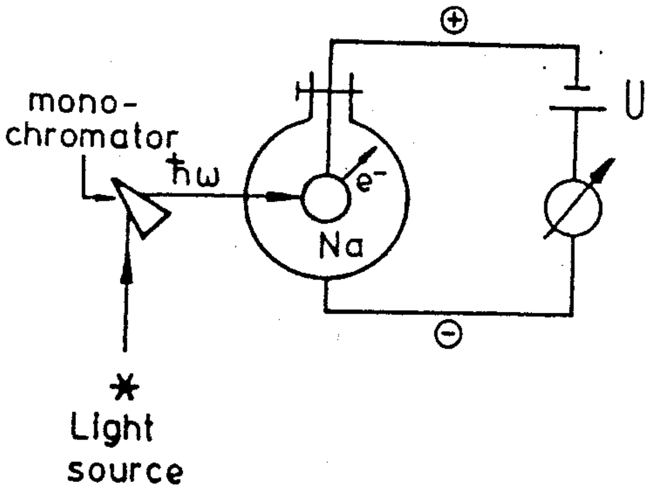
☆Surface (Interface) Sensitive （5～30Å）

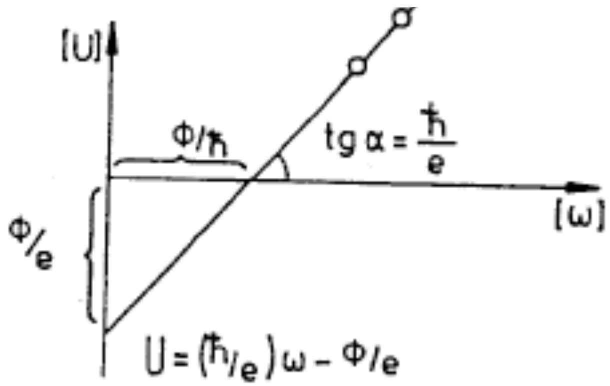
☆Direct Determination of Electronic States
- Chemical Shift
- DOS
- Band Diagram



Principle of photoemission spectroscopy : Photoelectric Effect

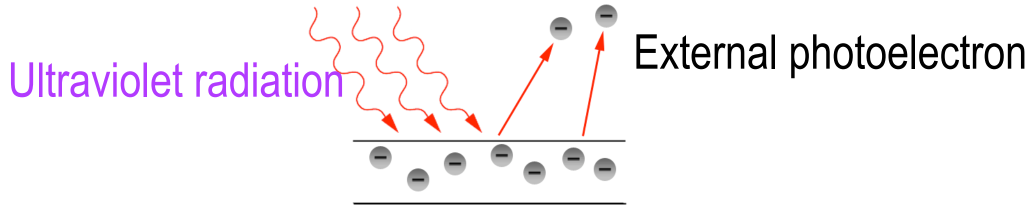
Schematic Drawing of an early "photoemission" experiment.





U: the retarding voltage

The phenomenon of photoemission was discovered by Dr. H.R. Hertz in 1887.



Dr. A. Einstein was able to explain the systematics by invoking the quantum nature of light (Novel Prize in 1921).

$$eU = E_{\mathrm{kin,\ max}} = \hbar\omega - \phi$$

ω : frequency of the light

$E_{\mathrm{kin,\ max}}$: the maximum electron kinetic energy

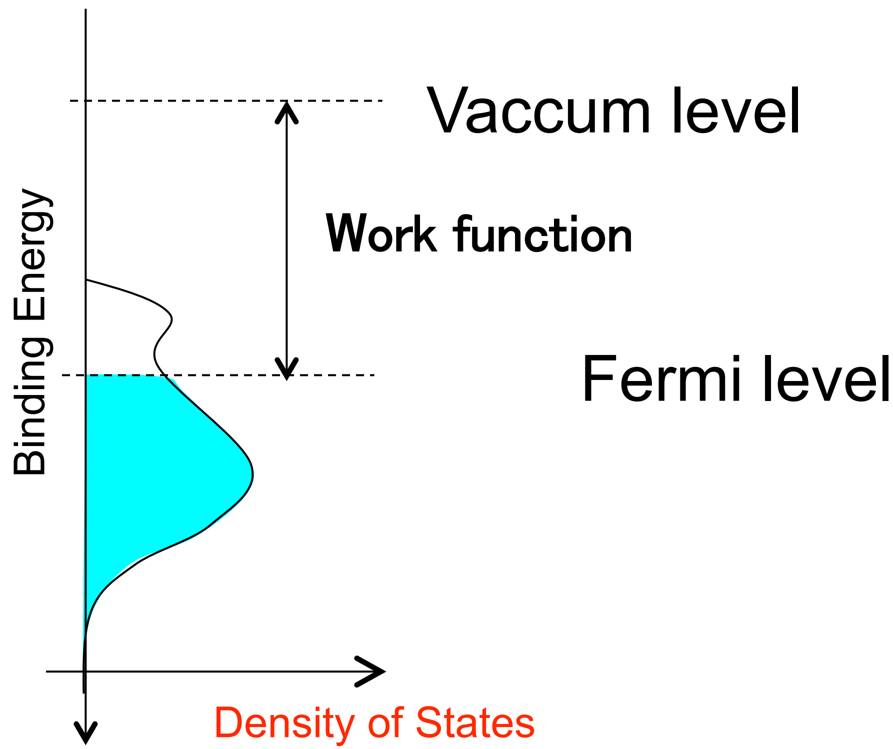
h : Planck's constant

ϕ : Work function

Principle of photoemission spectroscopy : Work Functions

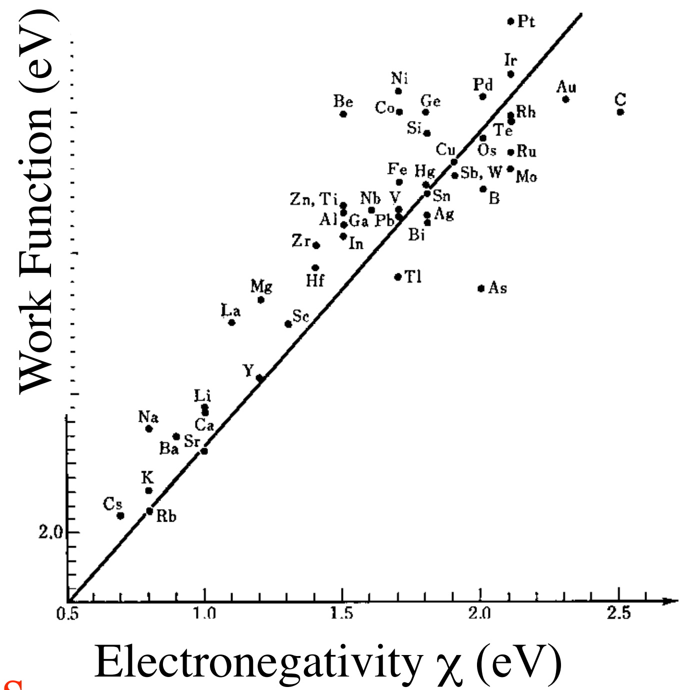
The **work function** is the minimum energy needed to remove an electron from a solid to a point outside the solid surface (or energy needed to move an electron from the Fermi level into vacuum).

Photoelectrons are emitted from the solid surface by irradiating the light.



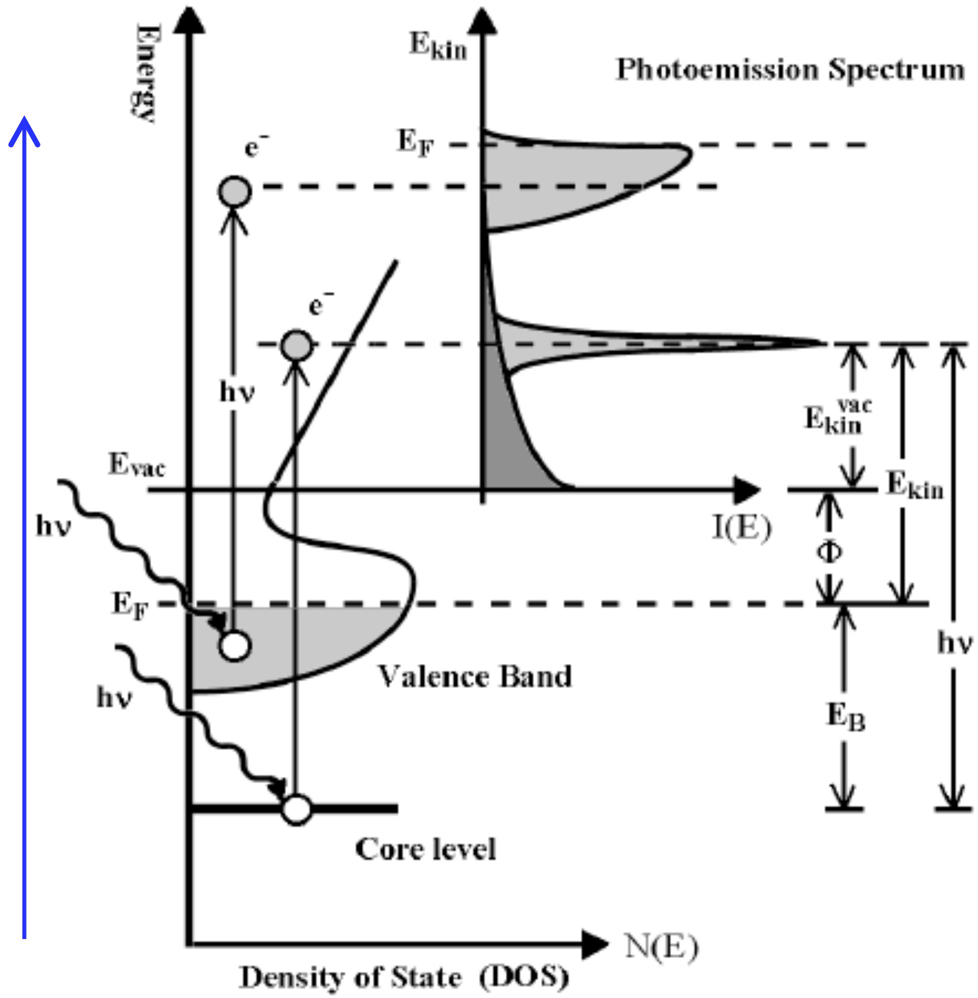
∝ Number of photoelectrons

Work functions



$$\phi = 2.27\,\chi + 0.34\ \mathrm{eV}$$

Principle of photoemission spectroscopy



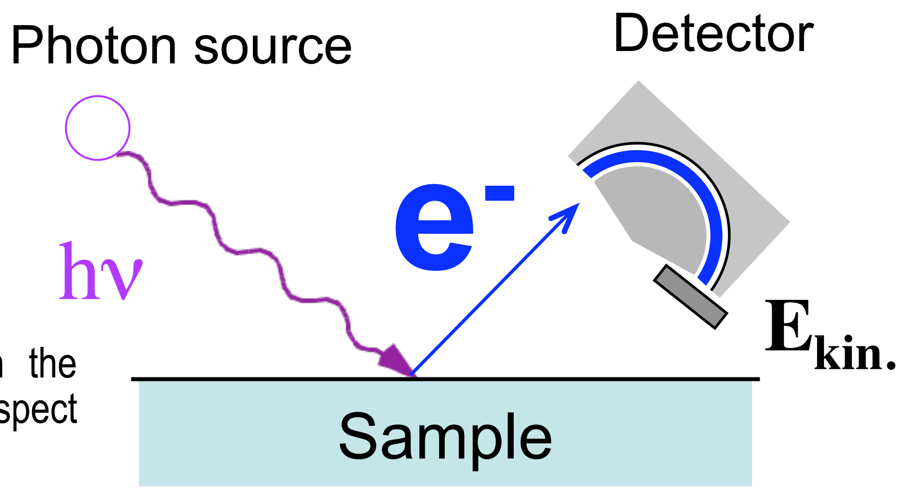
$$h\nu = E_B + E_{kin.} + \phi$$

E_B ; Binding Energy

$E_{kin.}$; Kinetic Energy of Photoelectrons

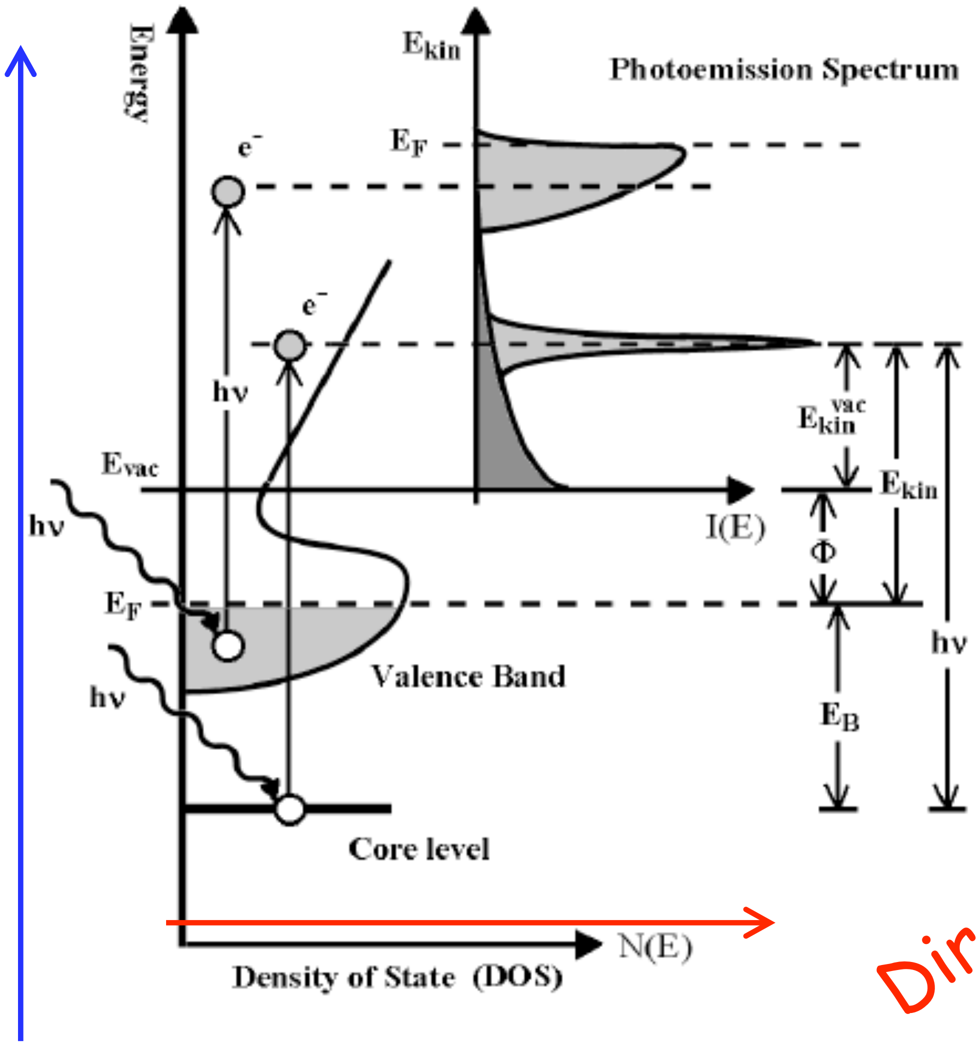
ϕ ; Work functions

Number of emitted photoelectrons with kinetic energy of Ekin.



The light radiated from the photon source impinges on the sample, and the photoelectron are then analyzed with respect with their kinetic energy in an electrostatic analyzer.

Principle of photoemission spectroscopy



$$E_B = h\nu - E_{kin.} - \phi$$

Fermi Golden Rule

Photoemission Intensity (I(w))

$$I(\omega) \propto \sum_k |\langle \Psi_n^{N-1}|a_k|\Psi_0^N\rangle|\delta(\omega - (E_0^N - E_n^{N-1} + \mu))$$

Density of states

Transition Matrix
(Photoionization Crosssection)
Depending on the photon energy

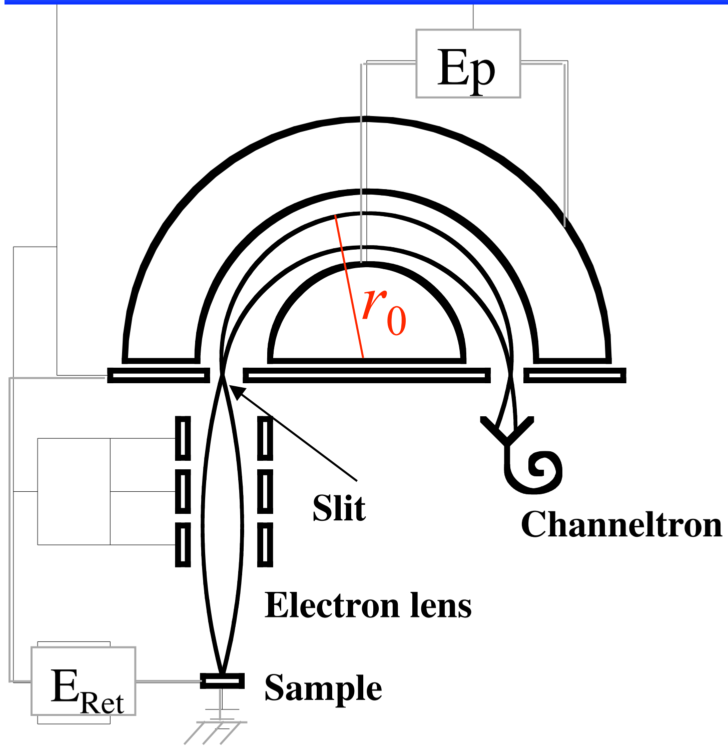
Detect the photoemission intensity as a function of binding energy.

