

Development of Laboratory HXPS system and Its Applications

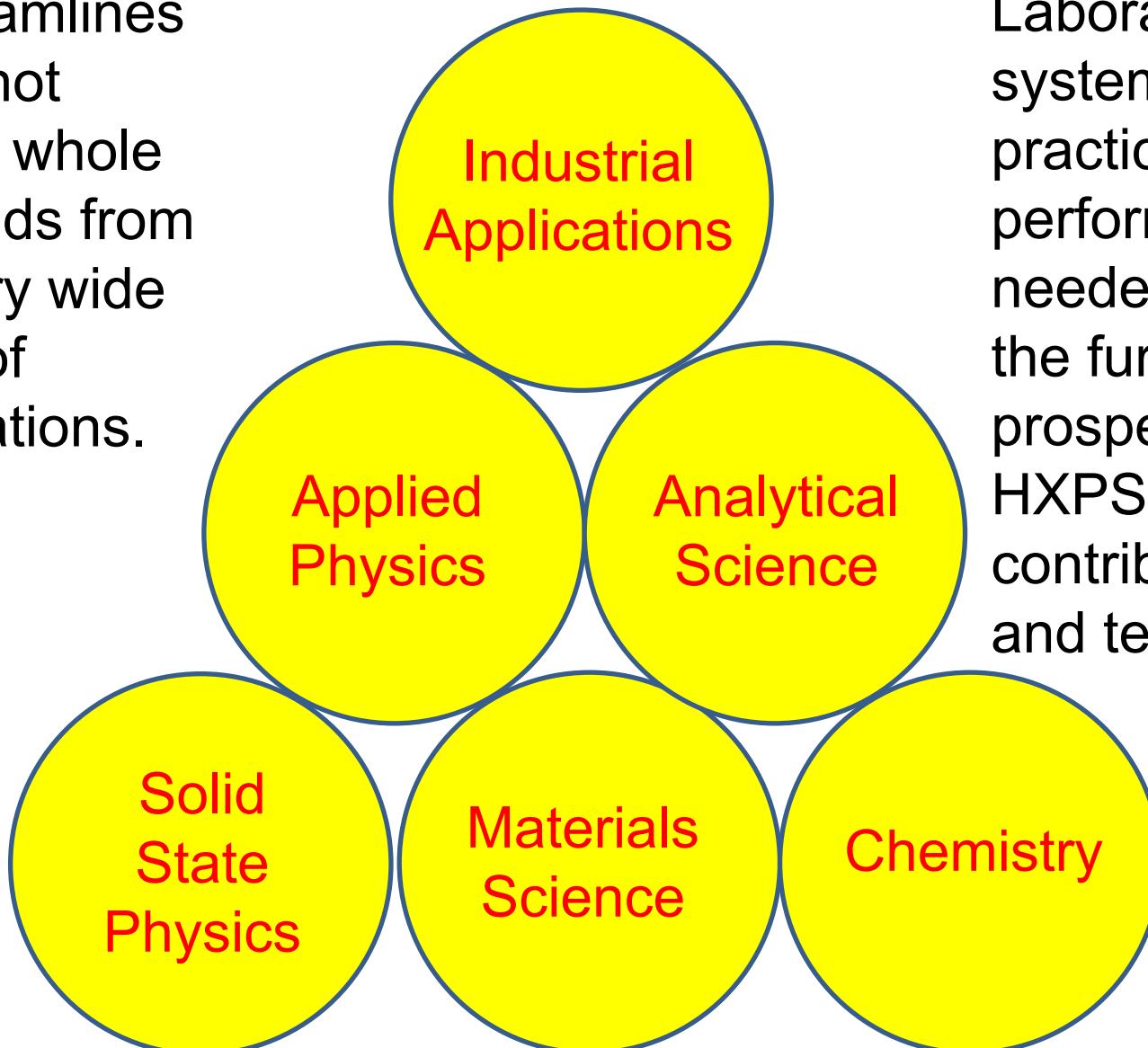
**High Energy Angle Resolved X-ray Photoelectron System for Laboratory Use
HEARP Lab**

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- 1) National Institute for Materials Science,
- 2) Synchrotron Radiation Center, Hiroshima university
- 3) Nara Advanced Institute of Science and technology
- 4) Ulvac Phy Corporation

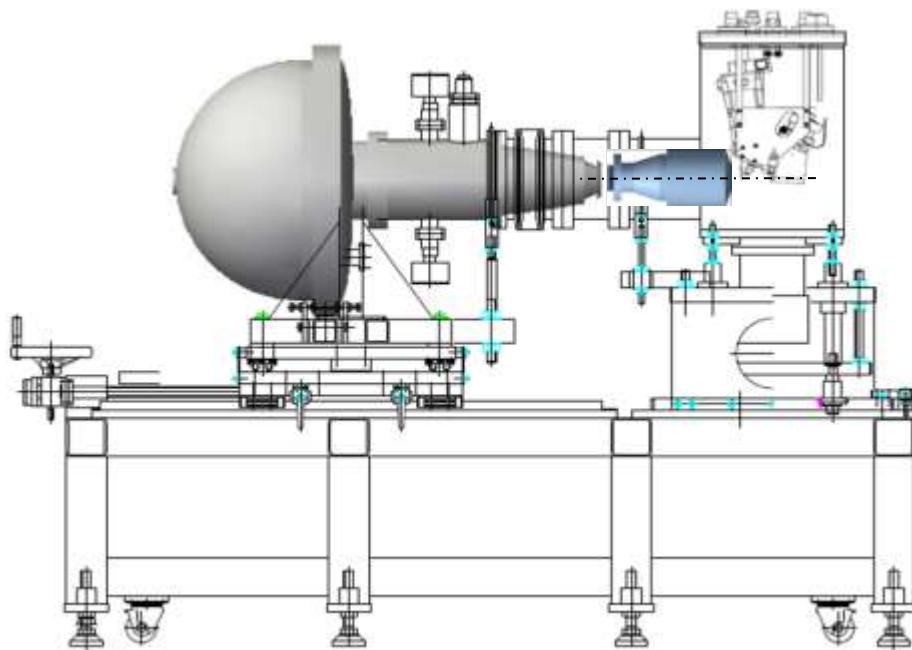
Application Field of HXPS

SR beamlines could not accept whole demands from the very wide fields of applications.