Directly

Density of States

Core level

Instruments: Electron Analyzer

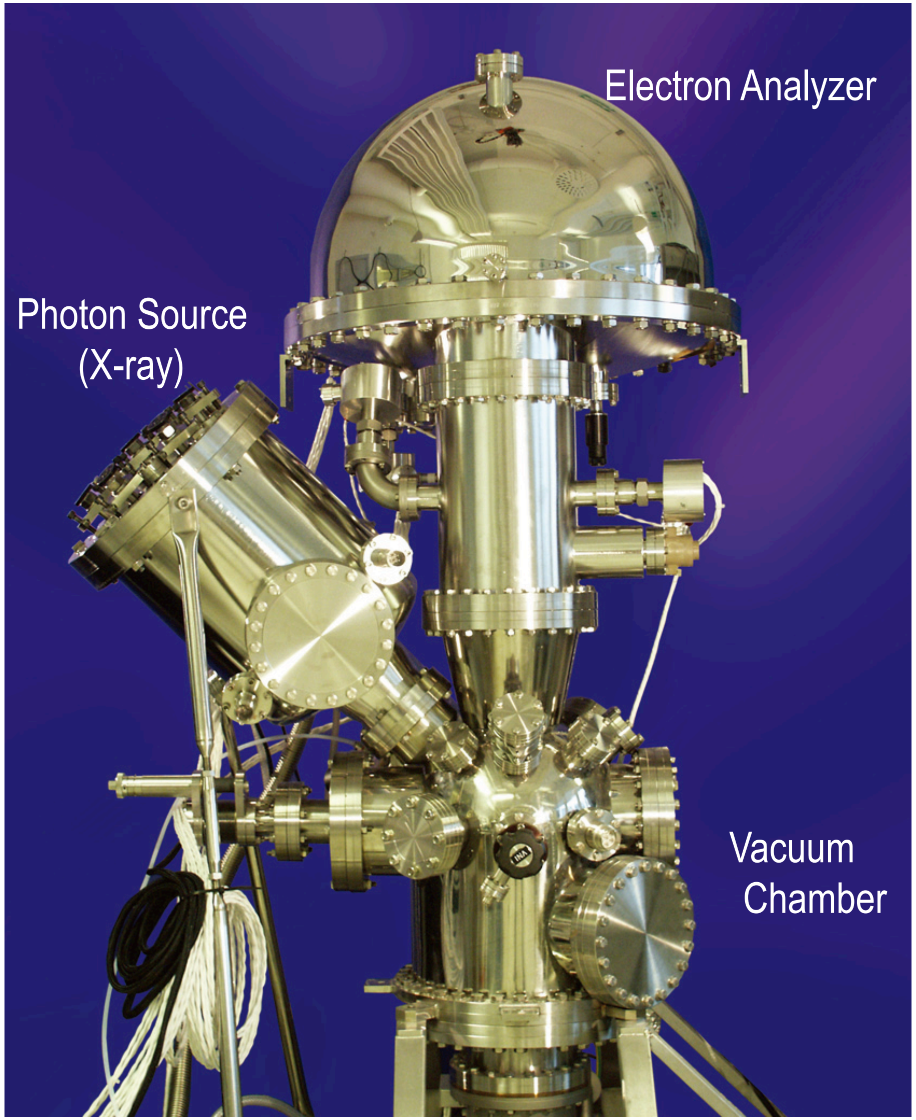


Energy Resolution

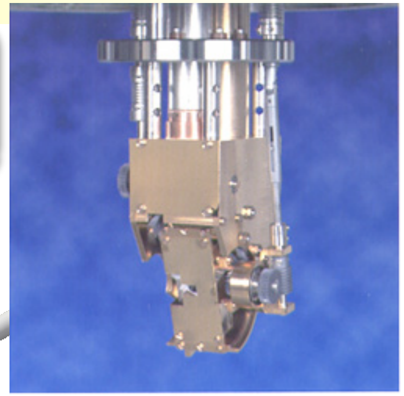
$$\Delta E = \frac{wE_p}{2r_o}$$

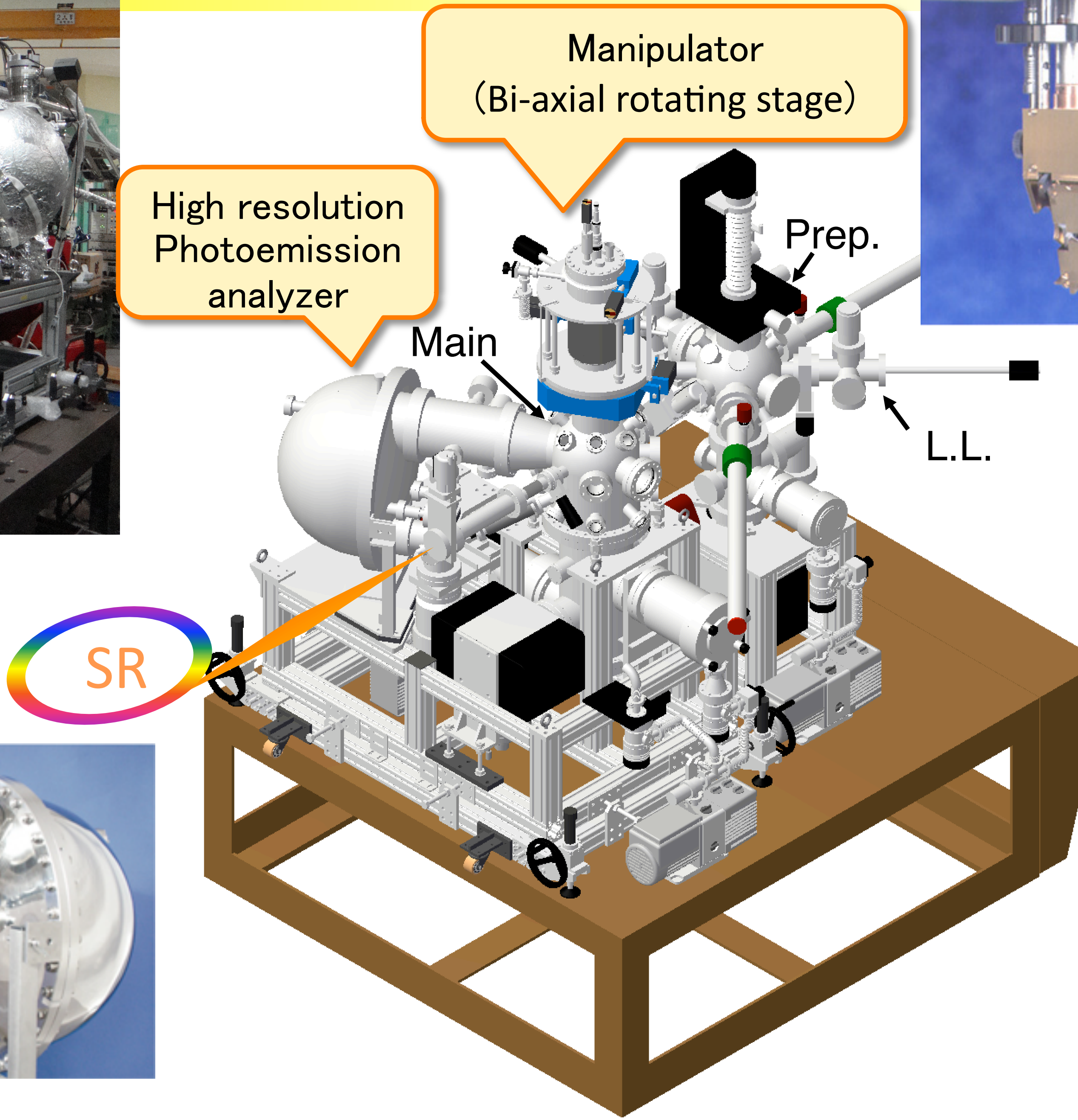
w ; Slit width

r_o; Radius of hemispherical analyzer

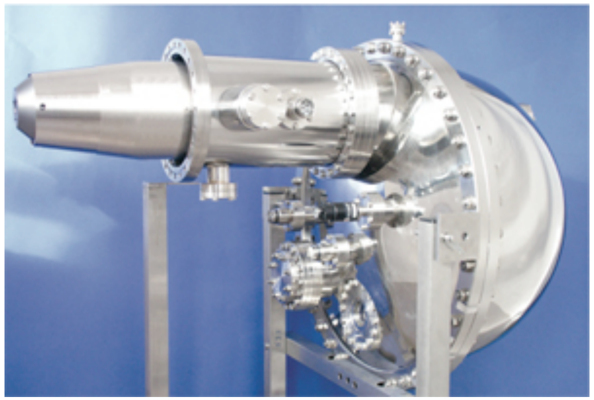


Photoemission Chamber@SR





VGScienta SES2002



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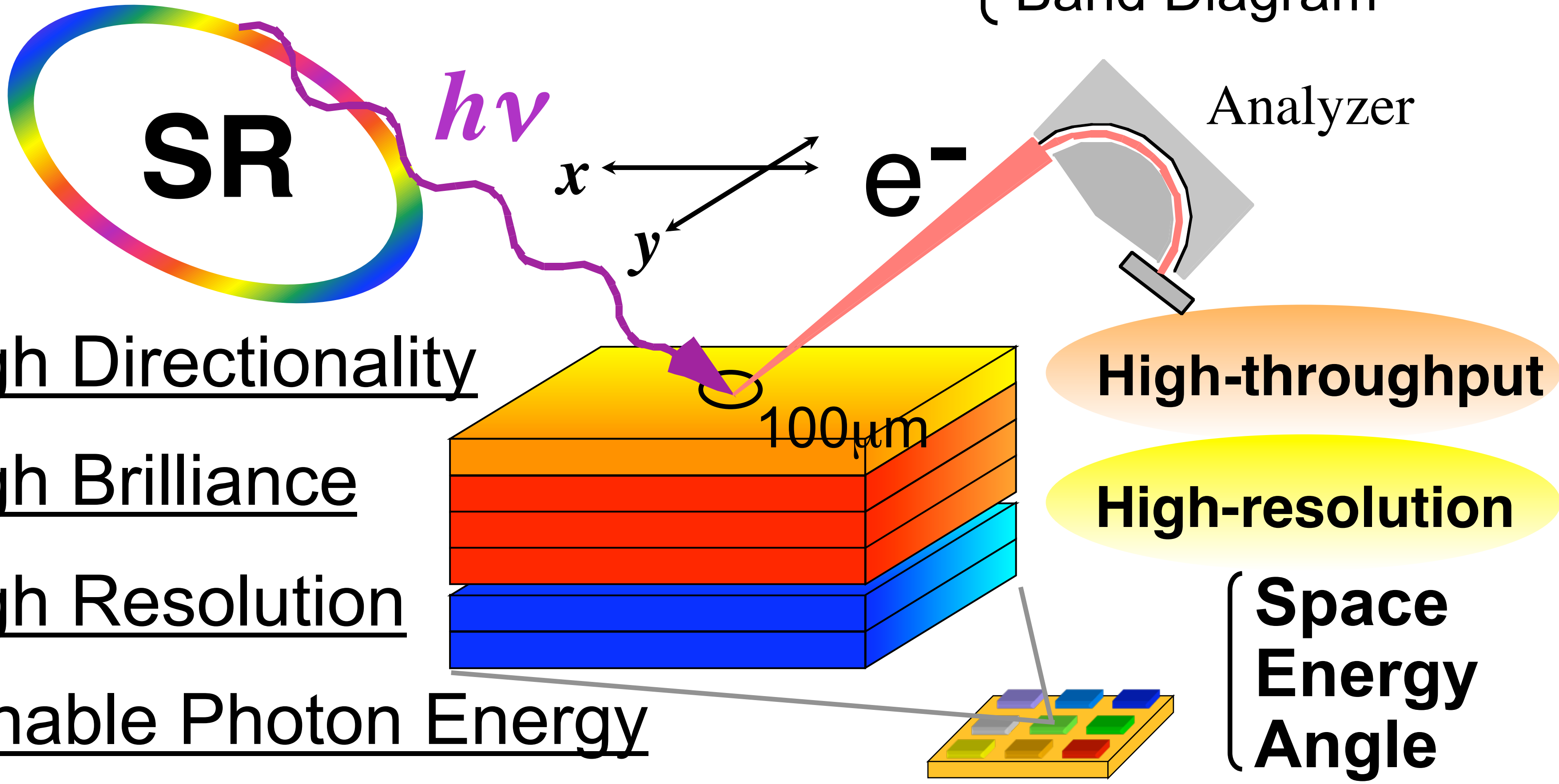
☆Surface (Interface) Sensitive （5～30Å）

☆Direct Determination of Electronic States
- Chemical Shift
- DOS
- Band Diagram



High Directionality

High Brilliance

High Resolution

Tunable Photon Energy

Photoemission in the soft-x-ray region

Photoemission spectroscopy (PES)

X-ray photoemission spectroscopy (XPS)

Mg Ka : 1253.6 eV
Al Ka : 1486.6eV

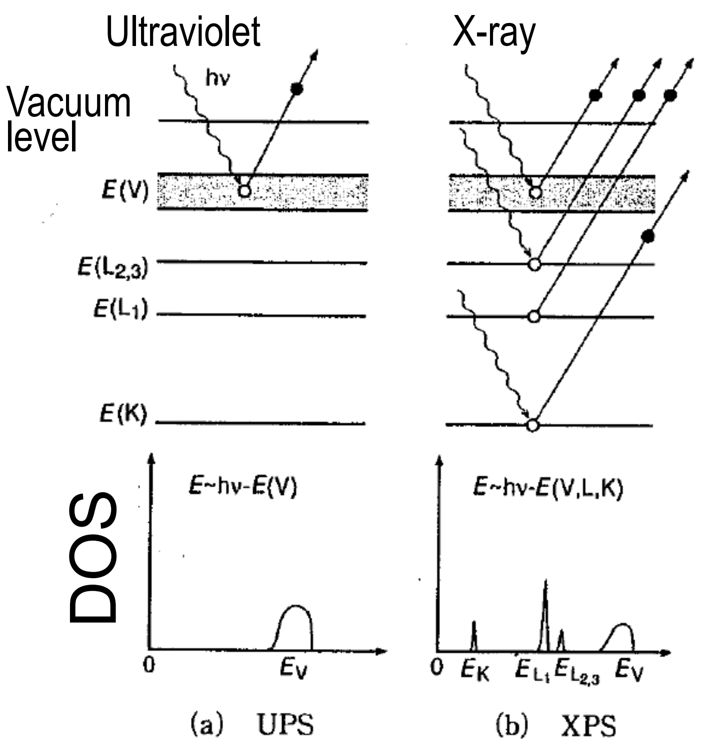
(Electron Spectroscopy for Chemical Analysis; ESCA)

⇨ Core level

Ultraviolet photoemission spectroscopy (UPS)

⇨ Valence band

He I : 21.22 eV
He II : 40.8 eV



Core levels

Valence band (UPS) → Density of States

Core levels (XPS) →Elemental selectivity

Chemical composition analysis

Chemical state analysis

XPS : Chemical composition analysis

Photoemission spectroscopy (PES)

X-ray photoemission spectroscopy (XPS)

Mg Ka ：1253.6 eV
Al Ka ：1486.6eV

(Electron Spectroscopy for Chemical Analysis (ESCA))

⇨ Core level   Elemental selectivity

Ultraviolet photoemission spectroscopy (UPS)

⇨ Valence band

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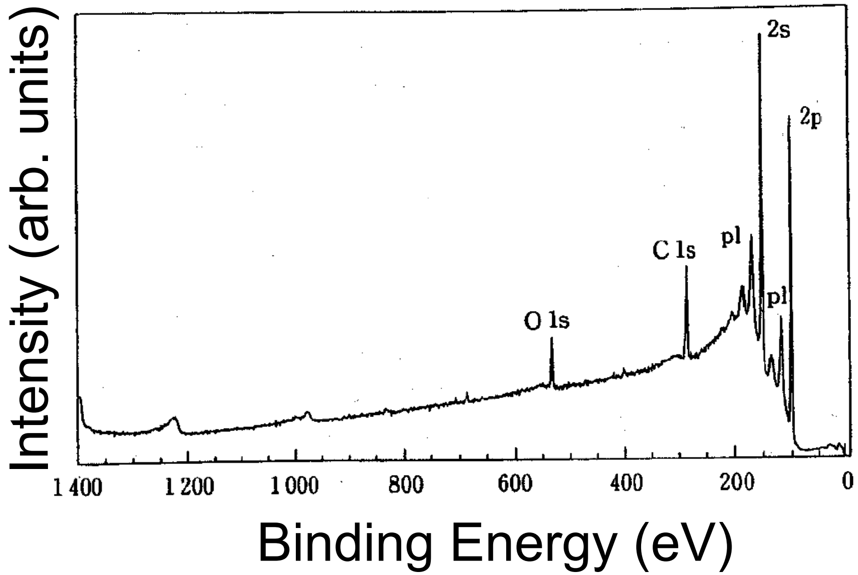


Si, O, and C

Contamination of Si wafers is some carbon oxides.

XPS spectra of Si.
(pl denote the prasmon)

XPS : Chemical composition analysis

Photoemission spectroscopy (PES)

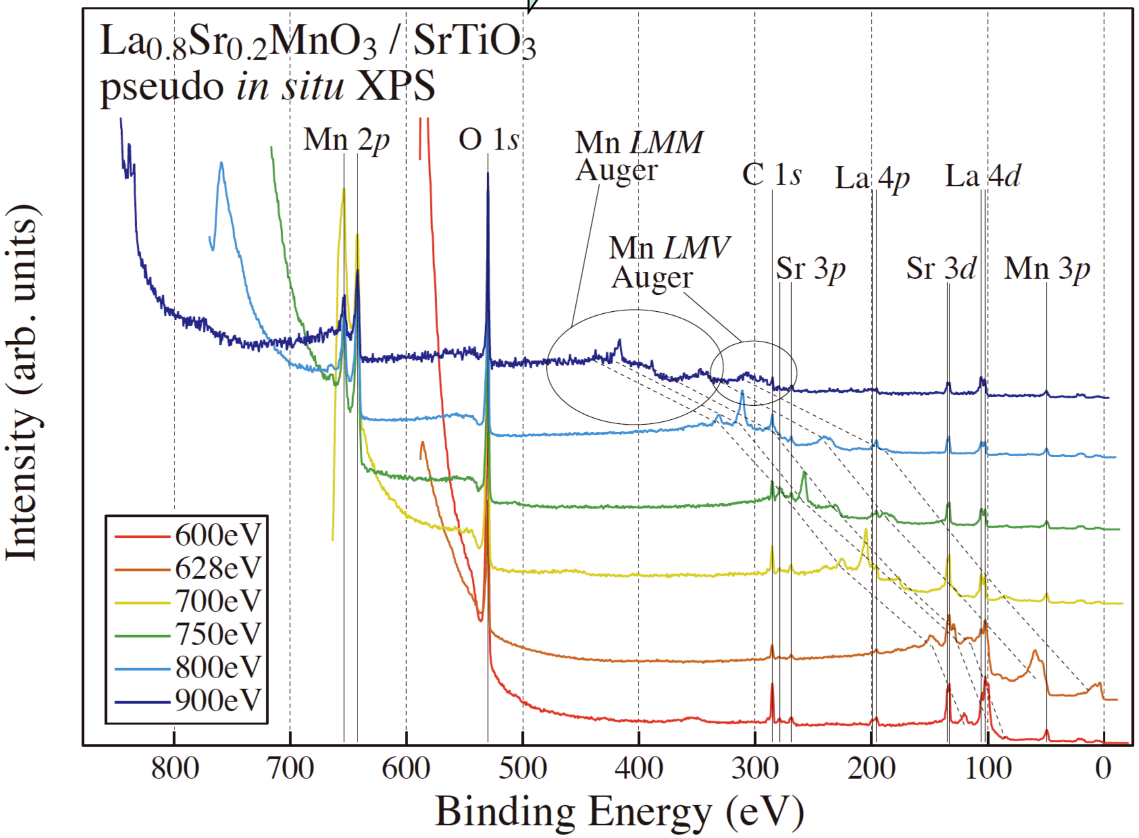
X-ray photoemission spectroscopy (XPS)

Mg Ka :1253.6 eV
Al Ka :1486.6eV

(Electron Spectroscopy for Chemical Analysis)

Soft x-ray@SR

Core level Elemental selectivity



XPS spectra of $La_{1-x}Sr_xMnO_3$ film

By analyzing the intensity of each core level, the chemical composition is estimated.

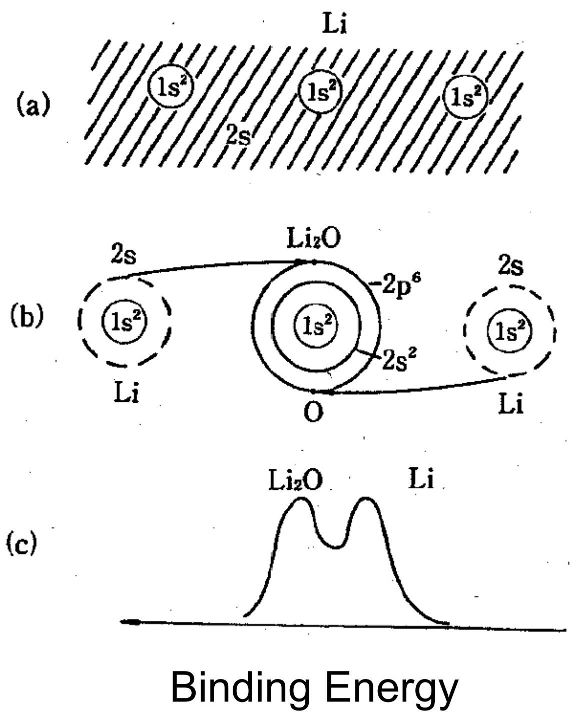
By changing the photon energy, the Auger peaks are distinguish.

XPS : Chemical states analysis

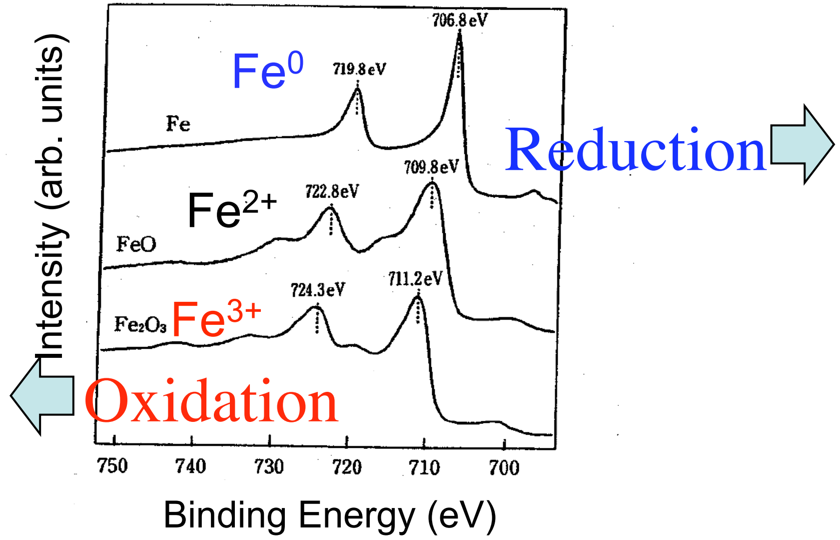
XPS→Elemental specificity、Chemical composition analysis

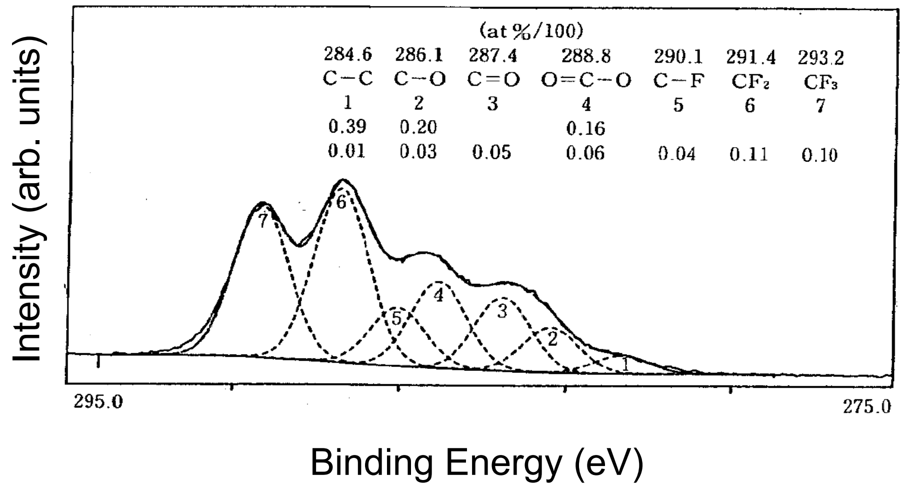
Chemical state analysis (Chemical shift)

The electric potential around core electrons is changed depending on the difference of chemical bonding. Therefore, reflecting the chemical bonding states, the energy position of the core level shifts.

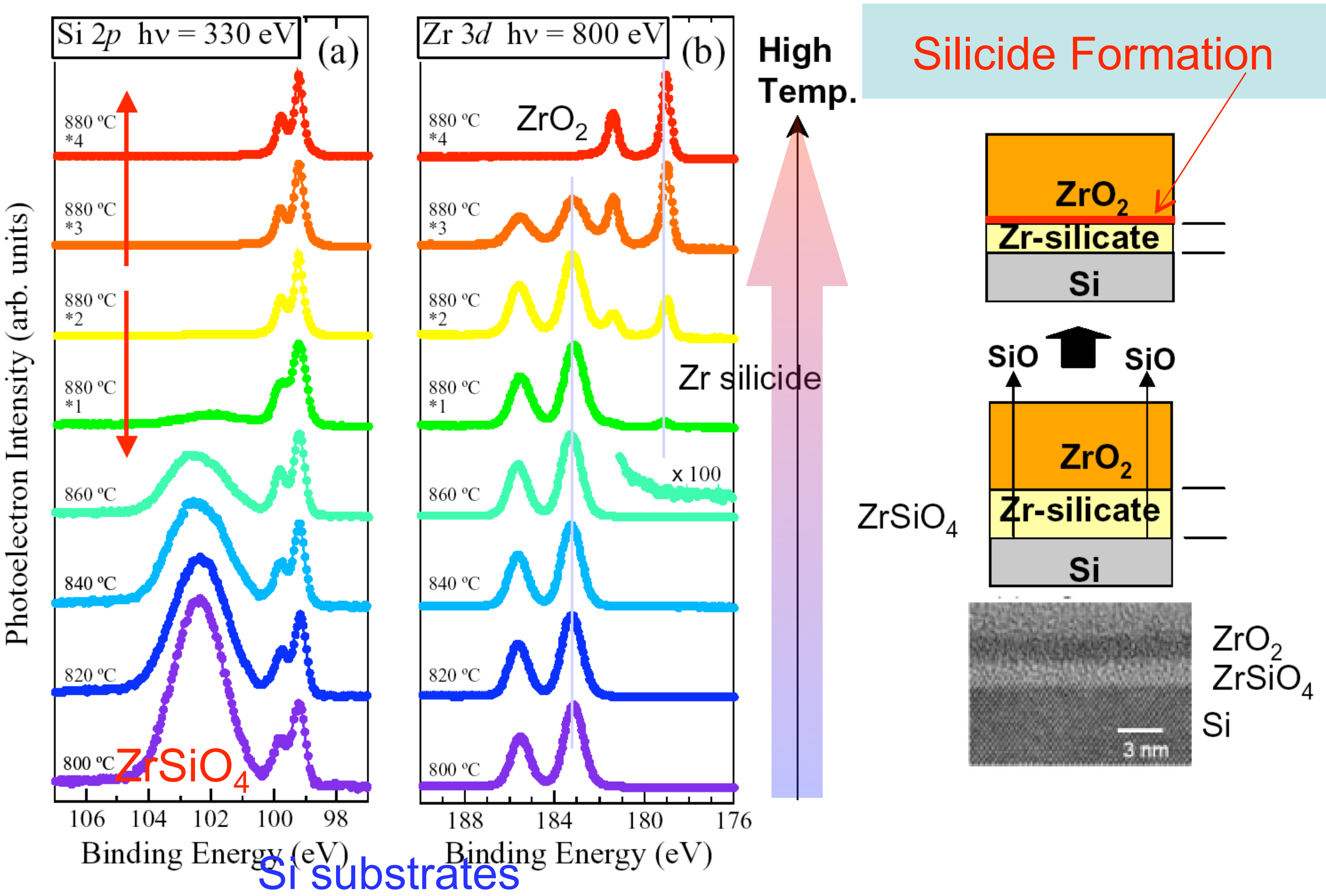


Chemical Shift of Li 1s core level.



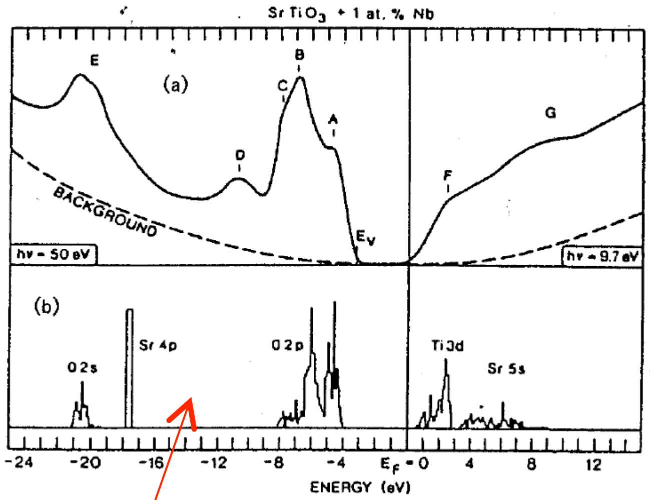


Analysis for high-k ZrO_2 gate



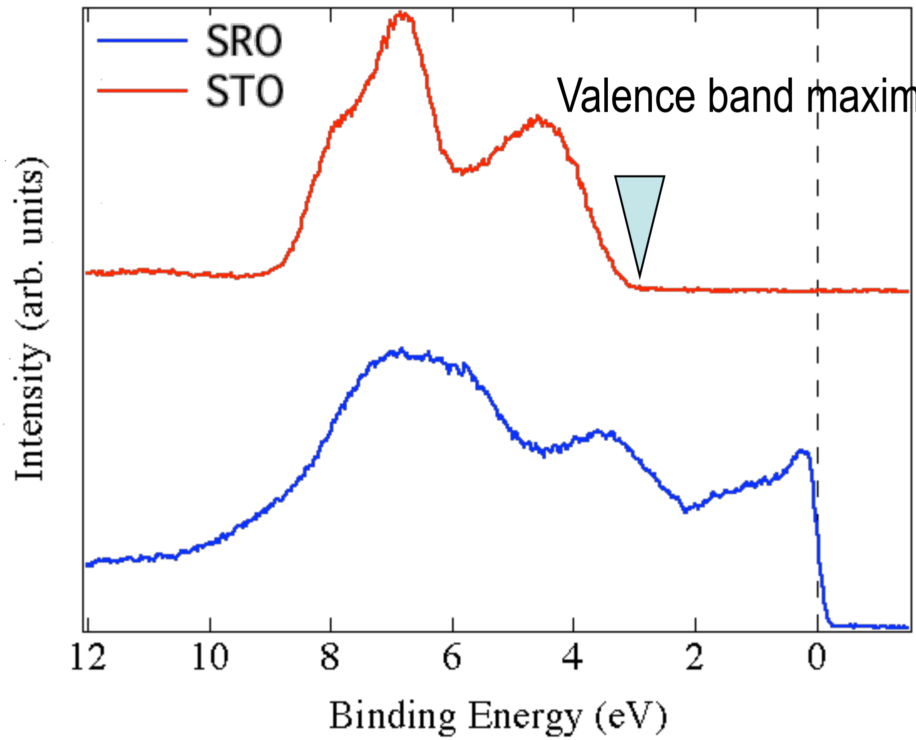
UPS : Valence Band Spectra

UPS →Direct determination of the density of states

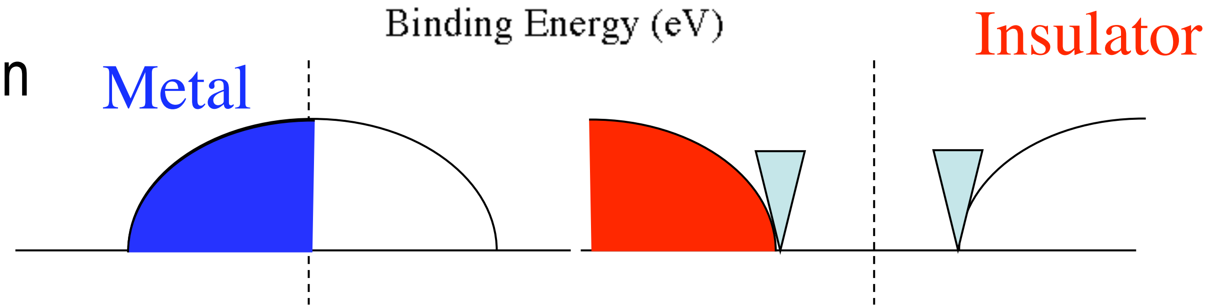


Band structure calculation

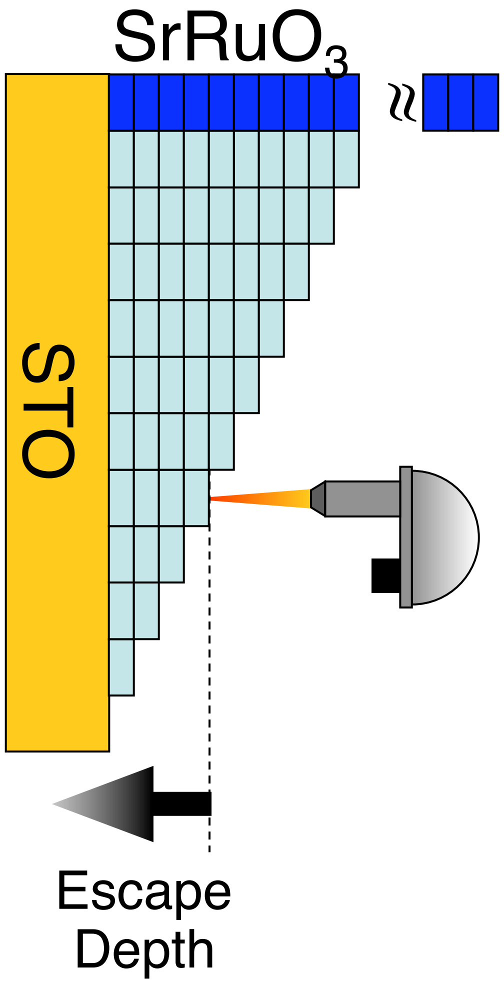
Metal or Semiconductor



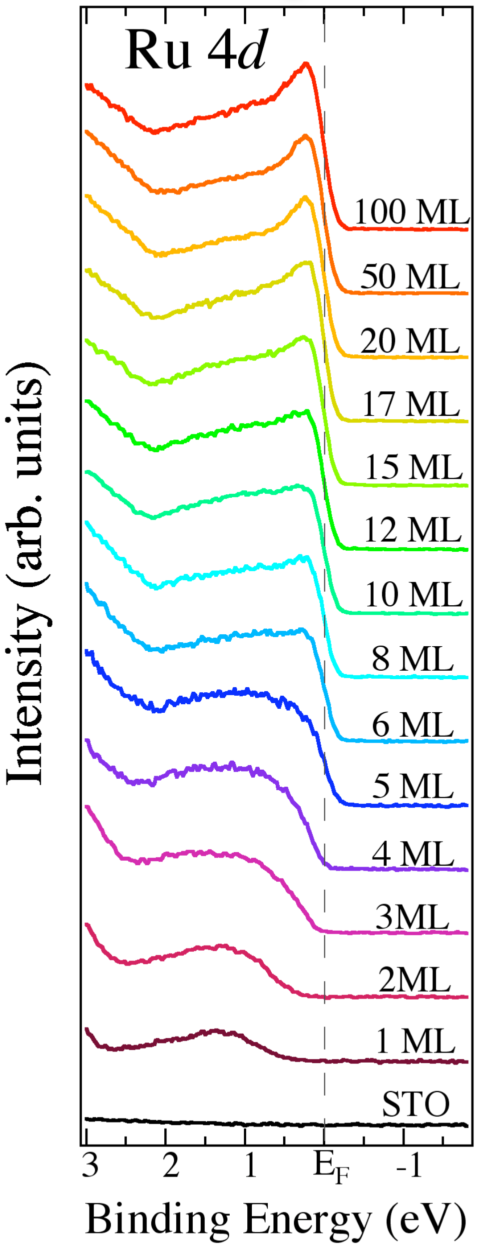
Insulator

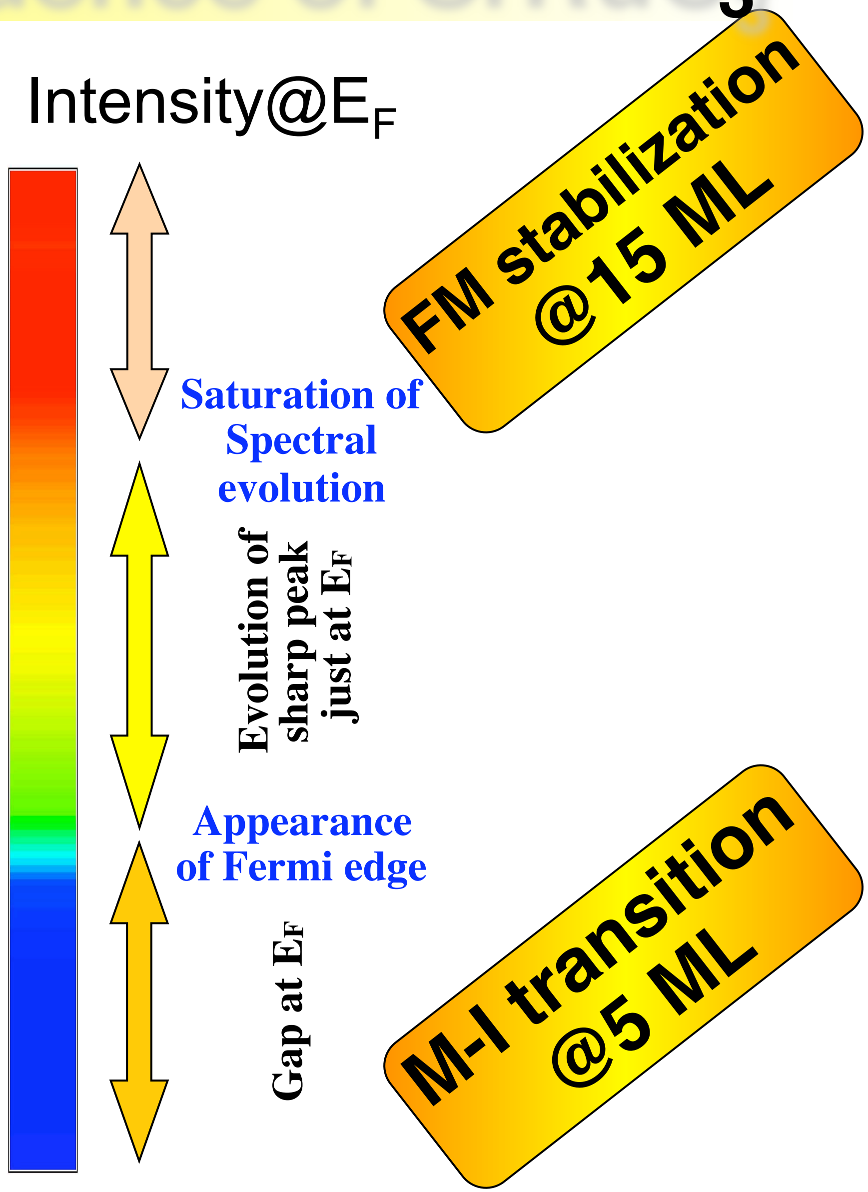


Thickness Dependence of $SrRuO_3$



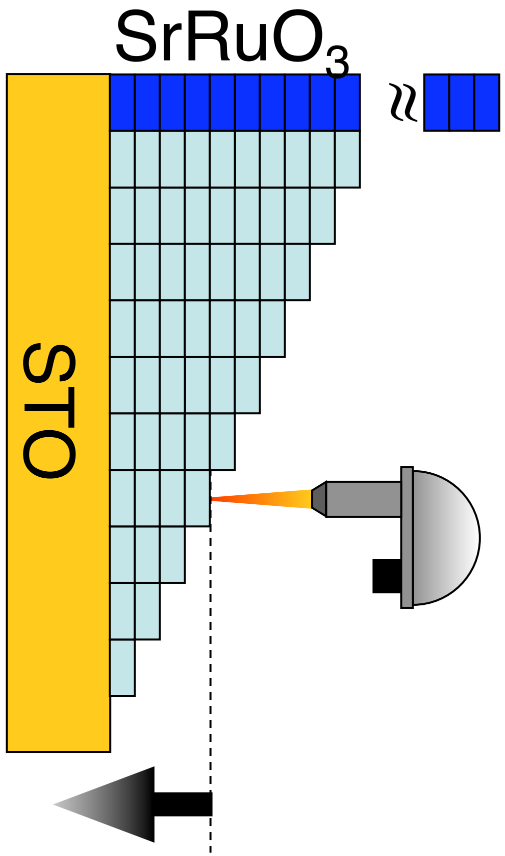
Obtained by *one-shot* experiment





D. Toyota *et al.*, Appl. Phys. Lett., **87**, 162508 ('05).

Thickness Dependence of $SrRuO_3$



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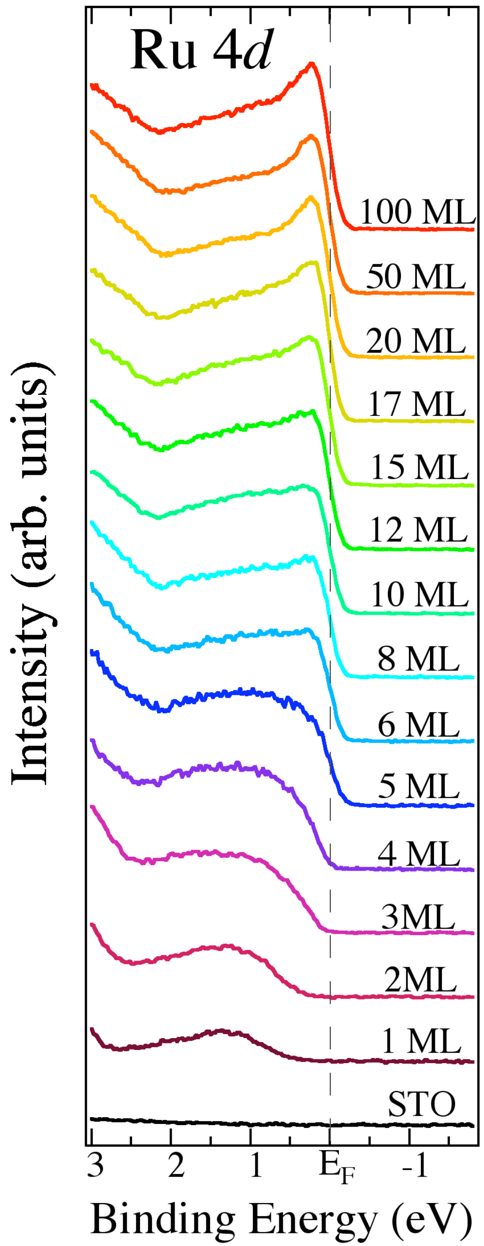