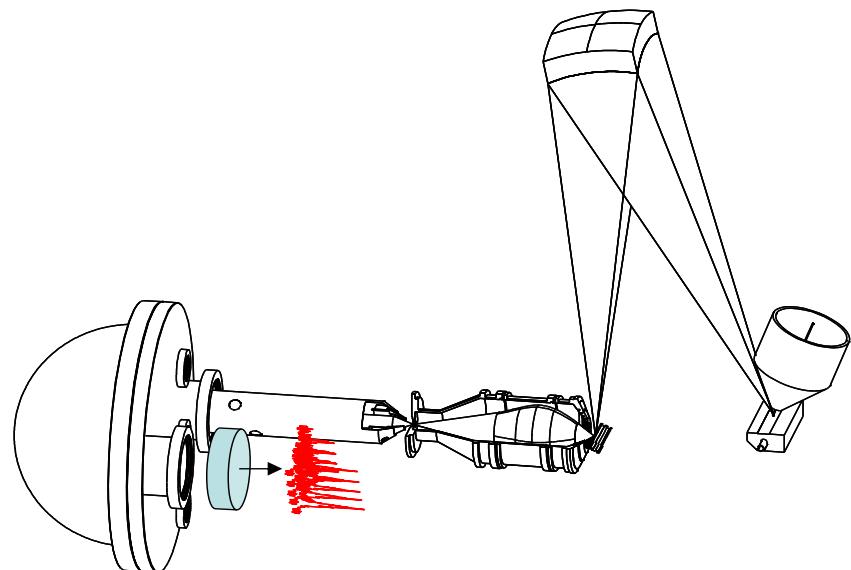
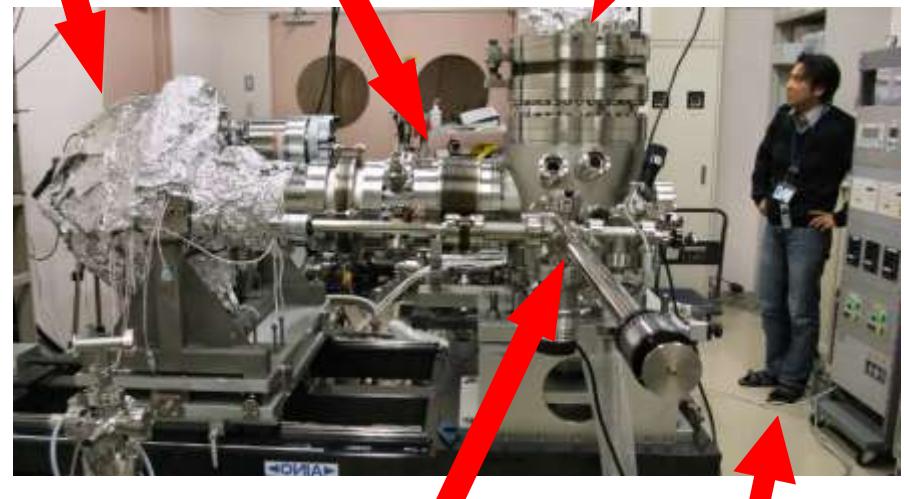


Laboratory HXPS system of practical performance is needed to widen the further prosperity of HXPS, to contribute science and technology.