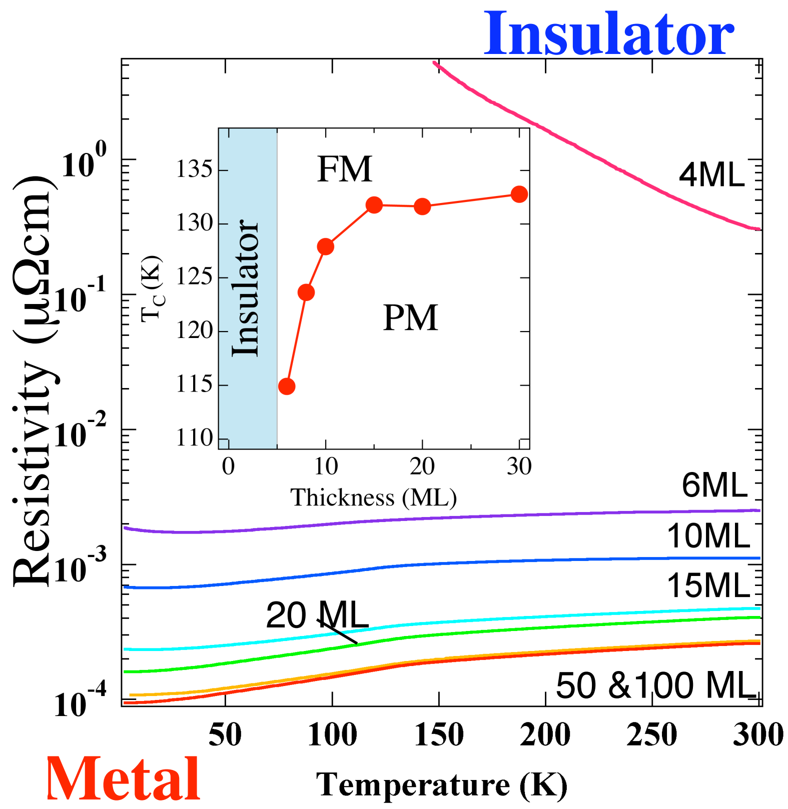

M-I transition@5 ML

FM stabilization@15 ML

D. Toyota *et al*., Appl. Phys. Lett., **87**, 162508 ('05).

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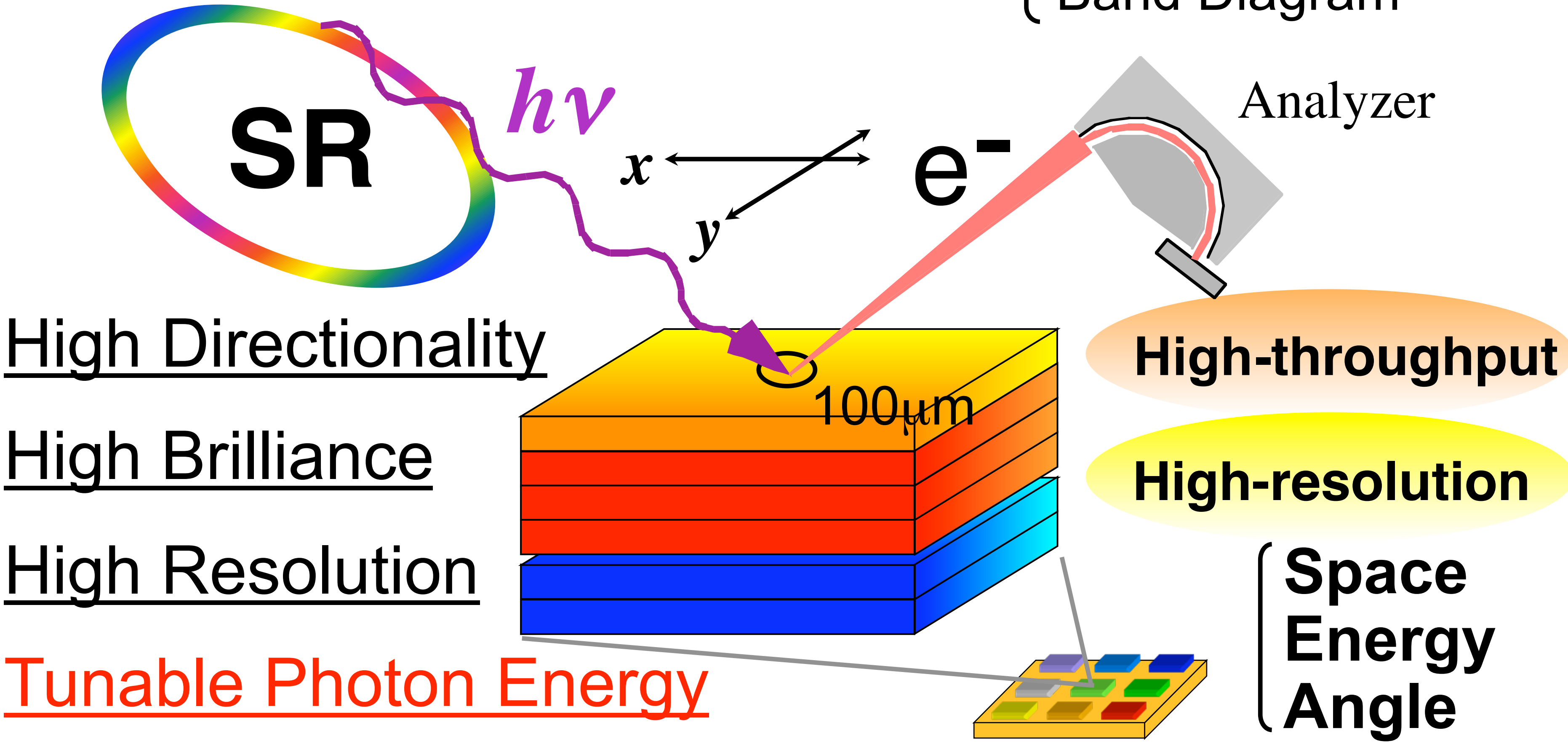
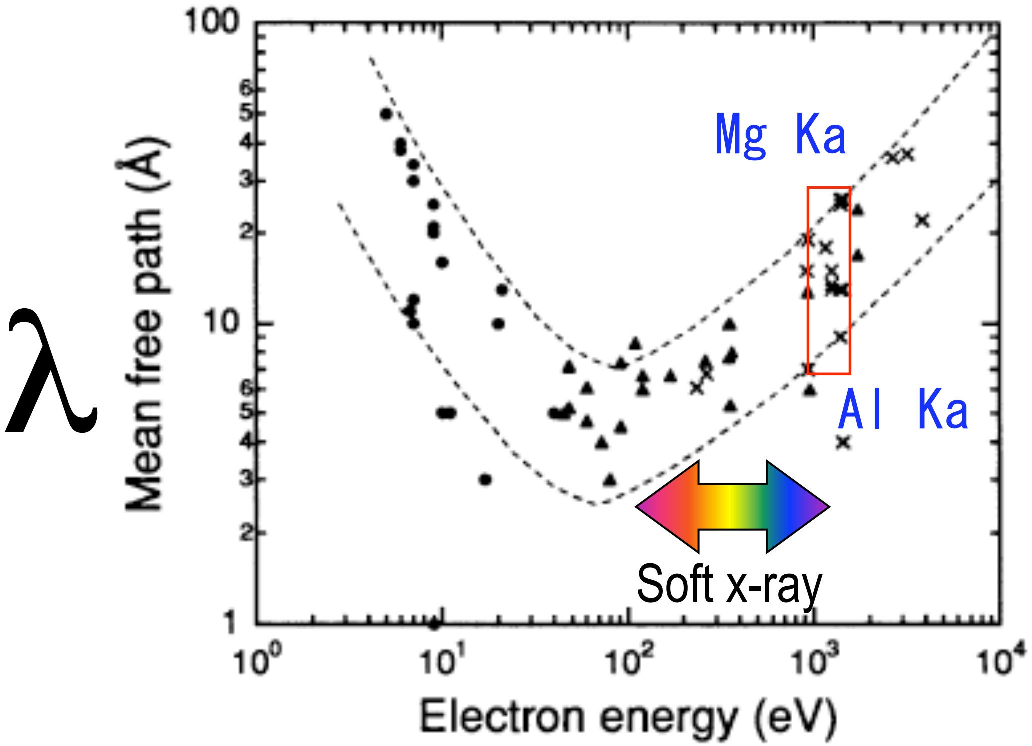


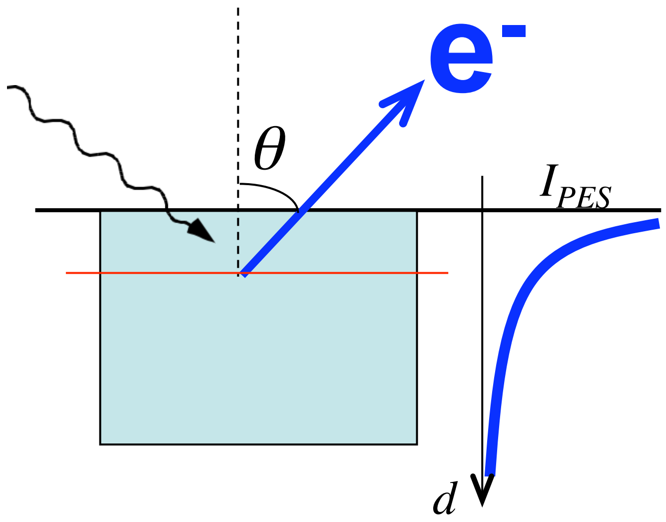
Probing depth

Photoemission is a surface sensitive prove.



Chemical states at the surface (interface).

$$I_{PES} = \exp(-d / \lambda \cdot \cos\theta)$$



Escape depth (mean free path) of photoelectrons depends on the kinetic energy.

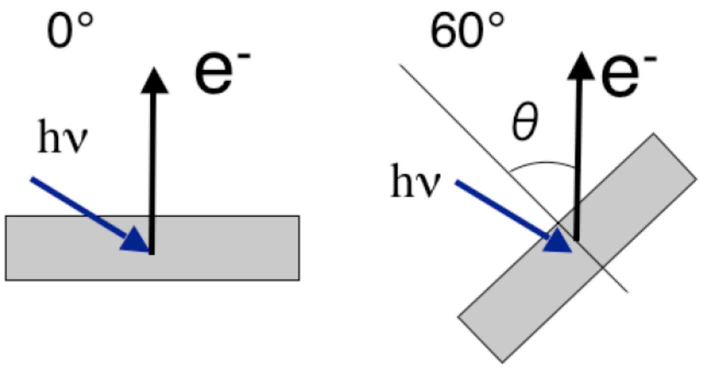
The escape depth in the soft x-ray region is ranged from 1 to 10nm. Thus, we studies the surface states of solid.

Surface sensitivity

Photoemission is one of the best prove to study the electronic structure at the surface and interface.

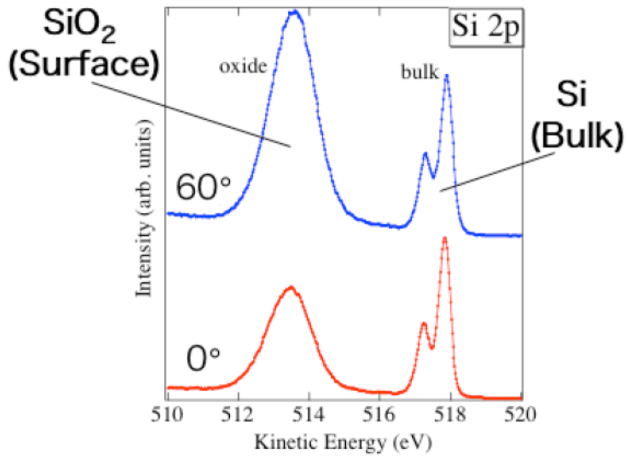
The intensity of photoelectrons is decade as a function of $\exp(-d\ /\lambda\cdot\chi o\sigma\theta)$. Therefore, we are able to extract the surface and/or interface components by changing the photon energy (kinetic energy of photoelectrons) and the angle between the incident light and the normal of the sample surface.

Si surface is oxidized.

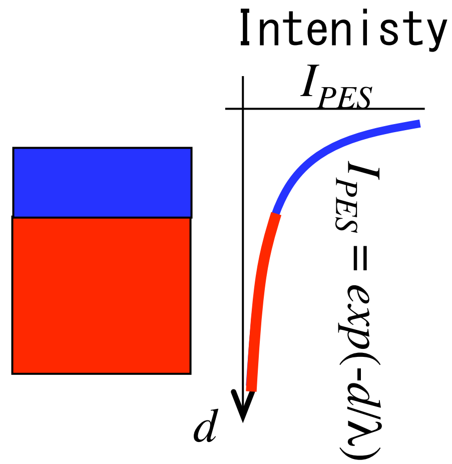


$\lambda(E_K, \theta) = \lambda(E_K)\cdot\cos(\theta)$

$I_{PES} = \exp(-d\ /\lambda\cdot\cos\theta)$



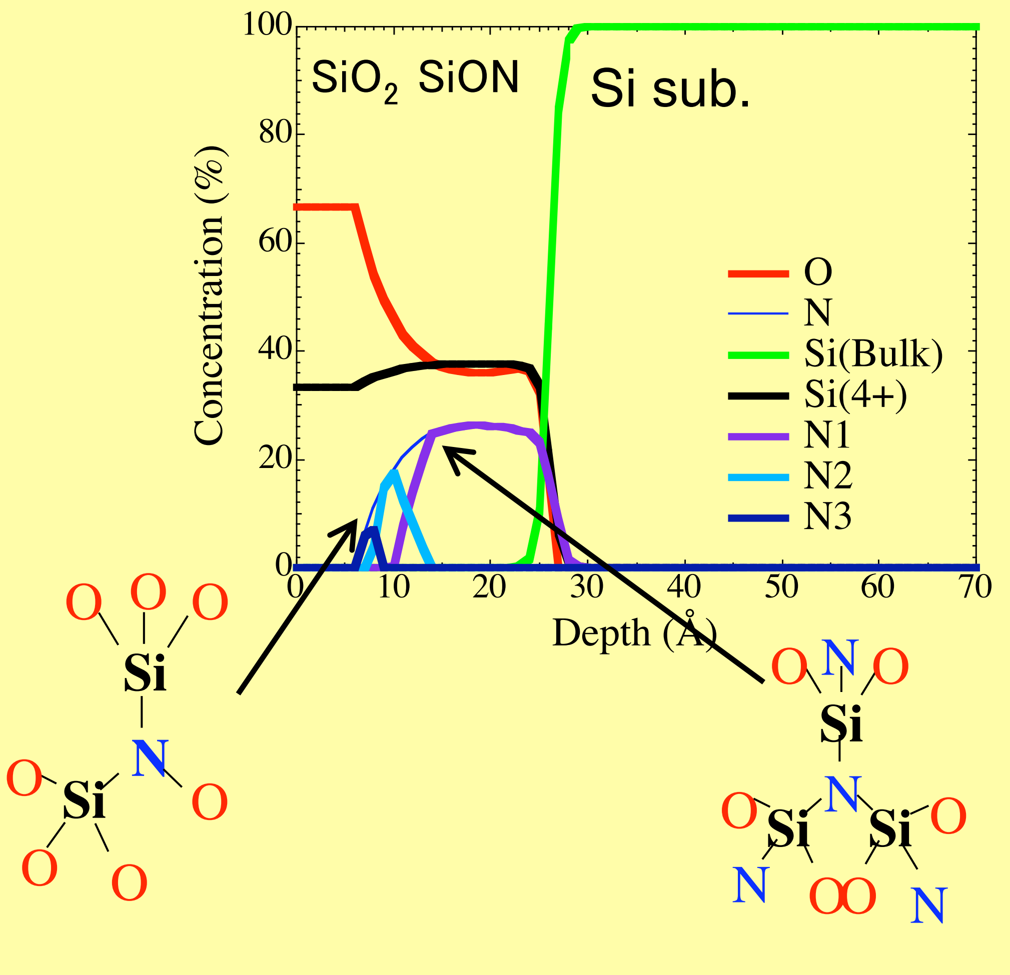
Chemical shift

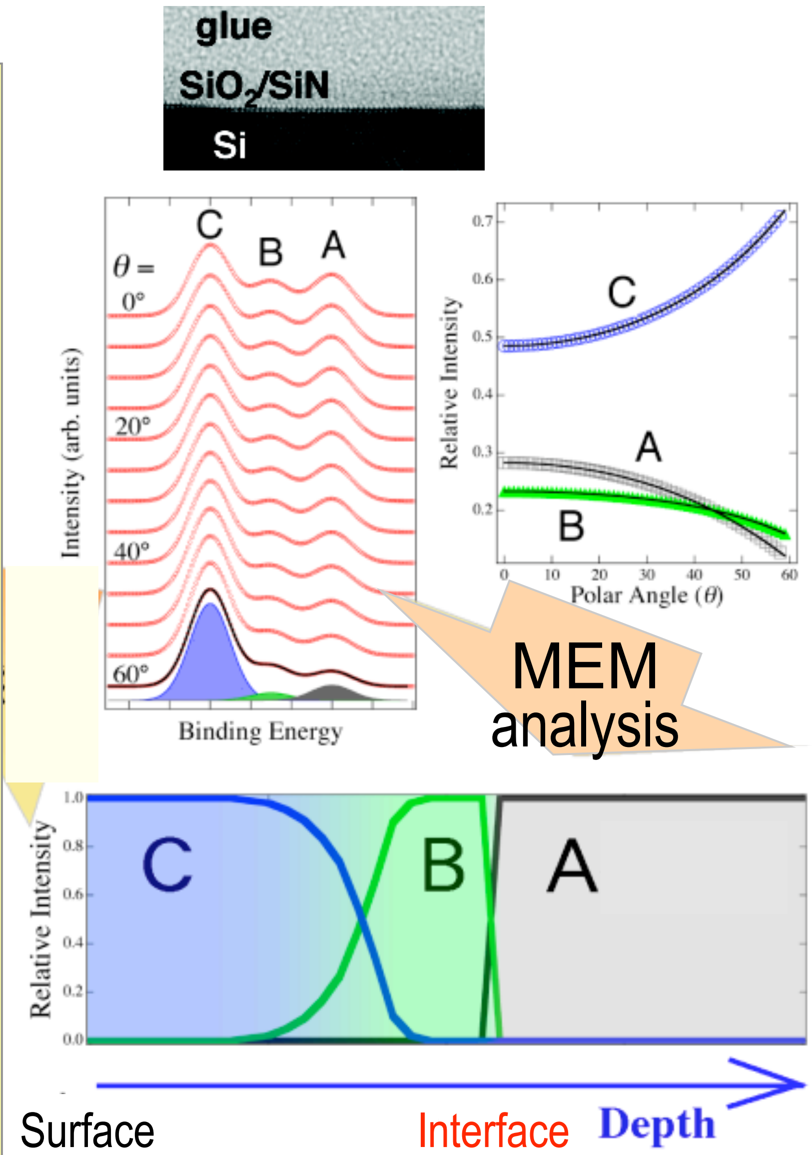


Interface

Depth profiling using angle dependent XPS

MEM analysis of SiON/Si





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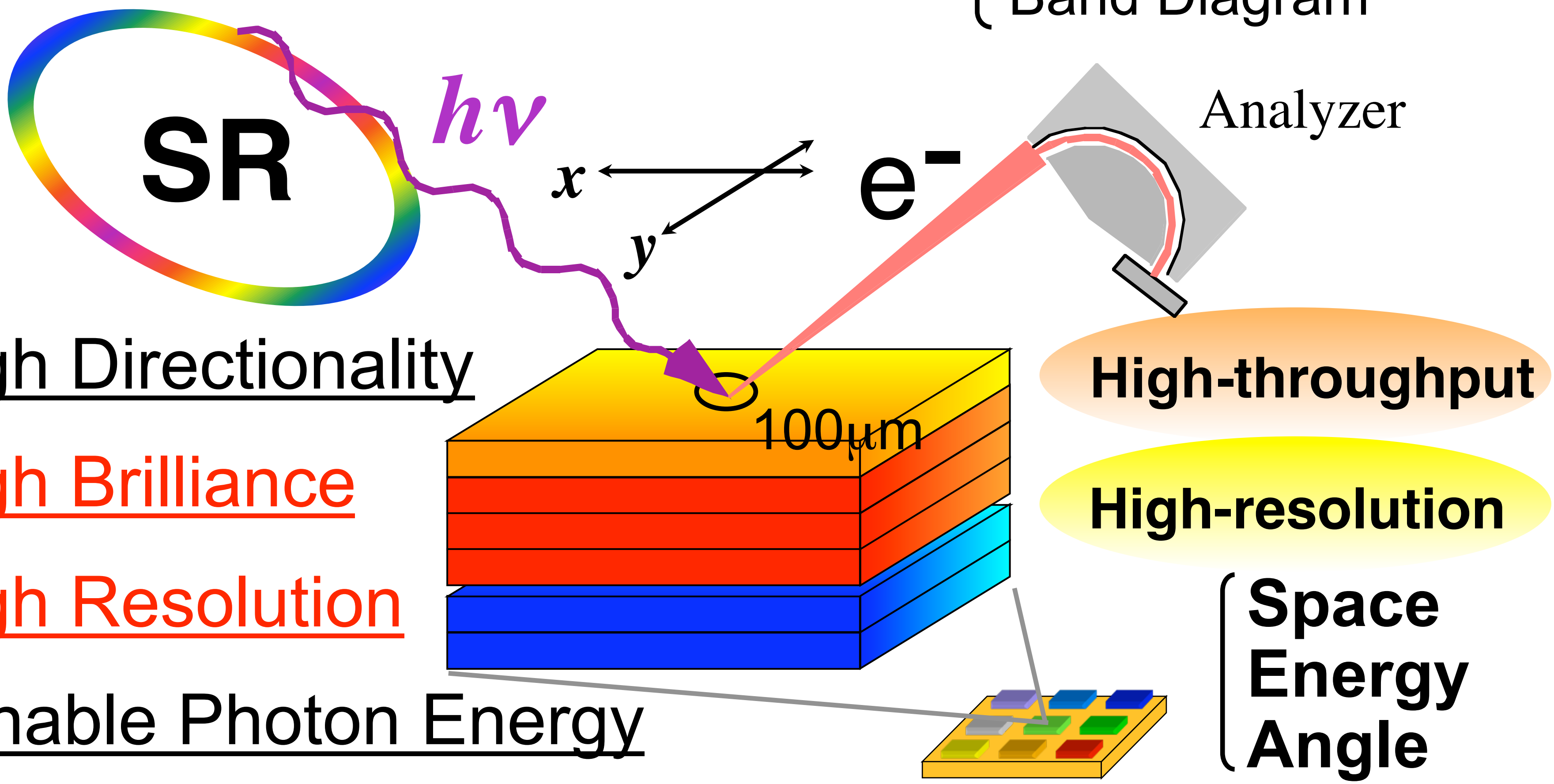