Lab. HXPS System:3 Key Components

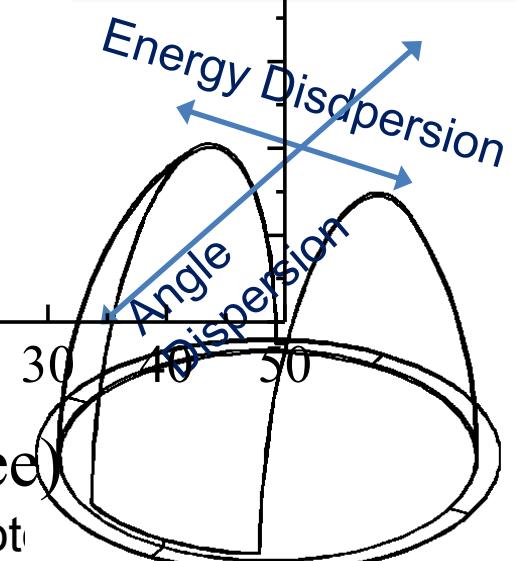
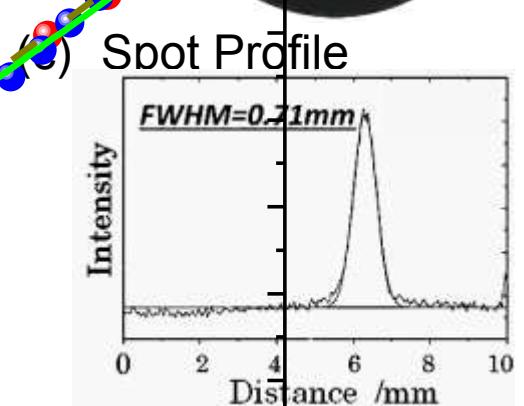
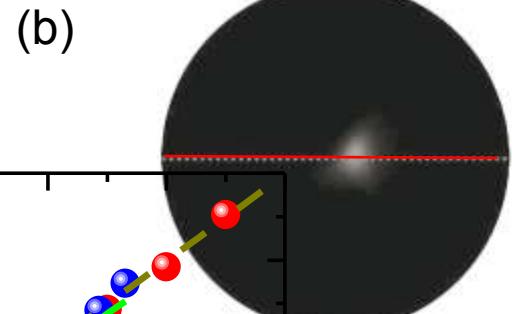
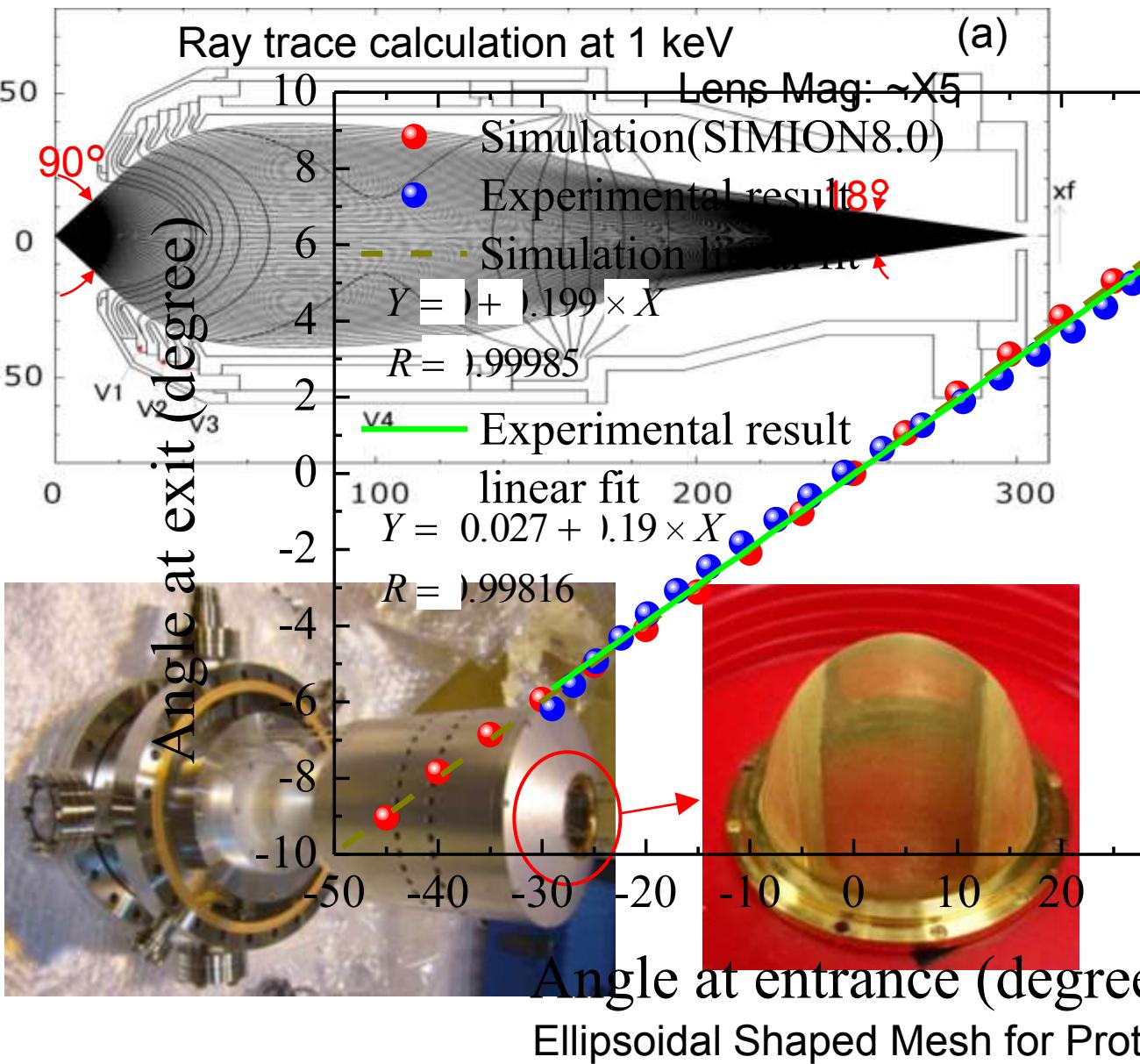


R4000 Wide Acceptance Lens Monochromatric Cr Ka X-ray Source

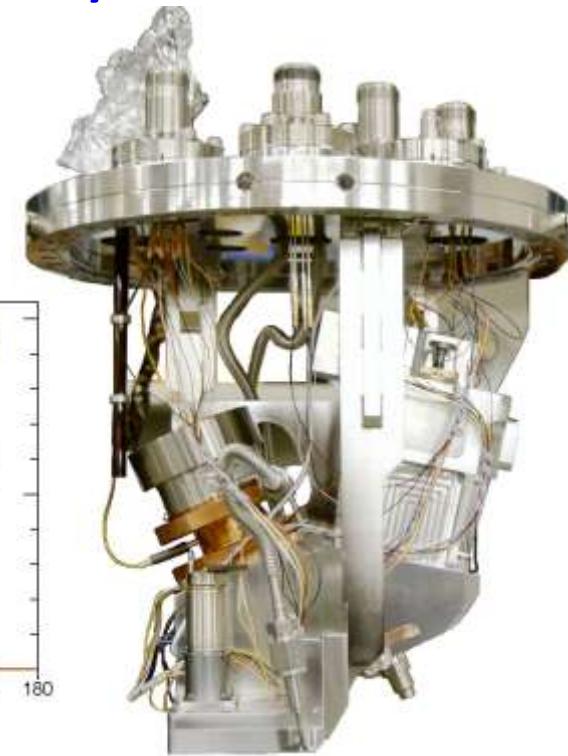
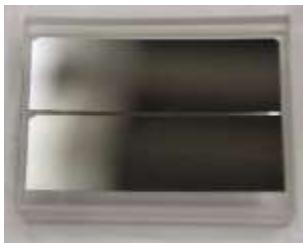
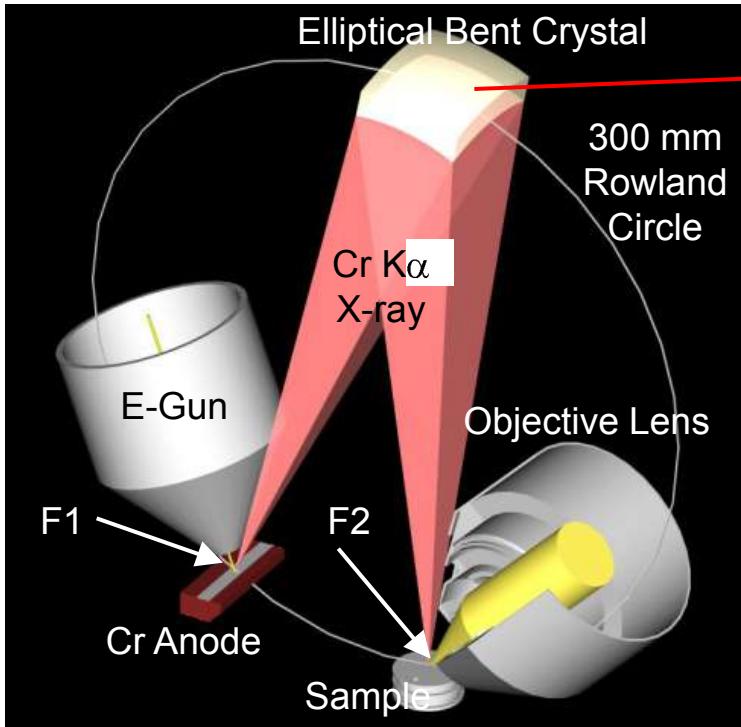


M. Kobata et al,
Anal. Sci., 26, pp.227-232 (2010)

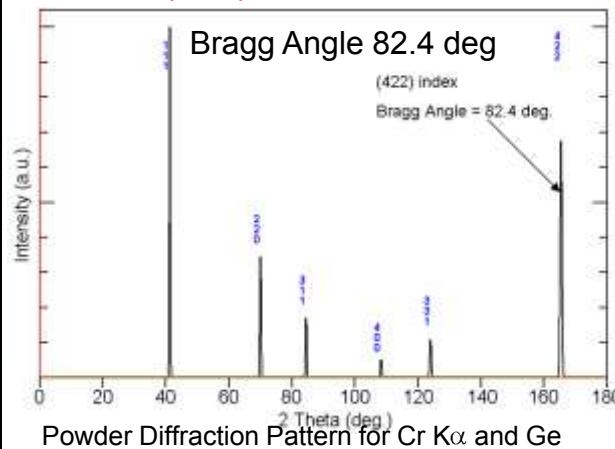
Wide acceptance angle objective lens



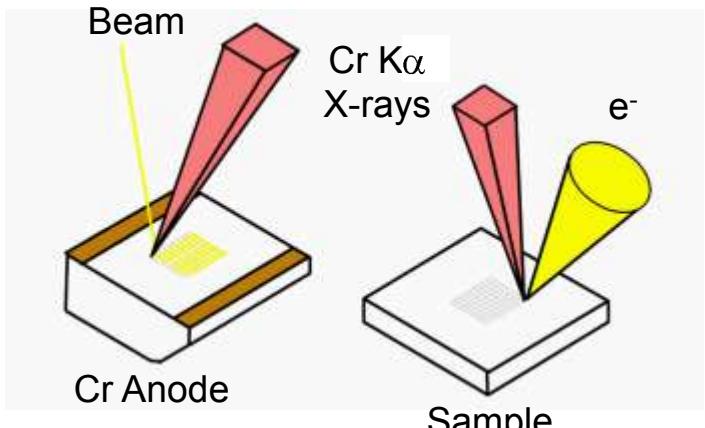
Monochromatic Cr K α Focused X-ray Source