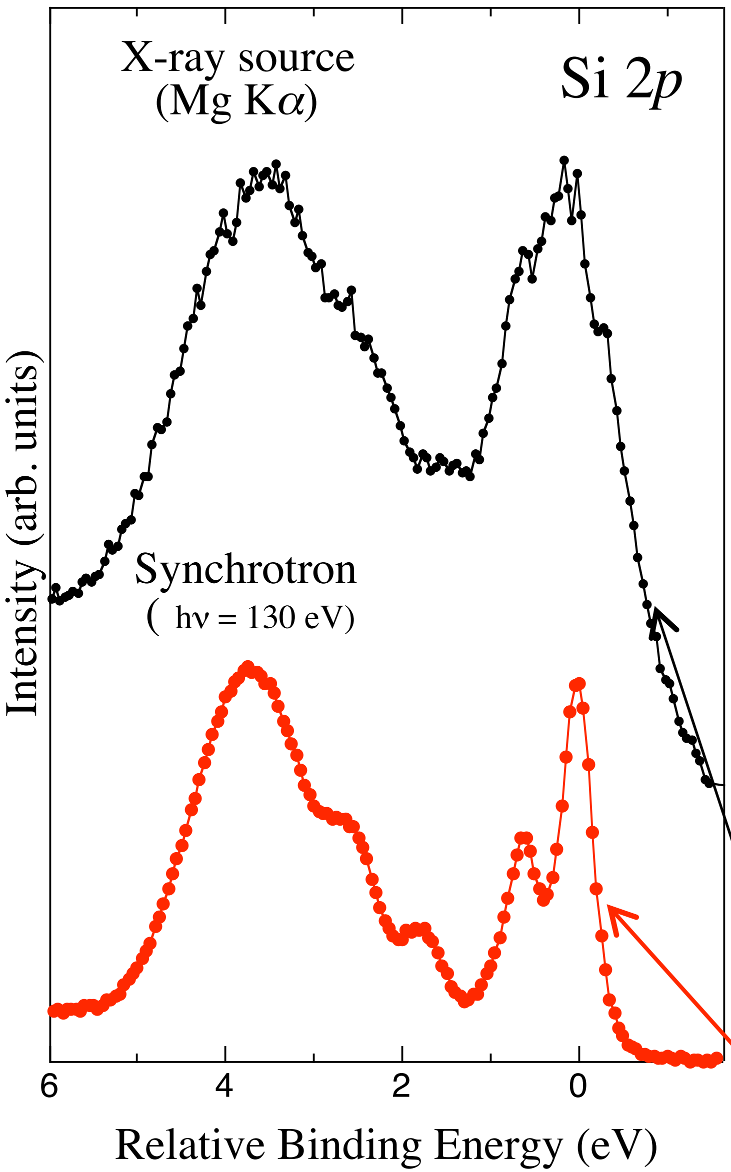
High Directionality

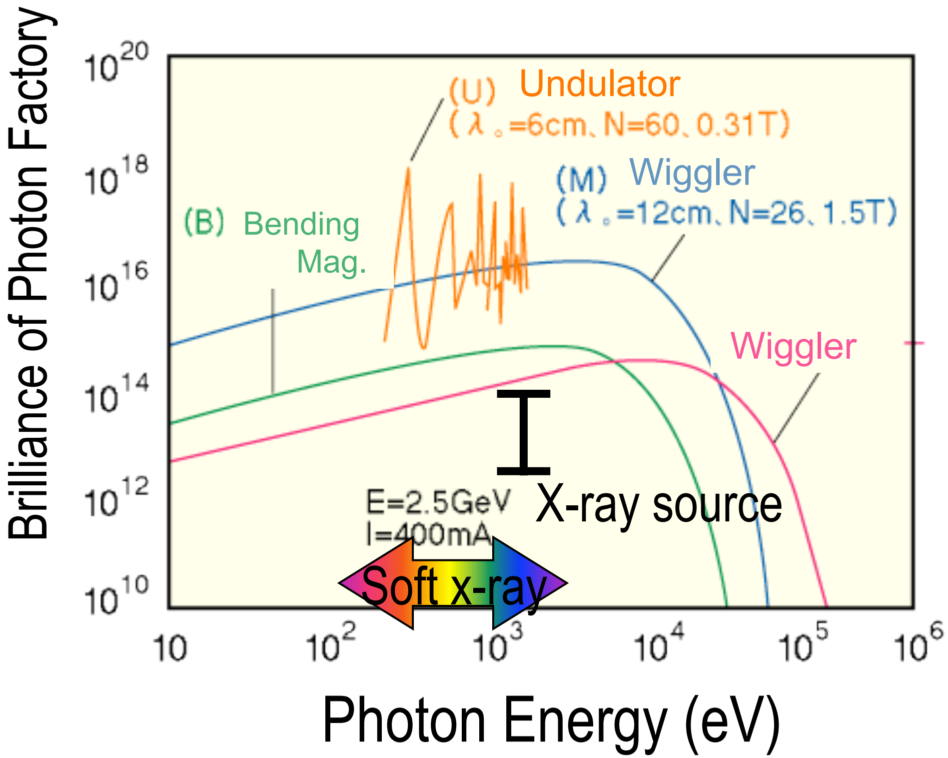
High Brilliance

High Resolution

Tunable Photon Energy

High brilliance and resolution: High-throughput and precise characterization

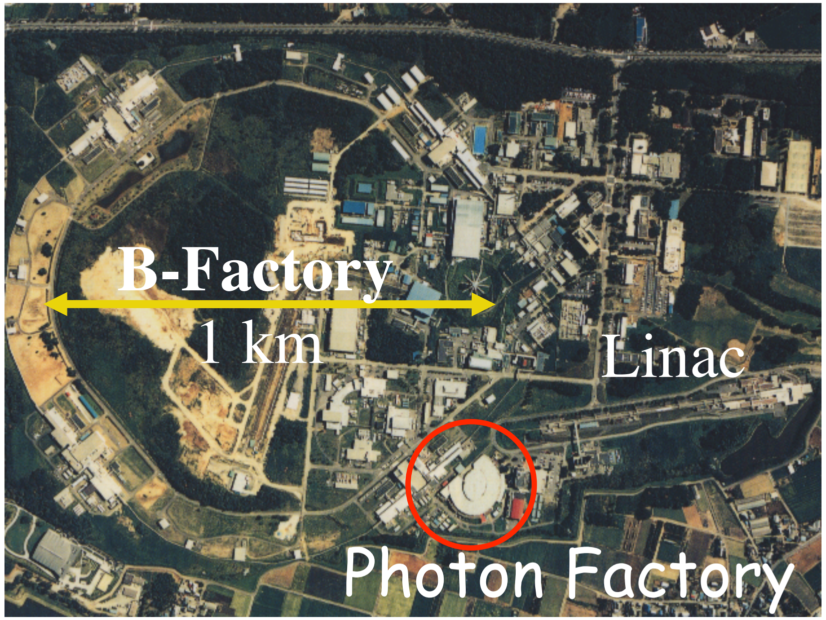




	Resolution	Acquisition Time
X-ray (Lab.)	1.0 eV	100 min
SR	0.1 eV	1 min

Application to the high-throughput characterization for devices

SPring-8

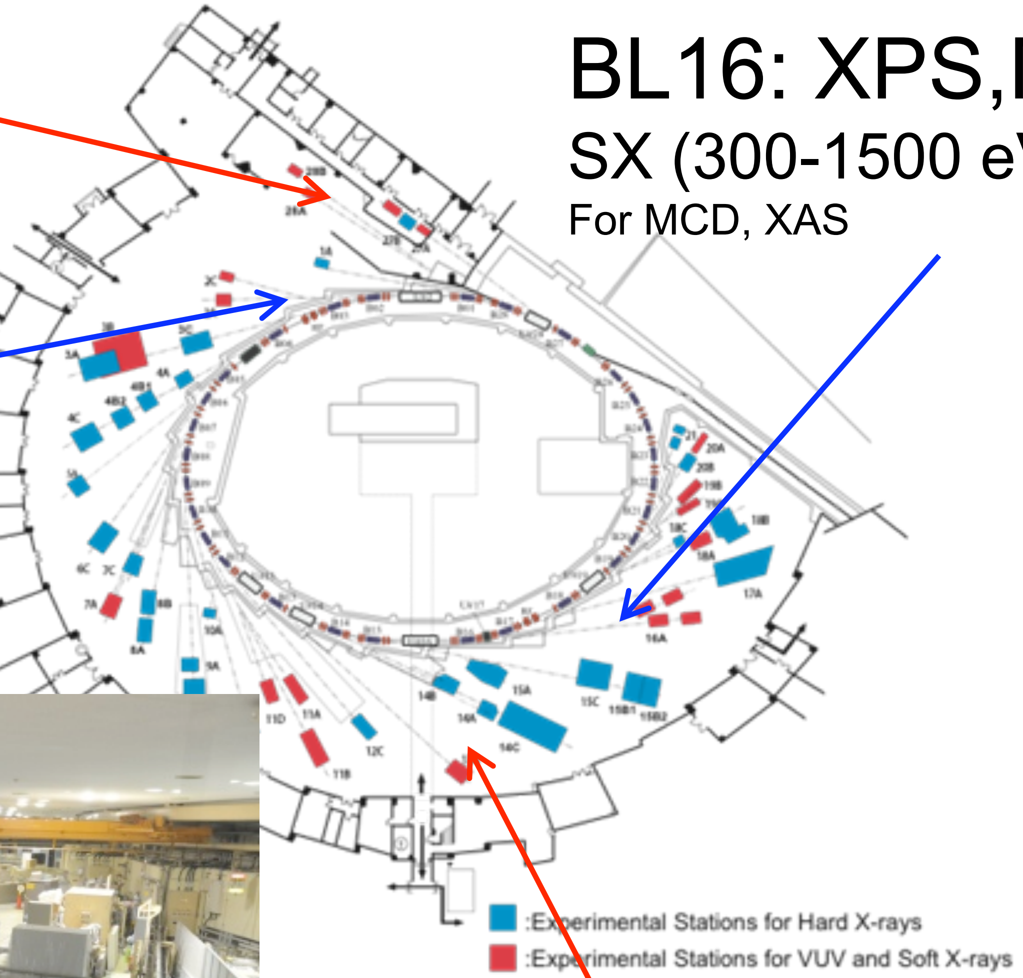


SR facilities (SX region) in Japan

PF Ring& Beam Lines for VUV-SX

BL28: UPS
VUV (30-300 eV)
For High-resolution PES&ARPES

BL16: XPS,MCD
SX (300-1500 eV)
For MCD, XAS



BL2C: XPS, XAS
SX (300-1500 eV)
For High-resolution XPS


Picture inside of PF

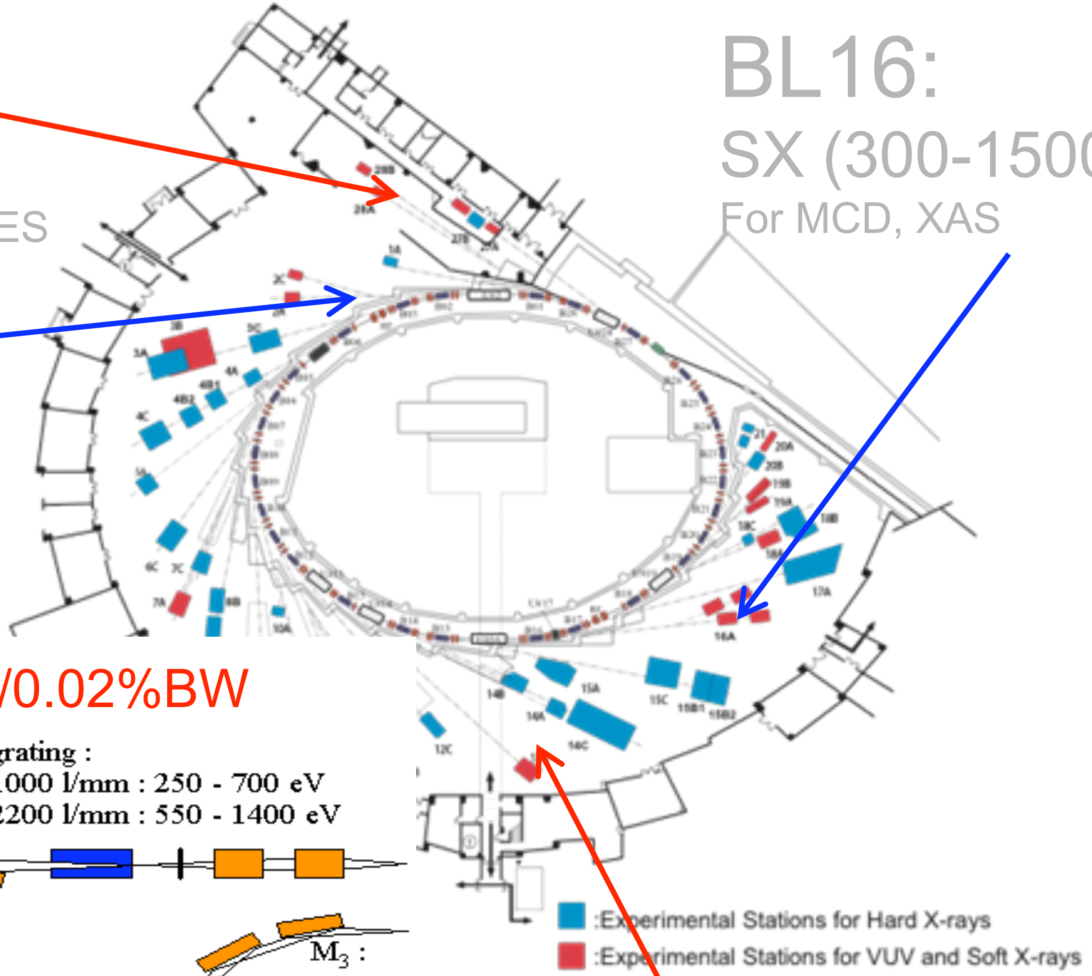
BL13: UPS
VUV (50-1000 eV)
For High-resolution PES&ARPES

Beam Line 2C: For High-resolution XPS

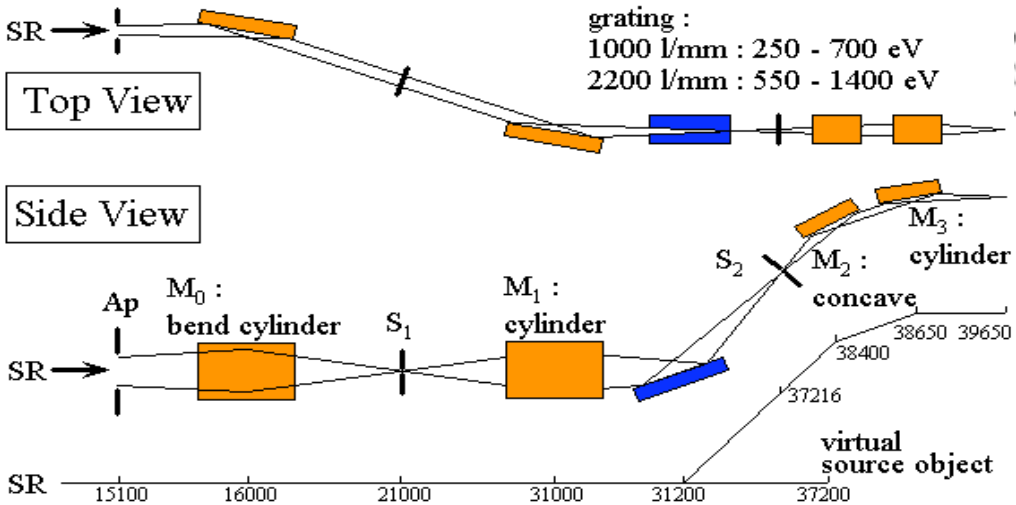
BL28:
VUV (30-300 eV)
For High-resolution PES&ARPES

BL16:
SX (300-1500 eV)
For MCD, XAS

BL2C:
SX (300-1500 eV)
For High-resolution XPS



E/ΔE ≦ ～ 10000
10^9 ～ 10^{10} photons /sec/0.02%BW



BL13:
VUV (50-1000 eV)
For High-resolution PES&ARPES

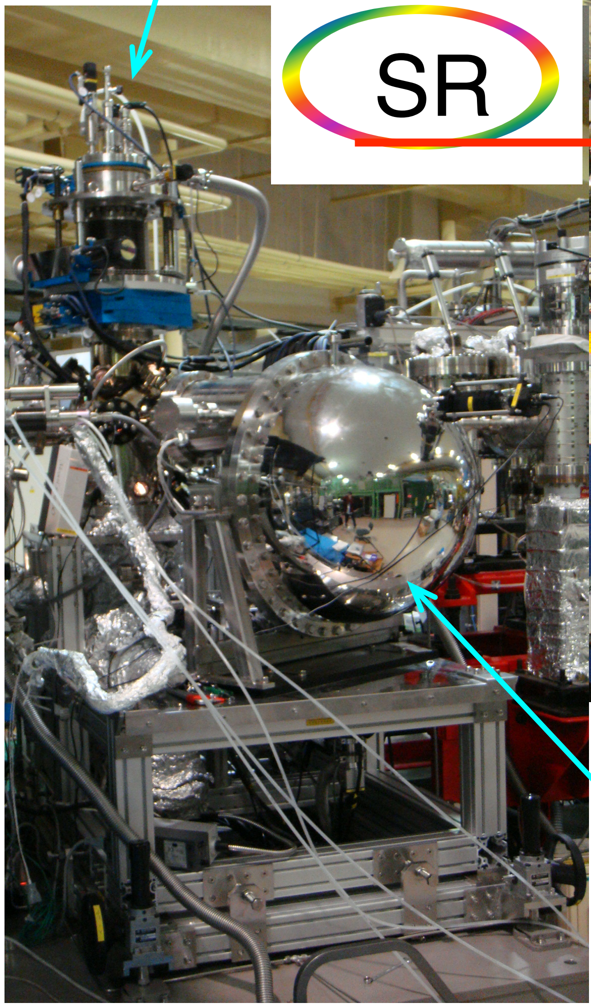
New in-situ PES + Laser MBE system

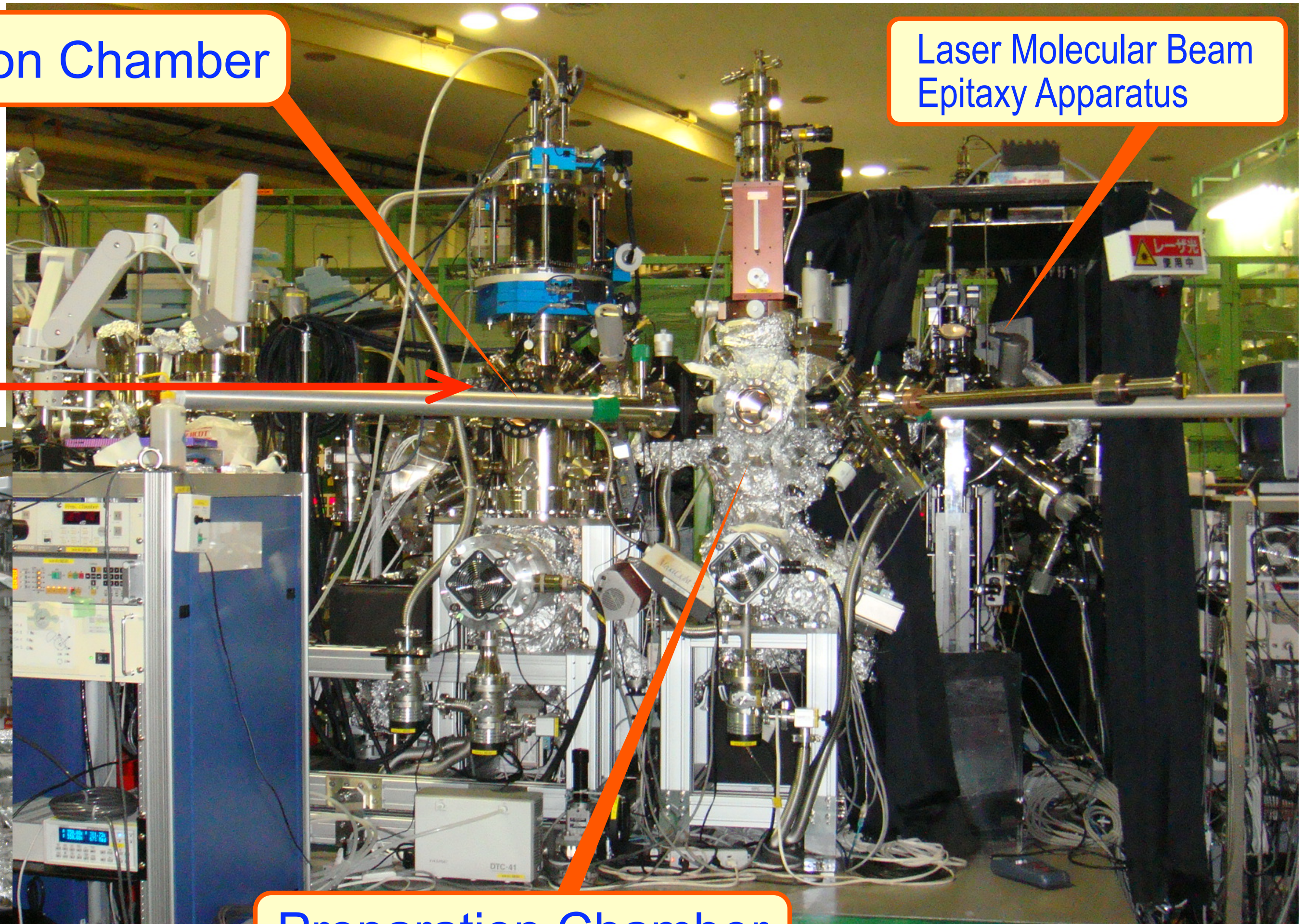
Photoemission Chamber

Laser Molecular Beam Epitaxy Apparatus

Manipulator (two-axial rotating stage)

SR





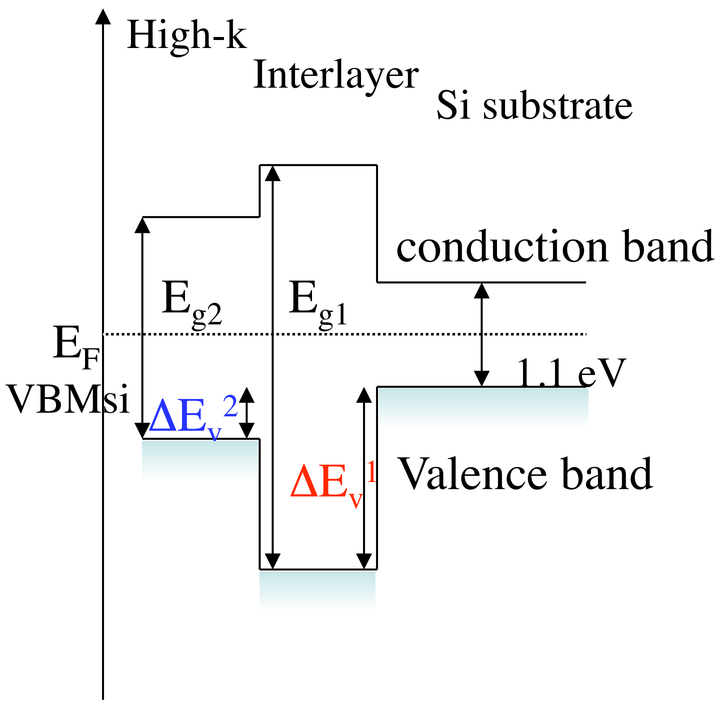
Preparation Chamber

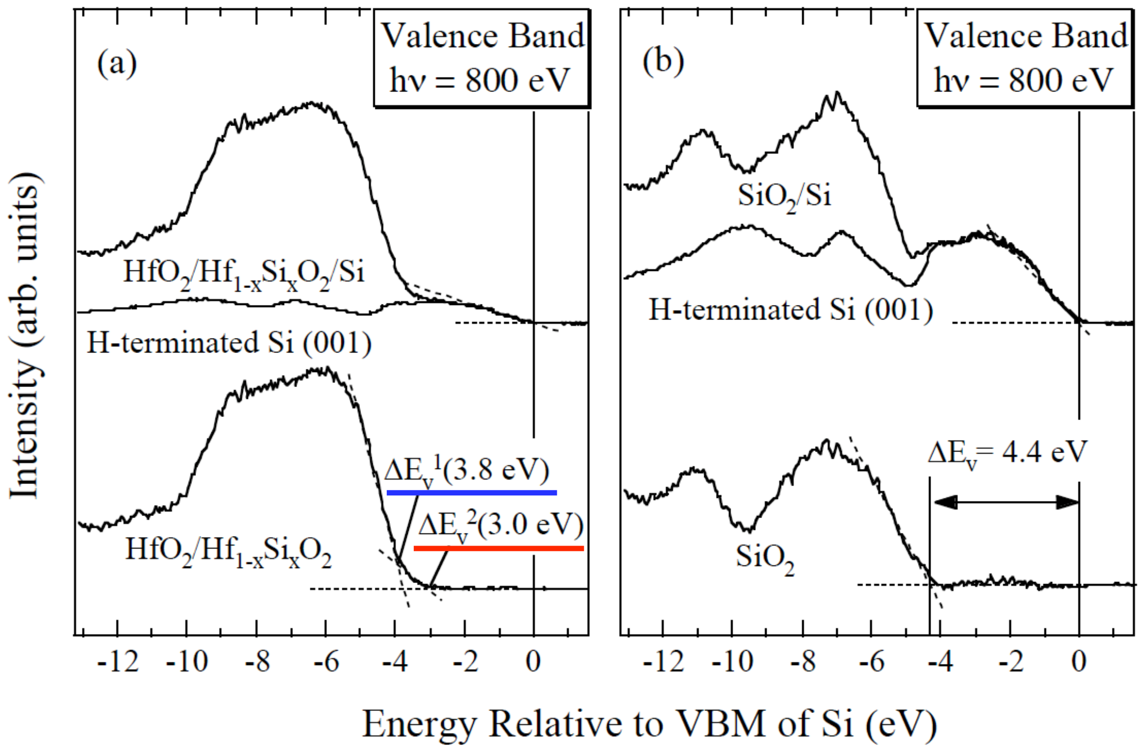
@KEK-PF BL-2C

High resolution photoemission analyzer
VG-Scineta SES2002

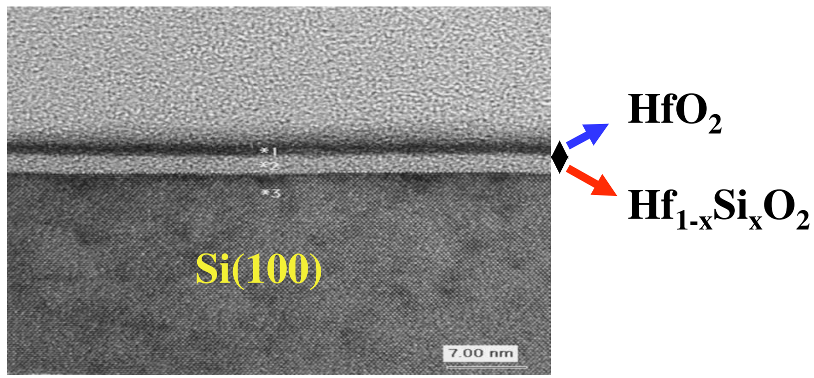
Energy-band offsets in high-k materials

Band diagram



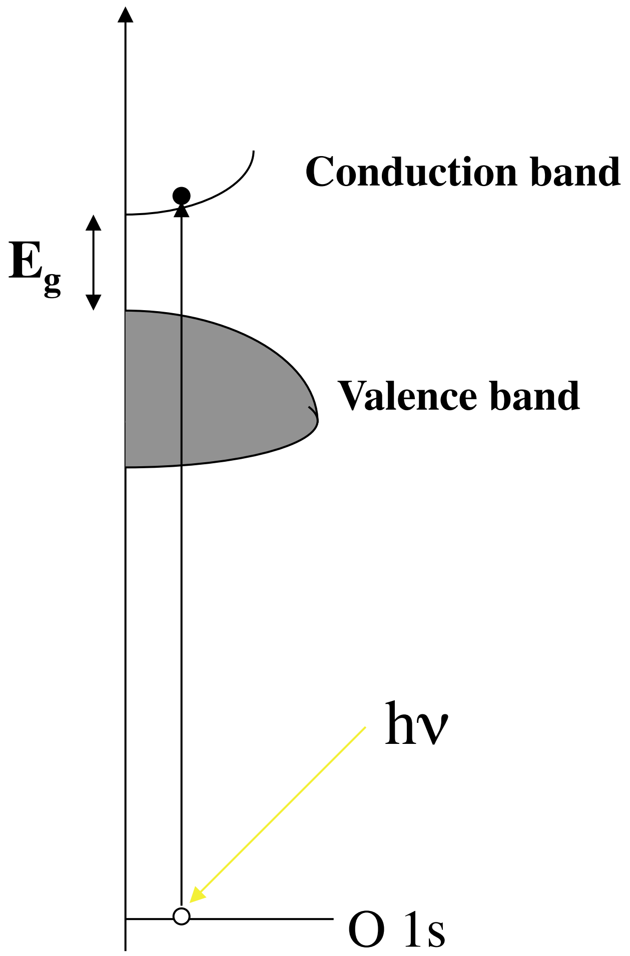


Determination of the band diagram of multilayer structures



Evaluation of the valence band maximum by photoemission

X-ray absorption spectroscopy (XAS)

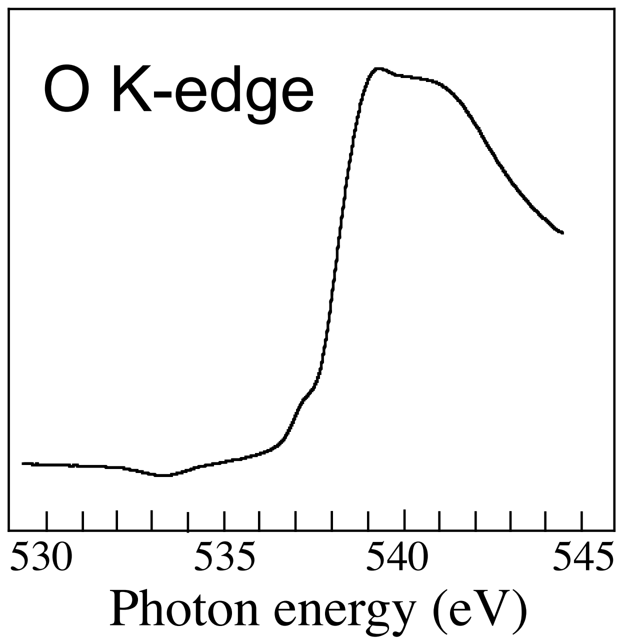


XAS;

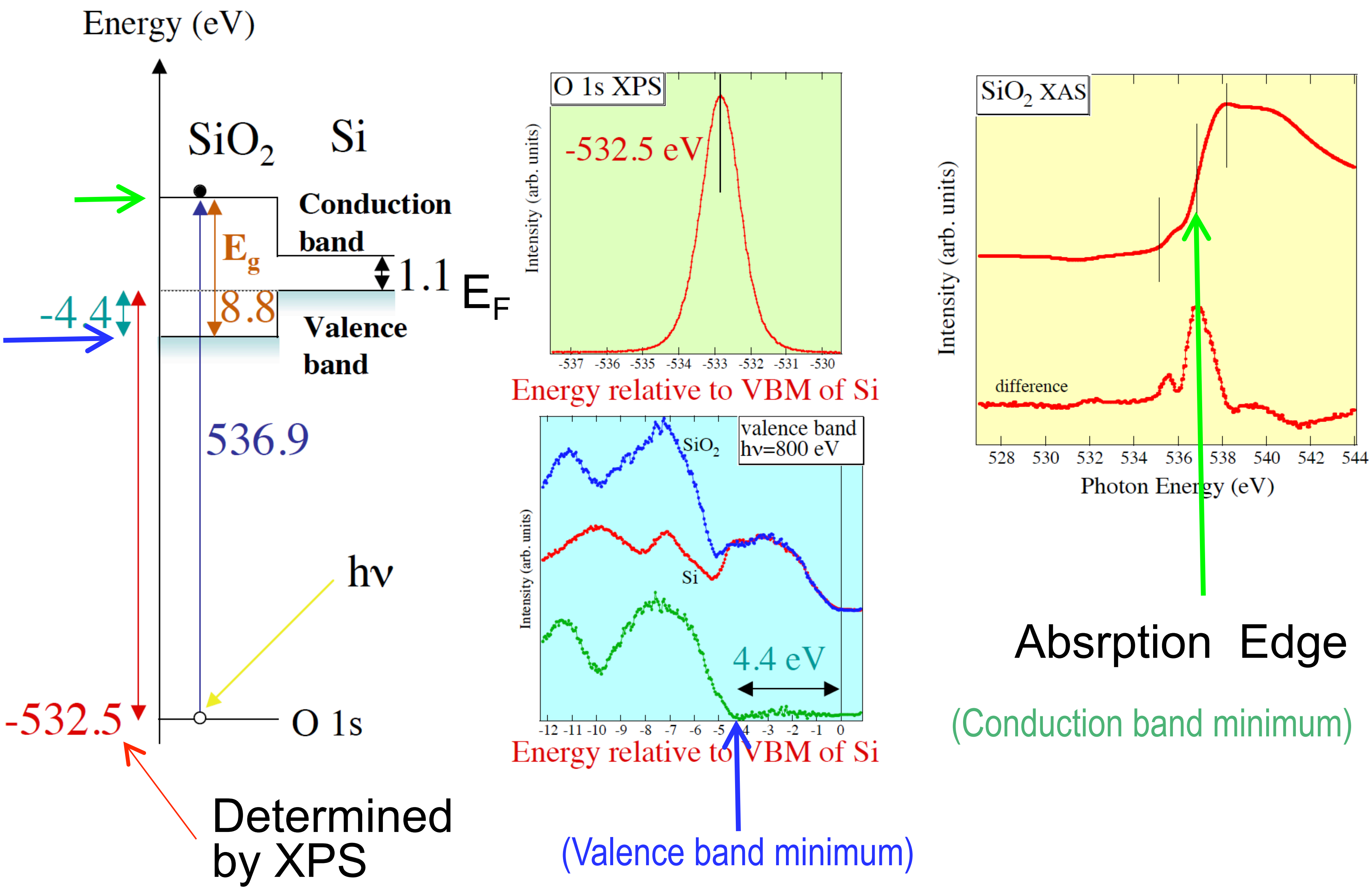
Measure the sample current (intensity of emitted electrons) by changing the photon energy.

Information of conduction band

Tunable Photon Energy provided from SR

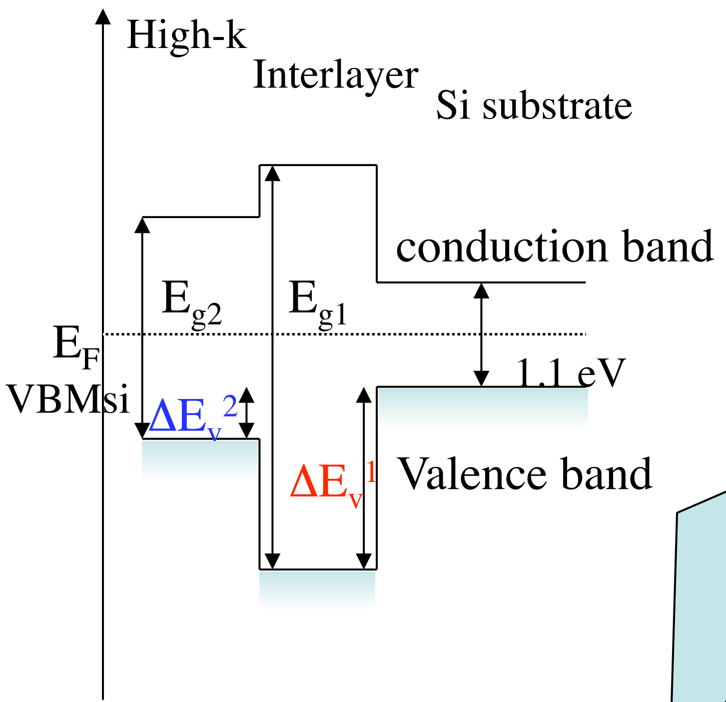


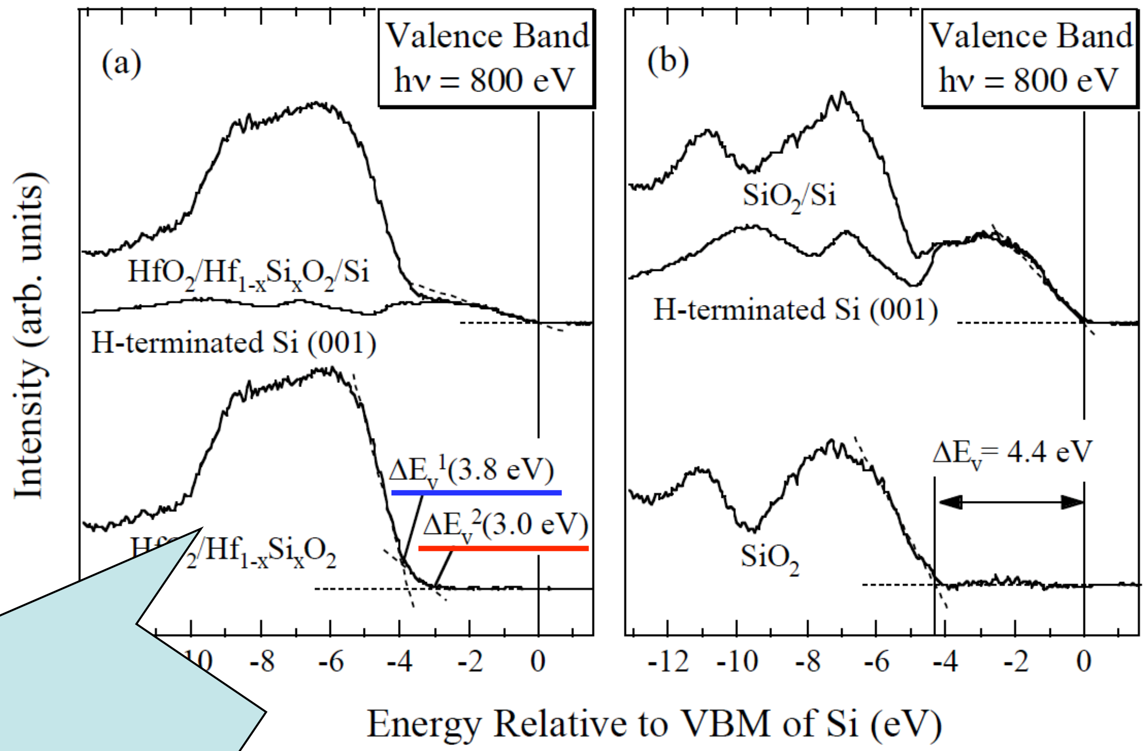
X-ray absorption spectroscopy (XAS)



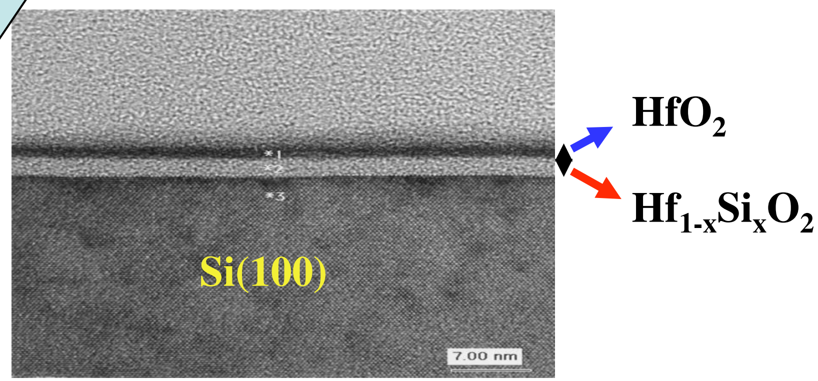
Energy-band offsets in high-k materials

Band diagram





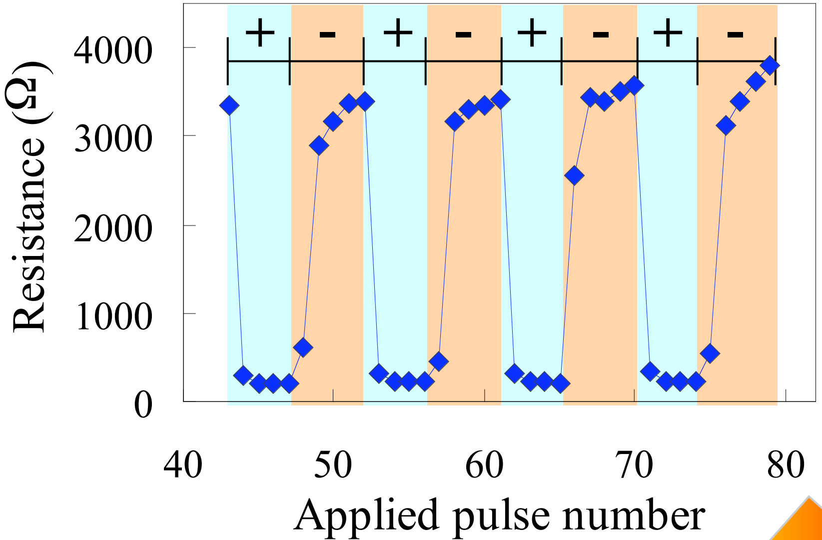
Determination of the band diagram of multilayer structures



Evaluation of the valence band maximum by photoemission

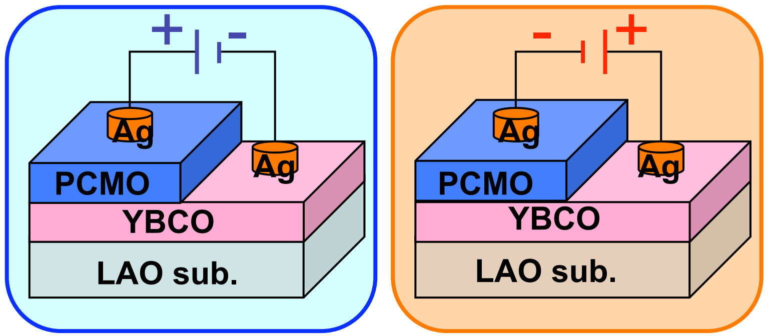
Resistance Changes by Application of Pulse Volatage

Resistance switching behavior in metal/oxide/metal structures



Two stable resistance states

S. Q. Liu *et al*., *Appl. Phys. Lett.* **76**, 2749 (2000).

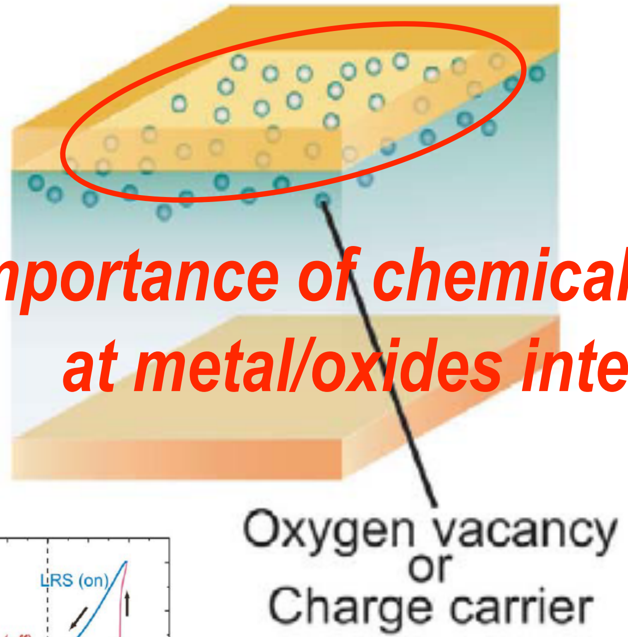


Resistance Random Access Memory (ReRAM)

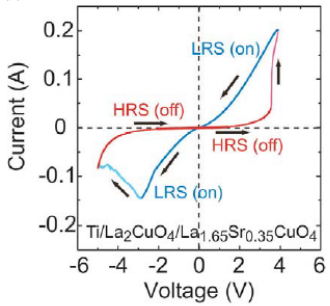
While various RS mechanisms have been proposed, the mechanism have not been fully understood yet.