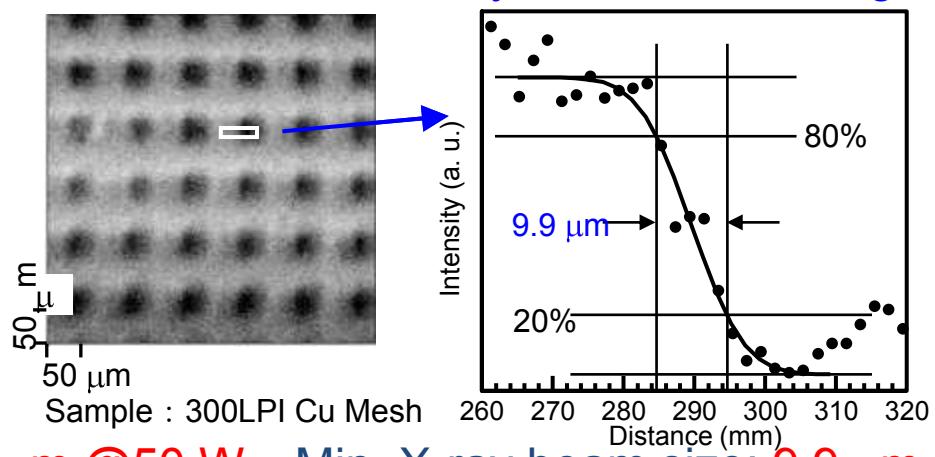
Ge (422) on the substrate



Electron Beam Intensity: $\sim 3.6 \text{E}+10 \text{ mm}^{-2}$



Beam Size from X-ray Induced SE Image

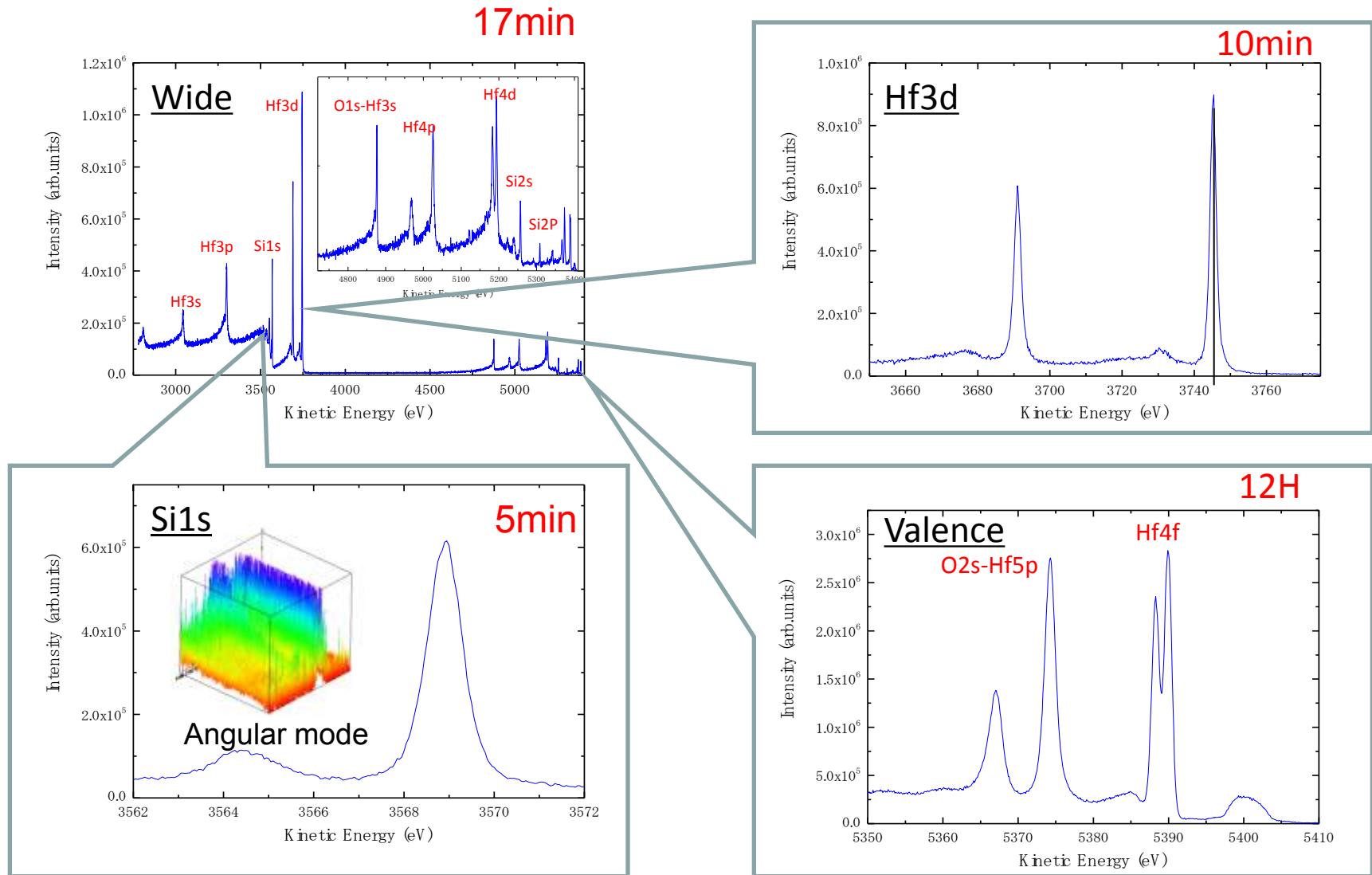


X-ray beam: 10 μm @ 1.0 W ~ 200 μm @ 50 W, Min. X-ray beam size: 9.9 μm

Basic performance

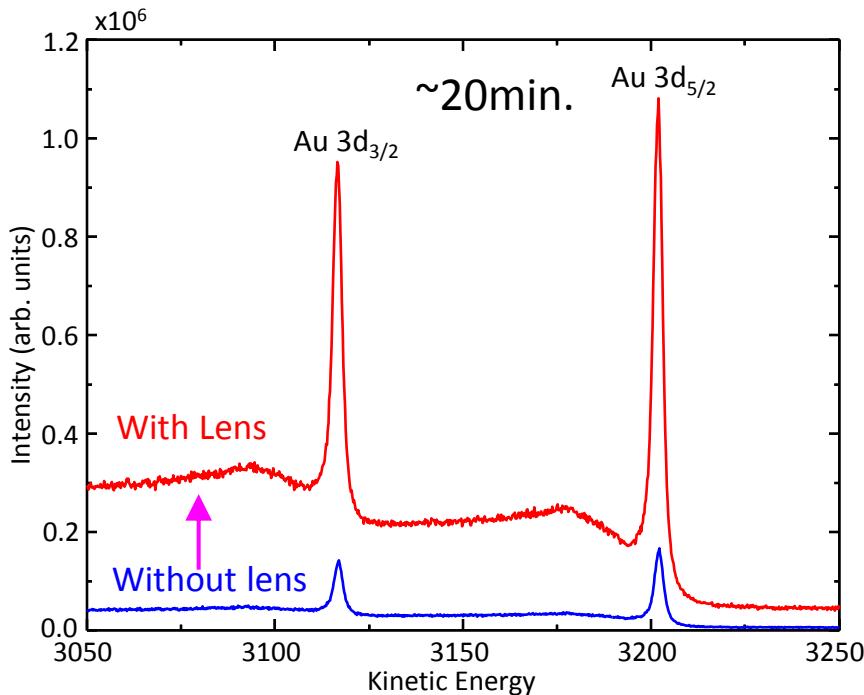
Basic Performance of HEXP Lab

HfO_2 (4 nm) / SiO_2 (1 nm) / Si(001)