Possible Mechanism for ReRAM

Interface type

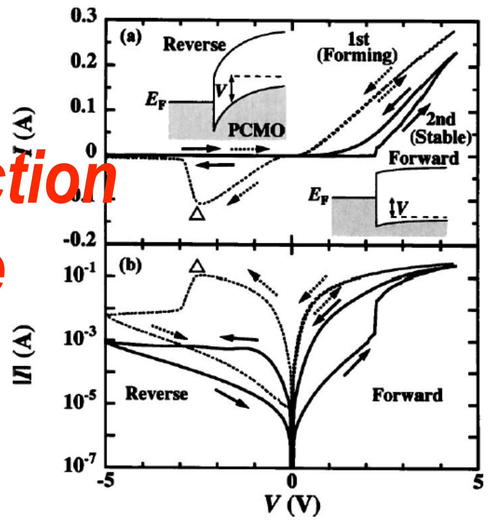


Importance of chemical reaction at metal/oxides interface



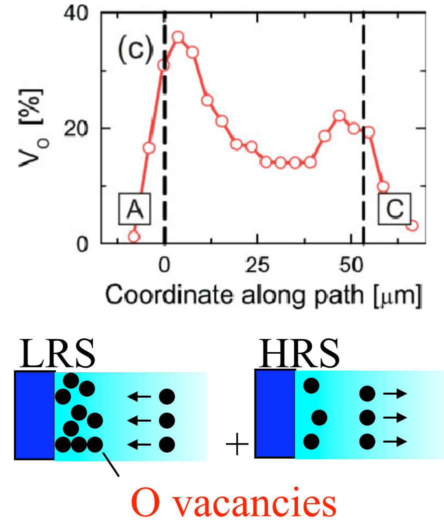
Bipolar switching

Modulation of Schottoky Barrier height



A. Sawa *et al.*, *Appl. Phys. Lett.* **85**, 4073 (2004).

Change in conductivity due to oxygen deficient

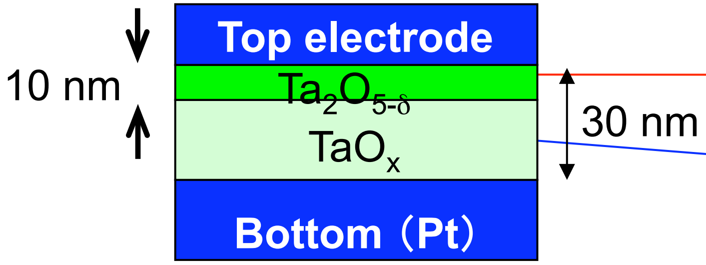


M. Janousch *et al.*, *Adv. Mater.* **19**, 2232 (2007).

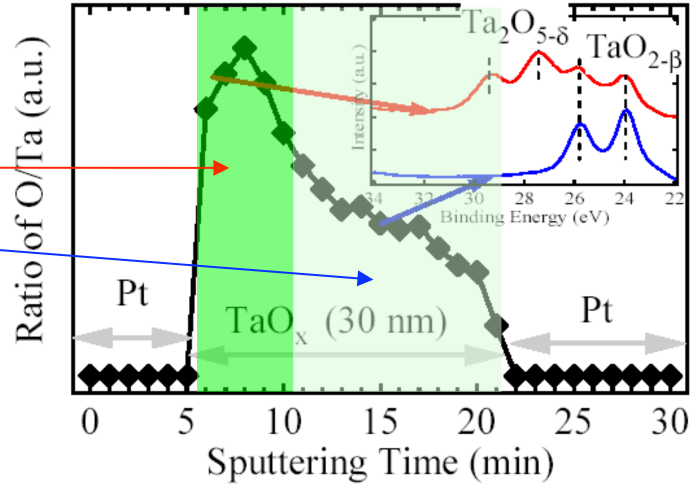
Chemical states at the interface → **Photoemission spectroscopy**

Characteristics of $Pt/Ta_2O_{5-d}/TaO_x$ ReRAM Device

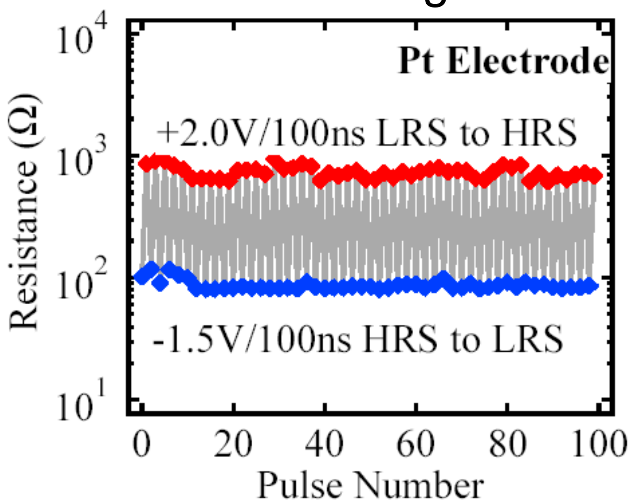
Device structures



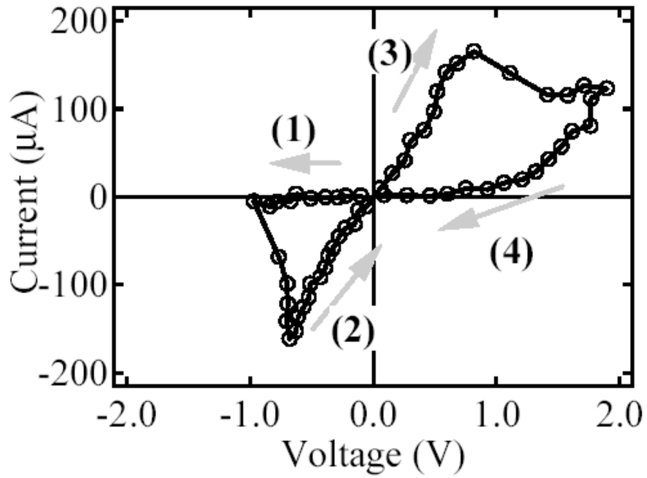
Depth profiling for Ta/O composition (Ar sputtering)



Resistance switching behabior



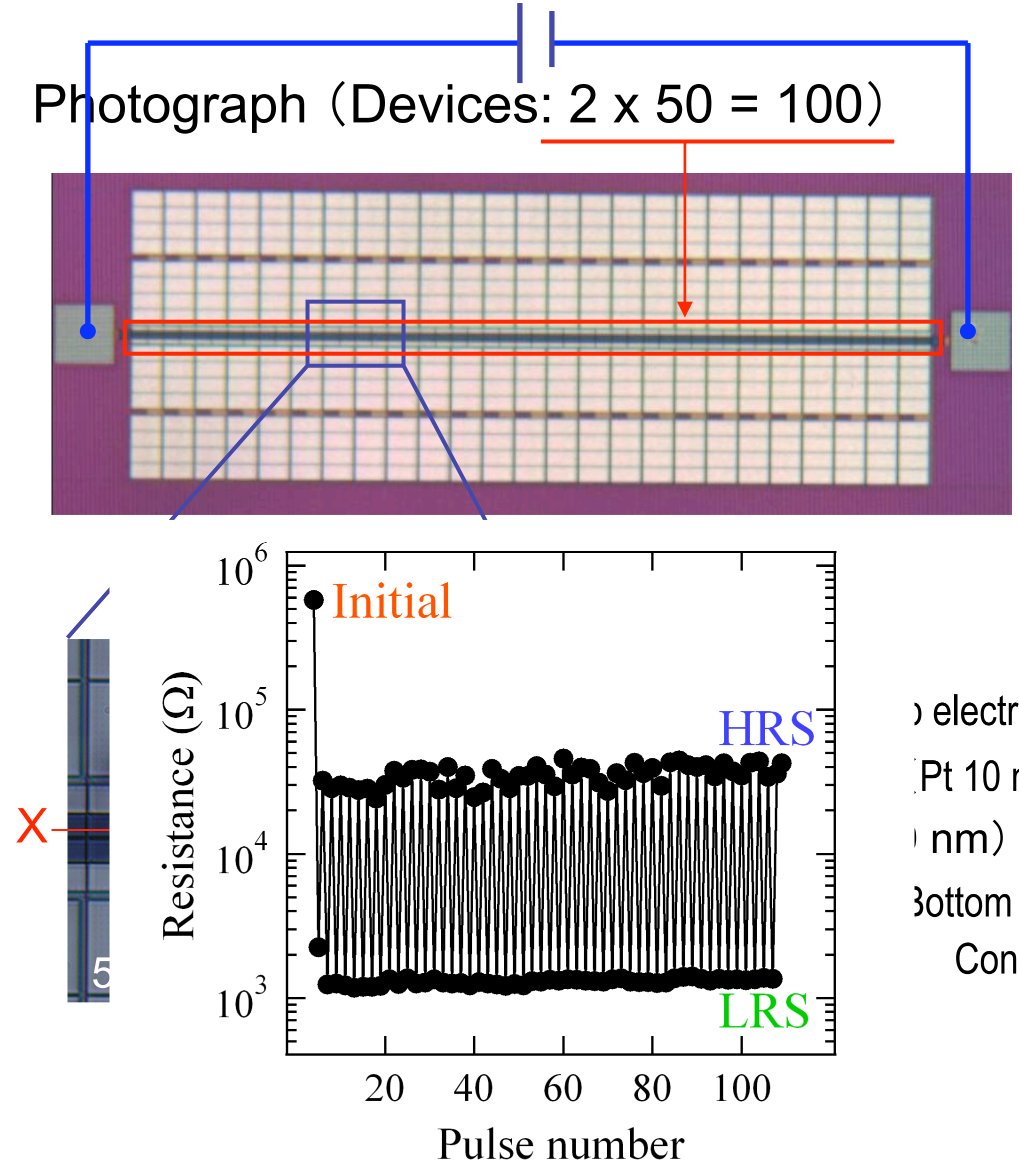
IV characteristics

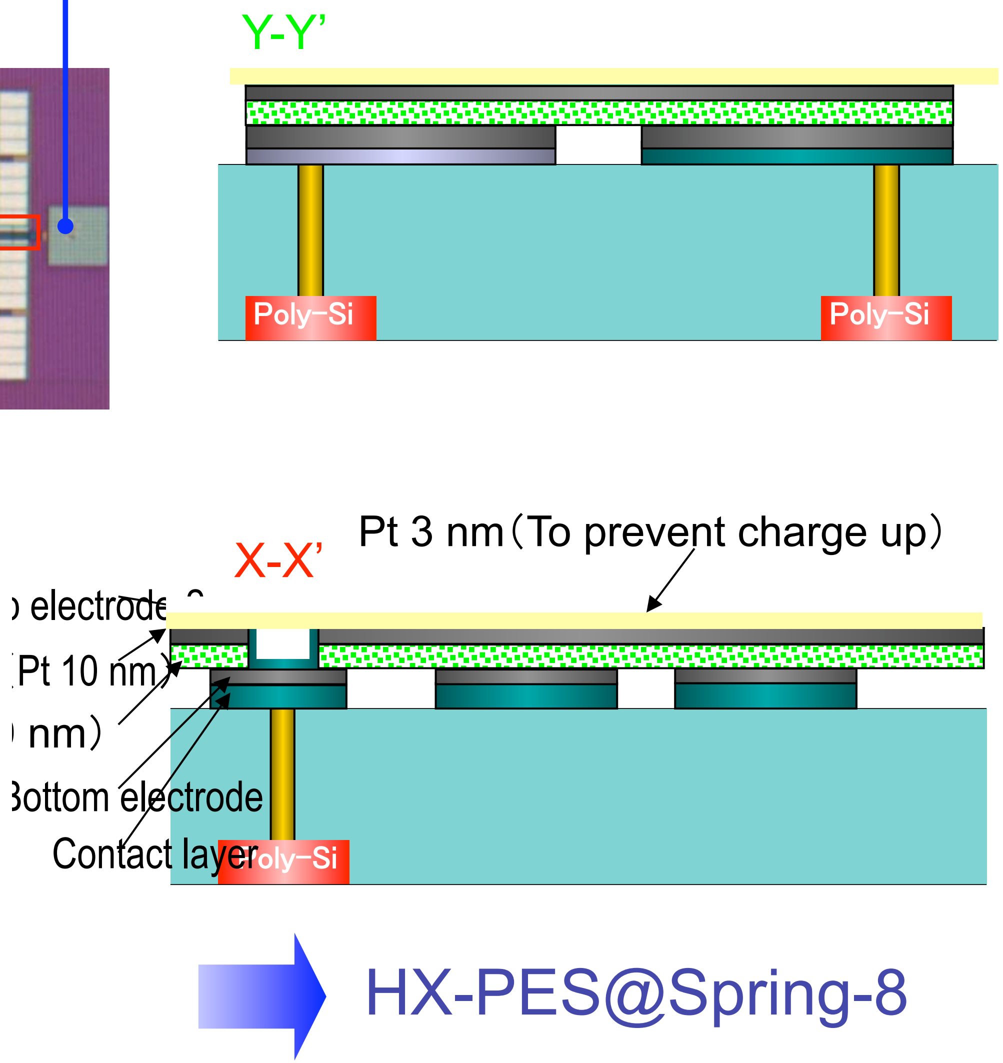


Bi-polar type resistance switching

Z. Wei *et al*., *IEDM Tech. Dig*. 293-296 (2008).

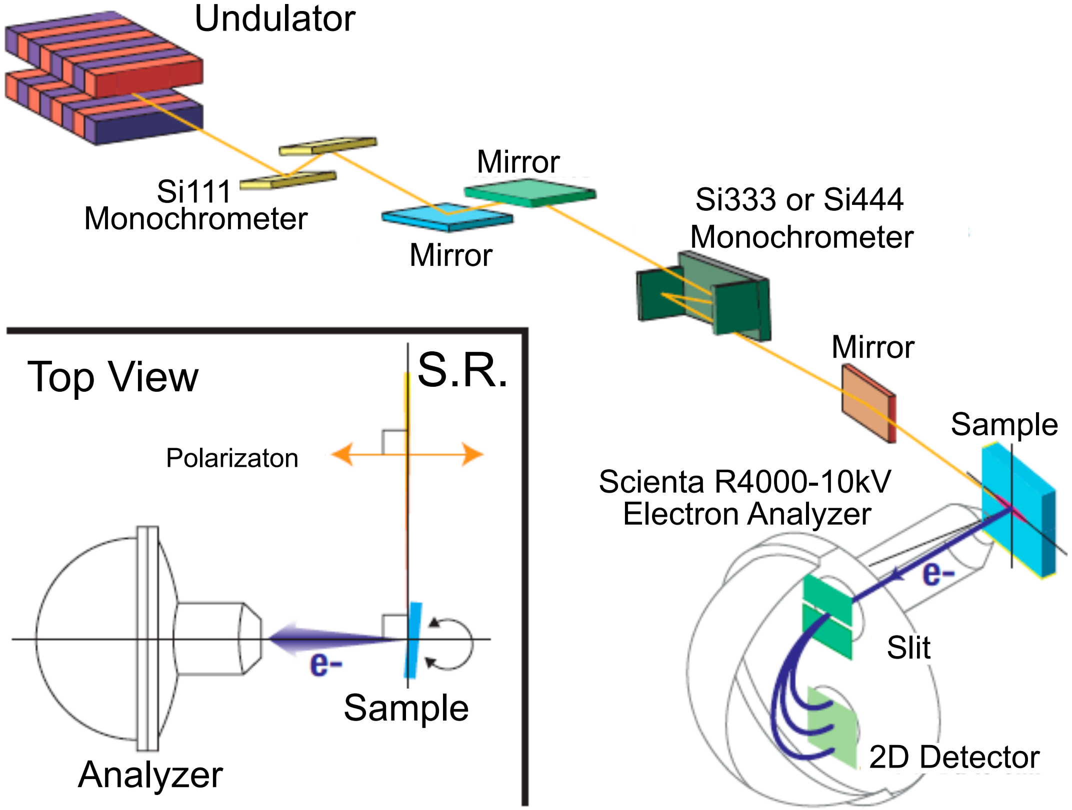
Device Structure for HXPES Measurements (Fablication Process)

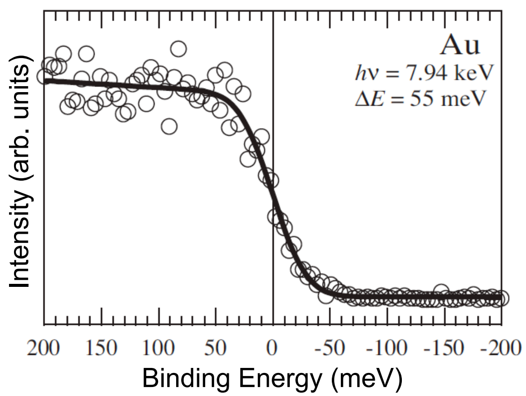


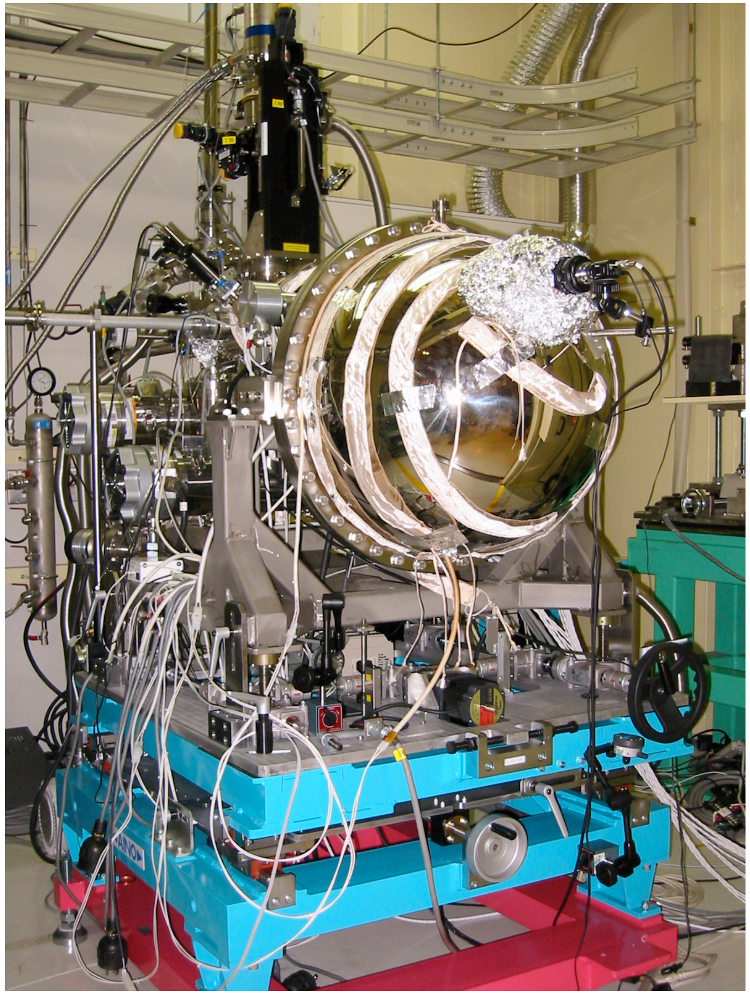


HX-PES@Spring-8

Hard X-Ray PES（BL47XU@SPring-8）

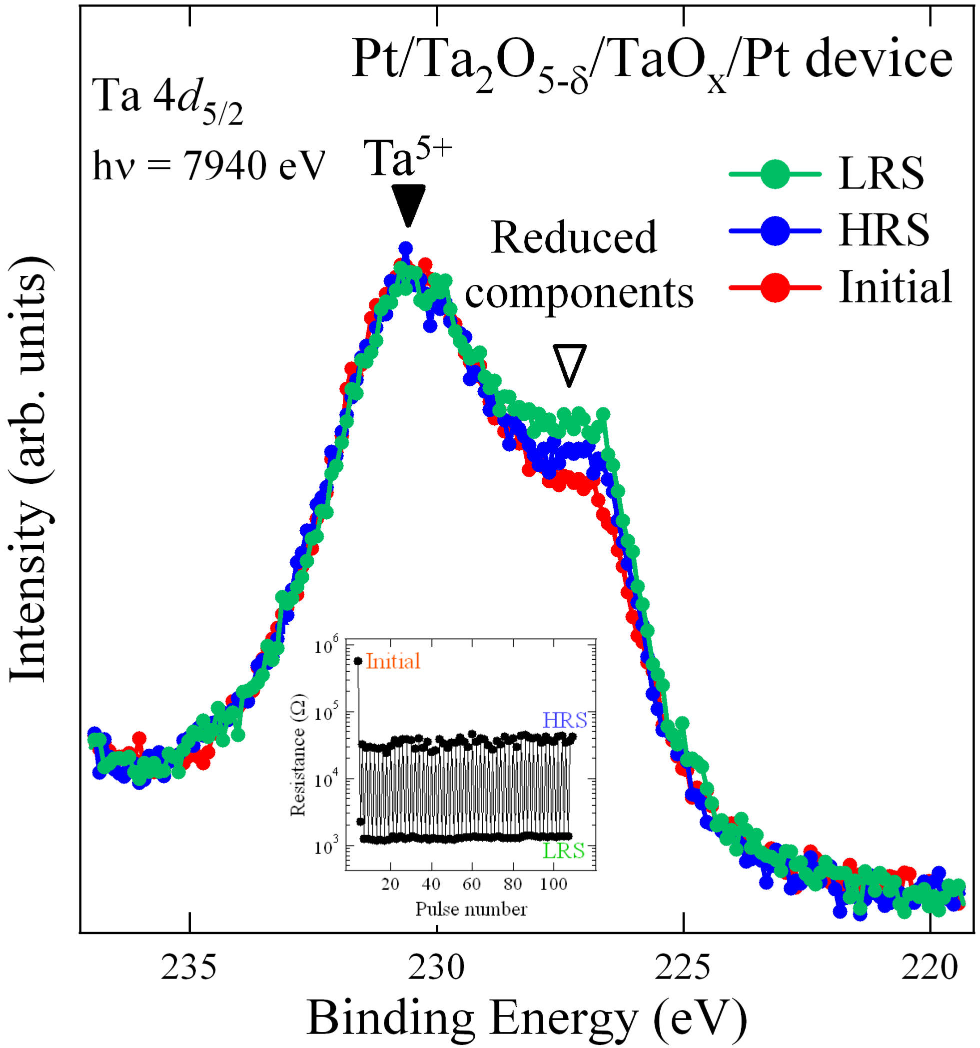


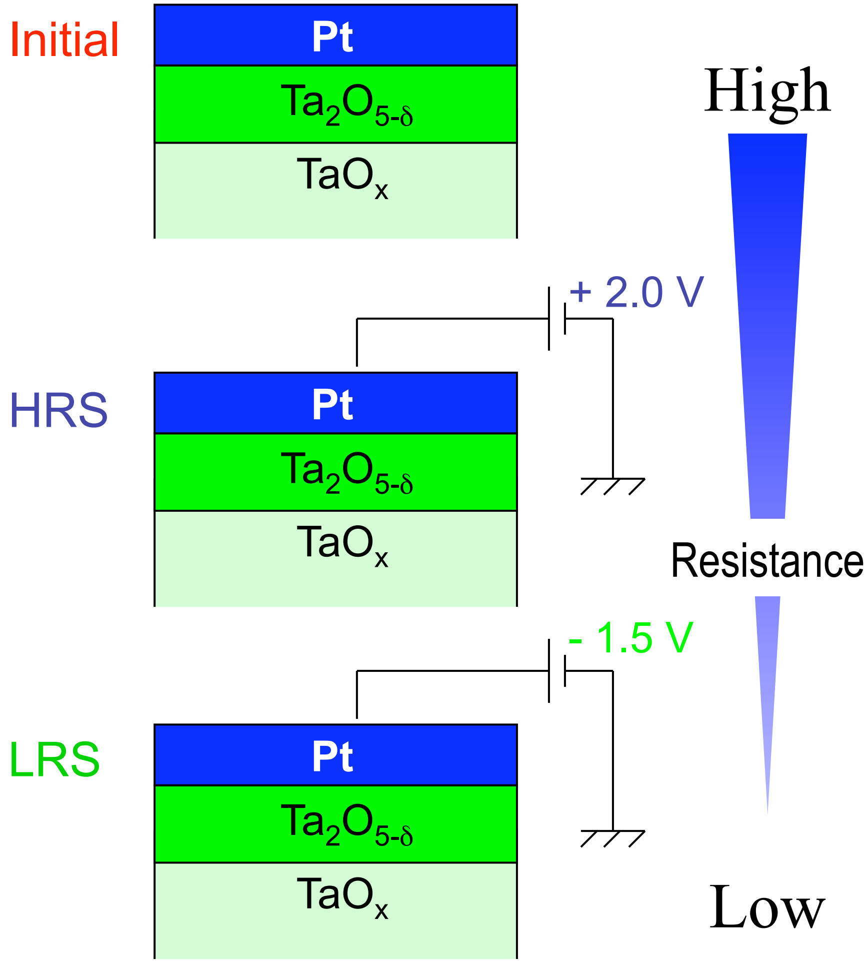




Photon Energy	**8 keV**
Energy Resolustion	**230 meV**

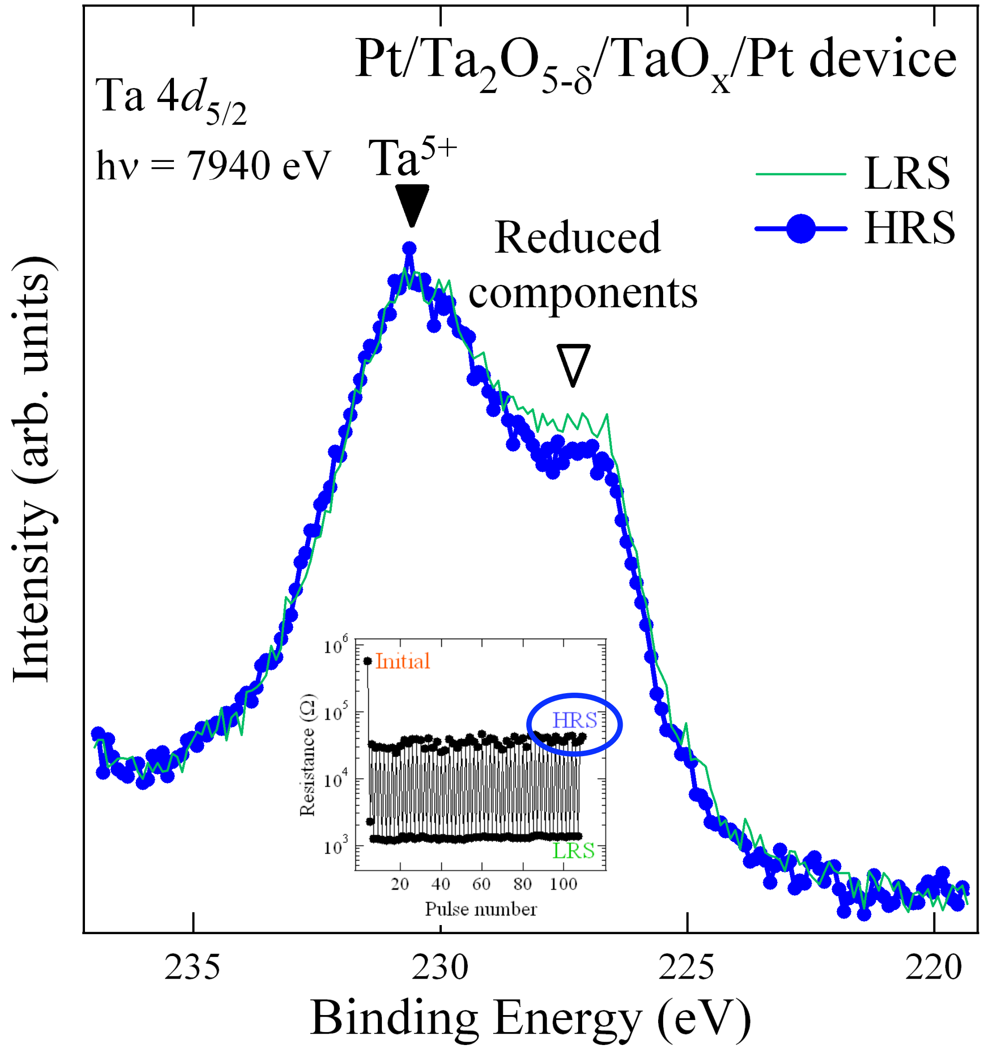
Change in Chemical States at On and Off States: Redox Reactions

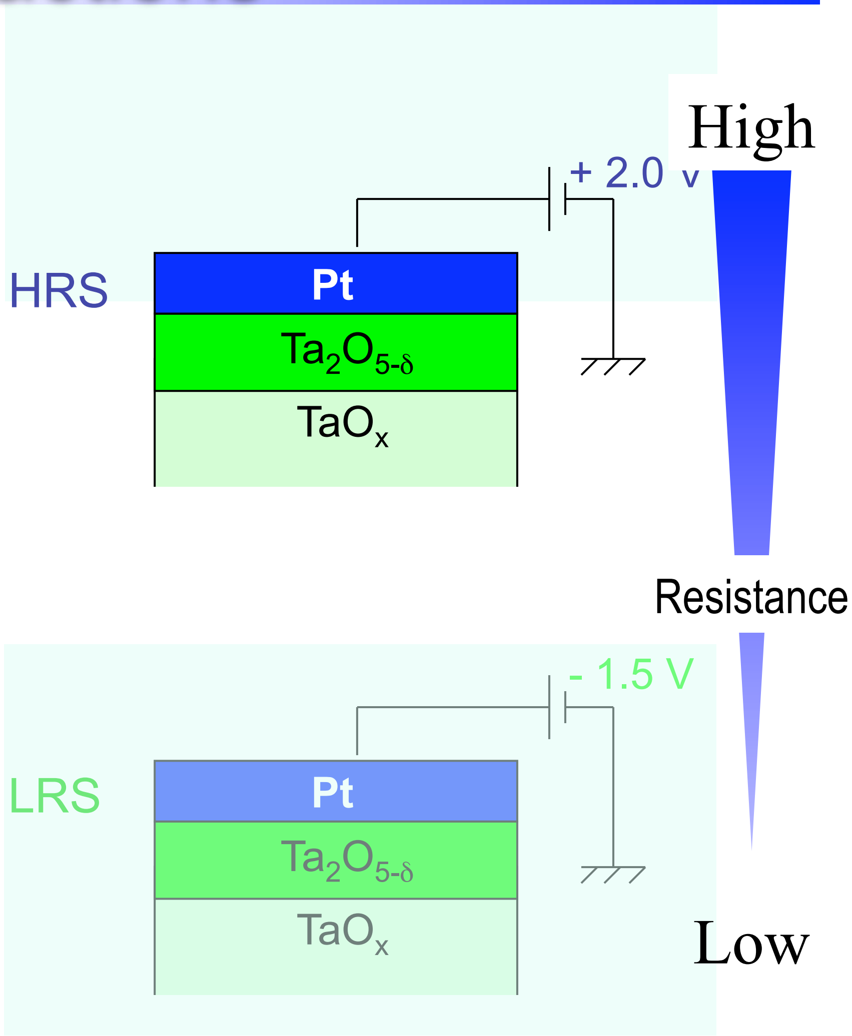




The intensity of reduced components changes with resistance switching.

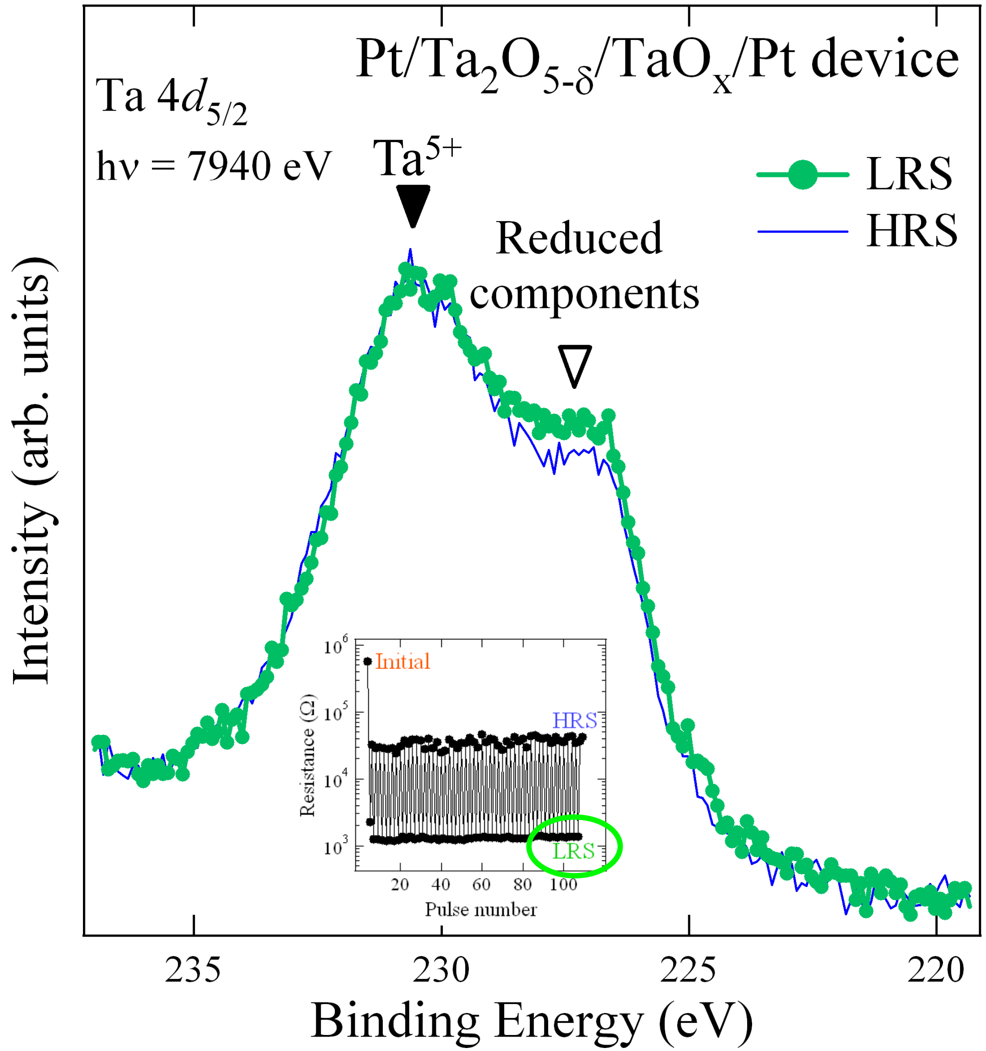
Change in Chemical States at On and Off States: Redox Reactions

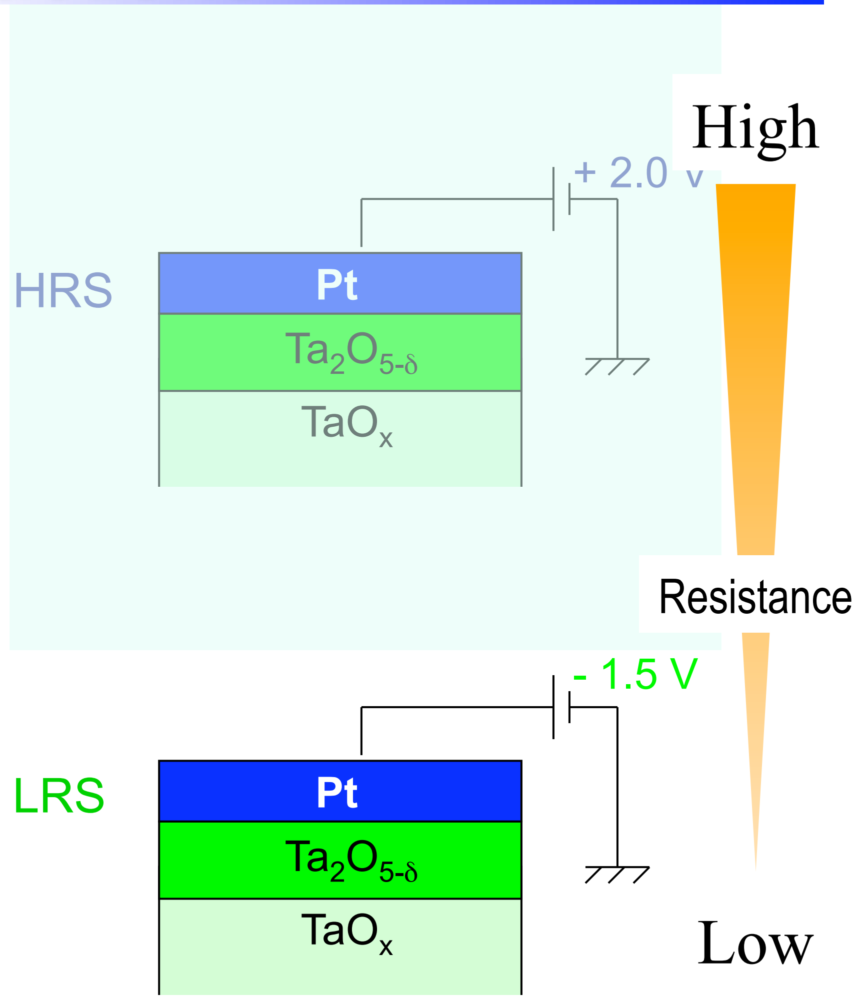




The intensity of reduced components changes with resistance switching.

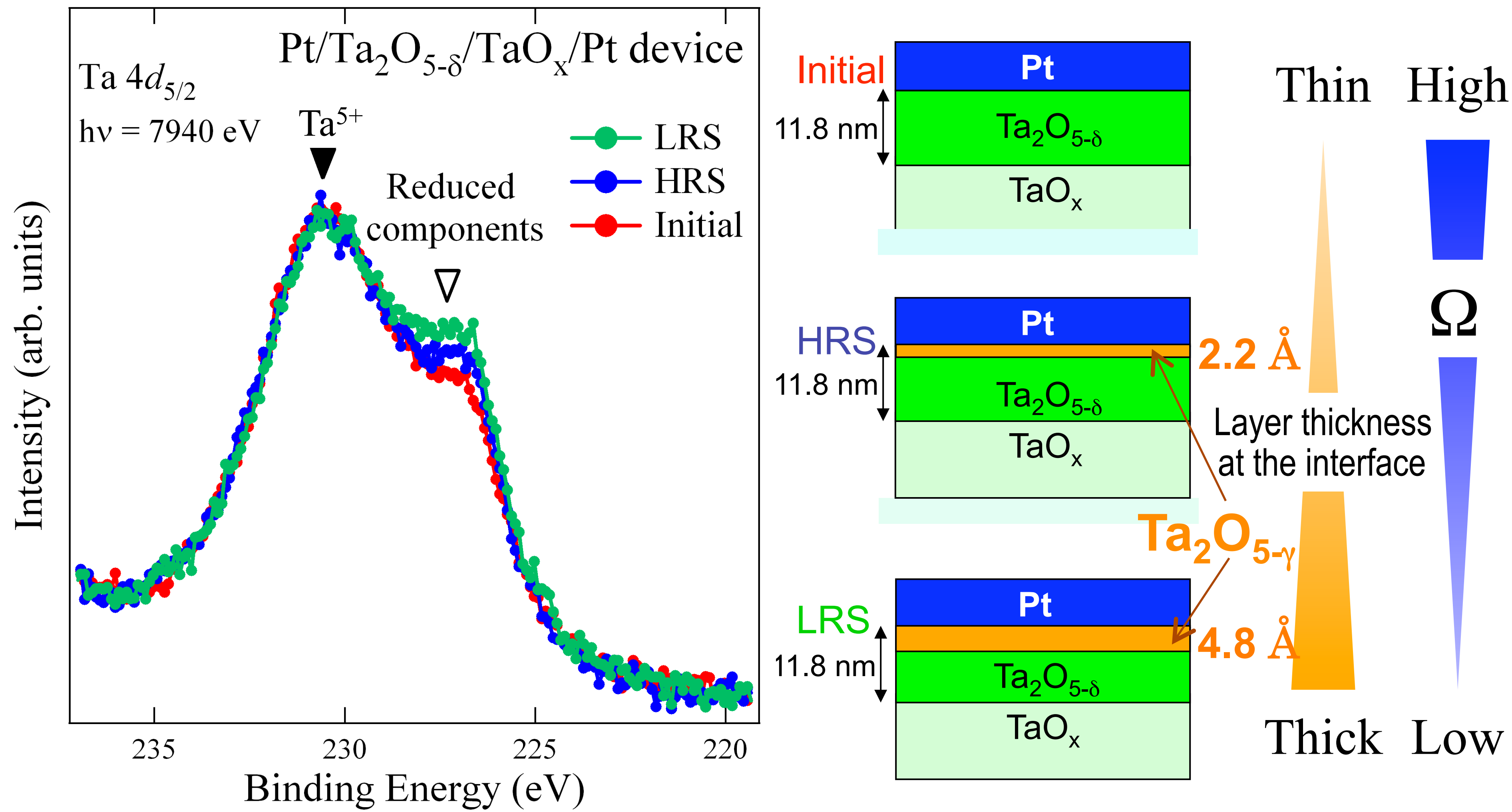
Change in Chemical States at On and Off States: Redox Reactions





The intensity of reduced components changes with resistance switching.

Chemical Changes of Ta_2O_{5-d} Asociated with Resistance Changes



Redox reaction at the interface induced by applicaton of pulse voltage is indispensable for ReRAM operation.

Summary

Photoemission spectroscopy combined with synchrotron radiation is powerful experimental technique to study the surface and interface electronic structures of devices.

Valence band spectra (X-ray absorption spectra)	Density of states Valence band maximum (Conduction band minimum)
Core level spectra	Chemical compositoin analysis Chemical state analysis

Direct observation of electronic structures.

"Simple is the best"