Basic Performance of HXPS Lab. System

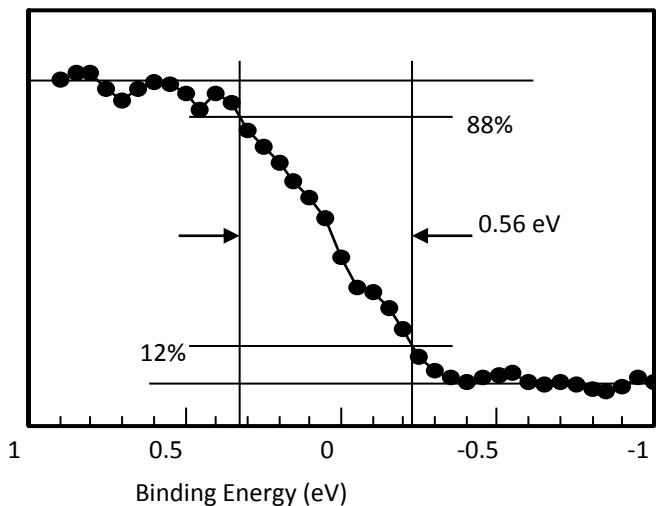
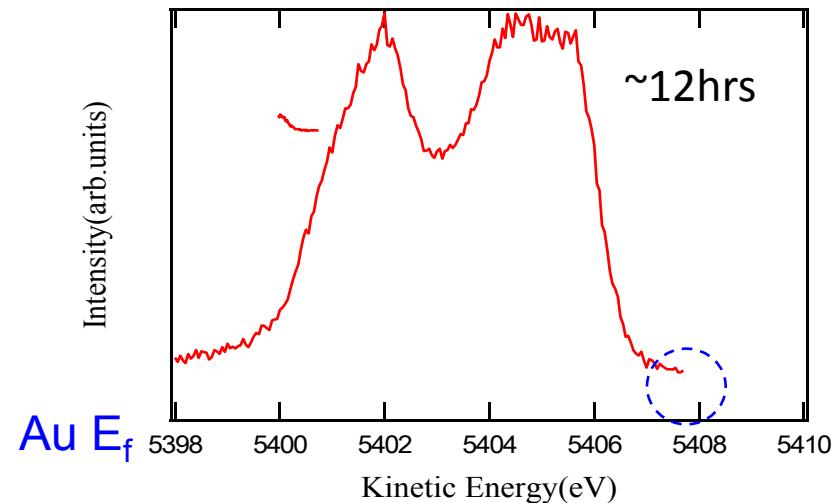
Sensitivity and Energy Resolution



	Au 3d _{5/2}		
	without lens	with lens	ratio
Area (cps*eV)	6.76X10 ⁵	4.91X10 ⁶	7.3
Height (cps)	1.55X10 ⁵	1.03X10 ⁶	6.6
FWHM (eV)	2.77	2.78	

~x7 Improvement by new objective lens

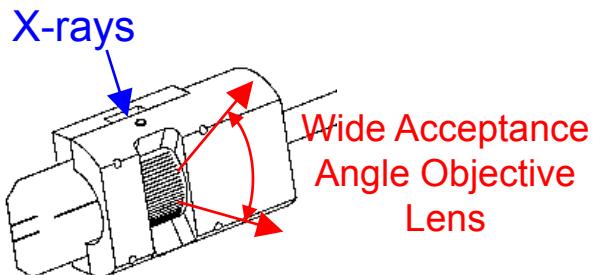
Au Valence band Spectrum



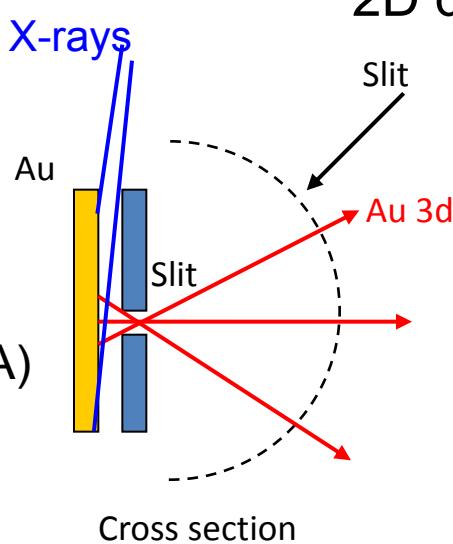
Total Resolution = 0.56 eV

Basic Performance of HXPS Lab. System

Acceptance Angle and Angle Resolution

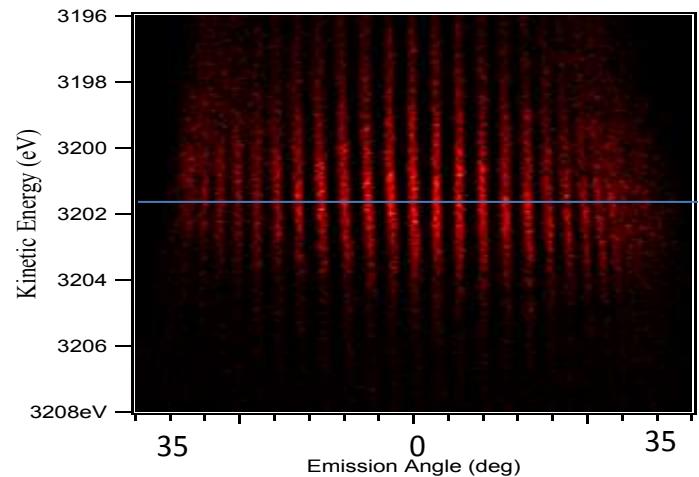


Angle test device(VG SCIENTA)

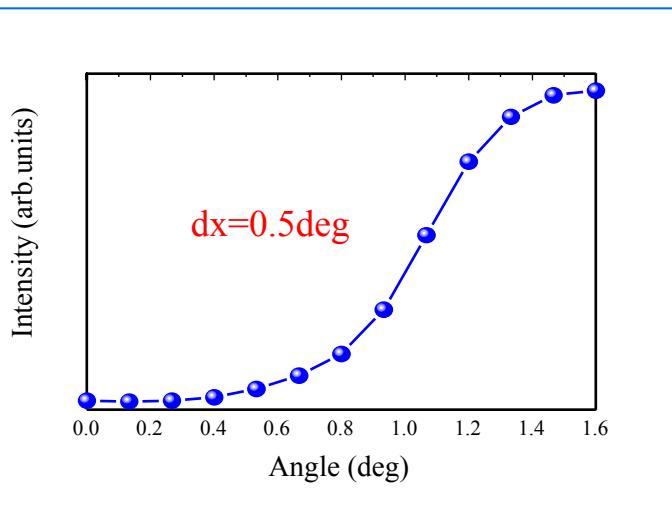


Cross section

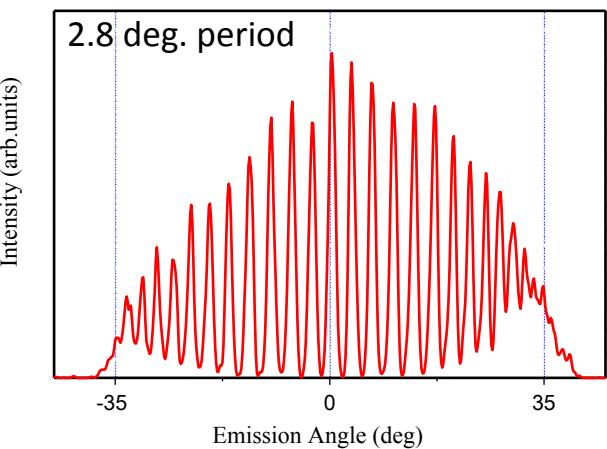
2D detector Image of *Au 3d (3.2 keV)*



Angle resolution at center



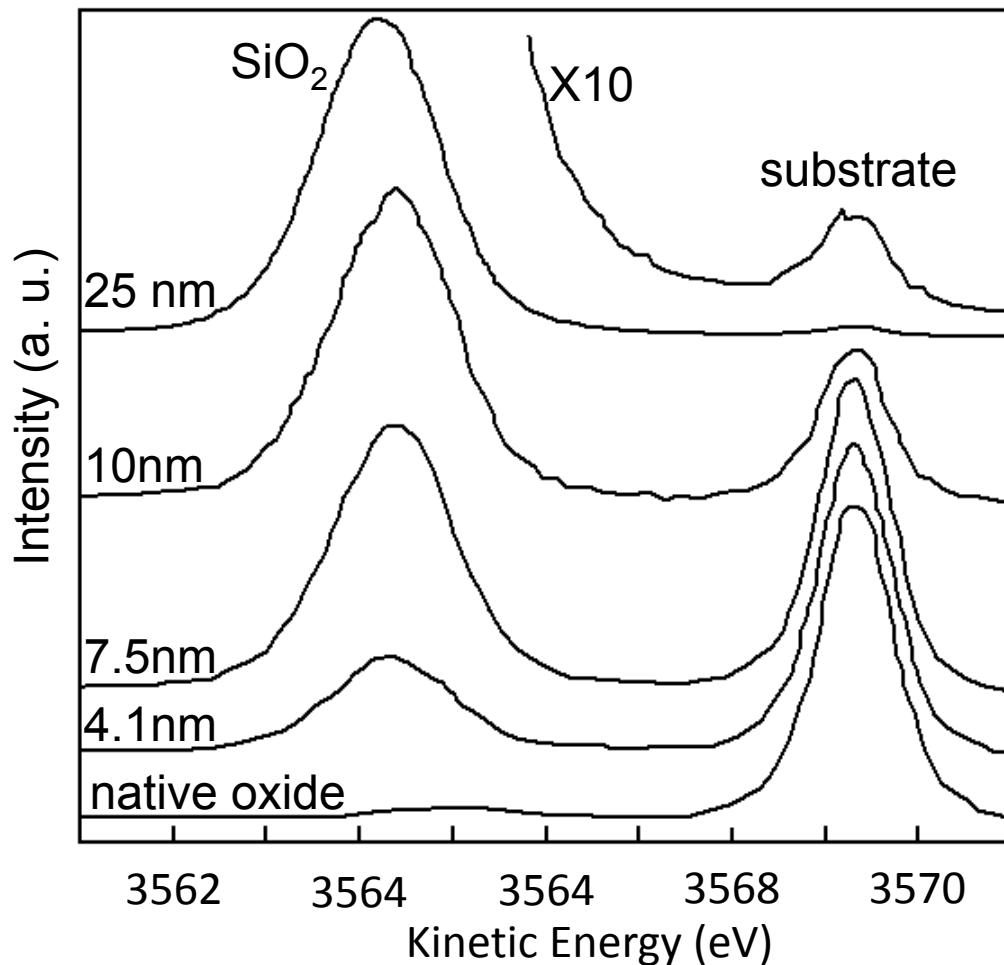
Lens mode: angular
PE=200eV,Slit:S4.0,Fixed
Beam Size200um(50W:CrKa)
Raster Scan(1mm×1mm)



Total Acceptance angle of ±35degrees

How deep can we see by HEAR PLab system?

Si 1s spectra at 80°take-off angle
on SiO_2 (4.1, 7.5, 10 and 25 nm)/Si



Si 1s in SiO_2 IMFP

~8.1 nm



The signal of 95% comes
from 3l in thickness, so the
substrate peak for 25 nm
 SiO_2 will appear.

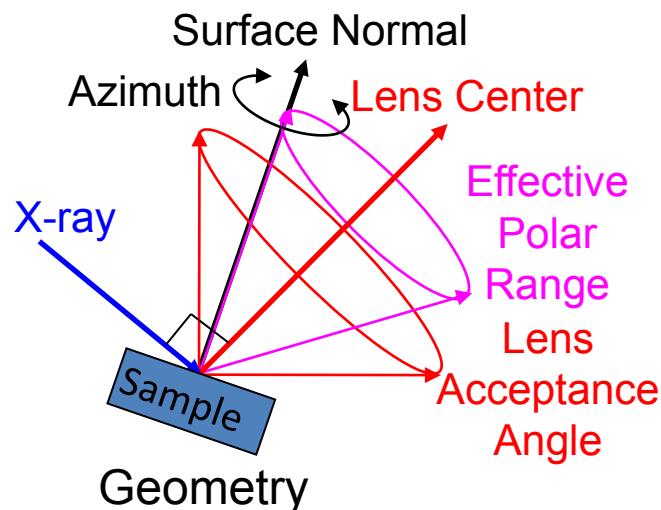
The applicability of the system to detect the depth information of layered materials more than 20 nm thicknesses was confirmed.

Comparison of performance

	Beamline system	Lab system
photon energy	6 / 8 keV	5.4 keV
X-ray spot size	1µm x 3µm	10/ 100/ 200 µm
typical IMPF (Si 1s)	10.7 nm (8 keV, cal.)	6.8 nm (5.4 keV, cal)
energy resolution	0.25 eV	0.5 eV
angular resolution	0.3 deg	0.5 deg
typical throughput (Au 4f _{7/2} , angle integrated mode)	1-2 sec	2-3 min (100µm)

Examples of Lab System Application in angle resolution mode

X-ray Photoelectron Diffraction of $\text{SiO}_2/\text{Si}(001)$



Acquisition parameters:

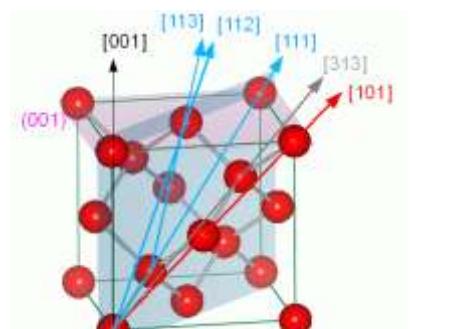
Azimuth range: $0\text{-}90^\circ$

(a four-fold symmetry operation was applied)

Azimuthal step: 2° (Stage)

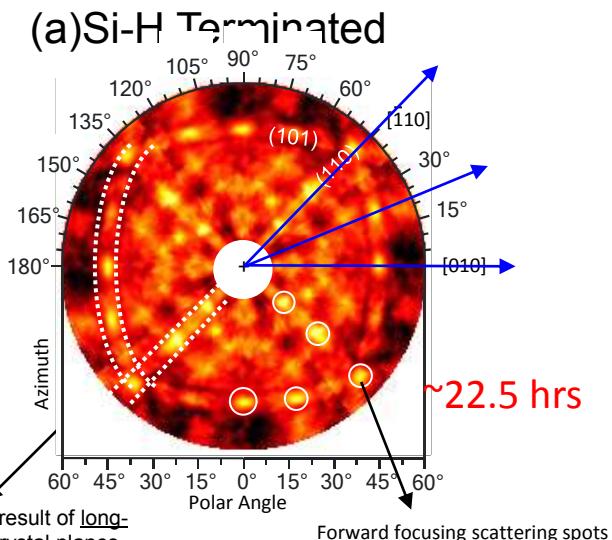
Polar range: $10\text{-}60^\circ$

Polar angle resolution: 1°

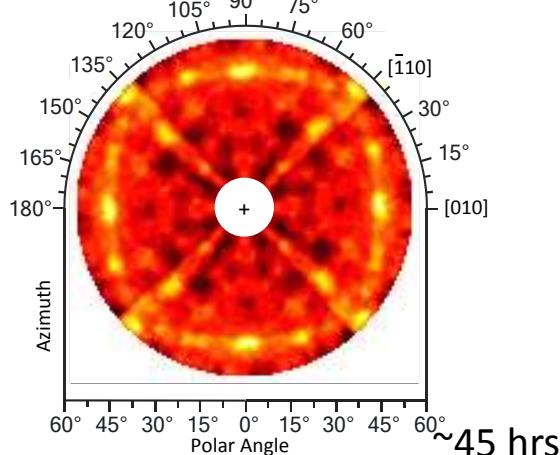


Model of ideal Si structure with some low index directions and planes.

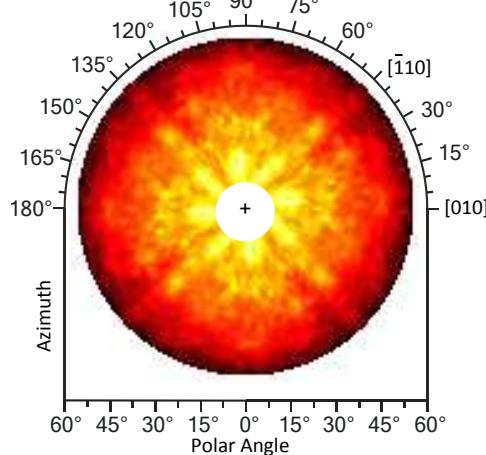
Kikuchi lines and bands are a result of long-range Bragg reflections from crystal planes.



(b) $\text{SiO}_2(4.1 \text{ nm})/\text{Si}(001)$



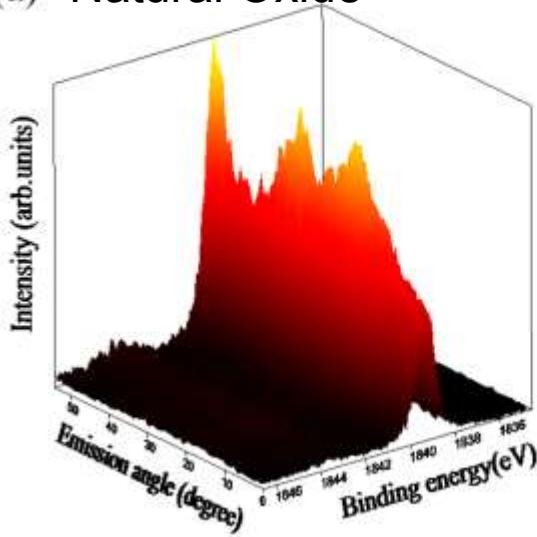
(c) $\text{SiO}_2(7.5 \text{ nm})/\text{Si}(001)$



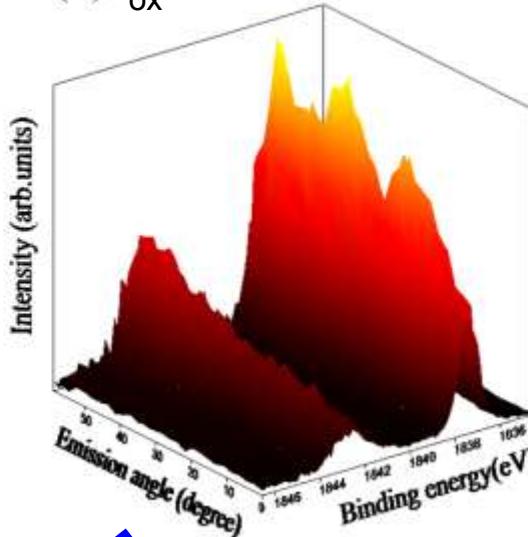
The kinetic energy of the Si substrate Si 1s photoelectrons was 3569 eV.

TOA dependence of Si 1s spectra

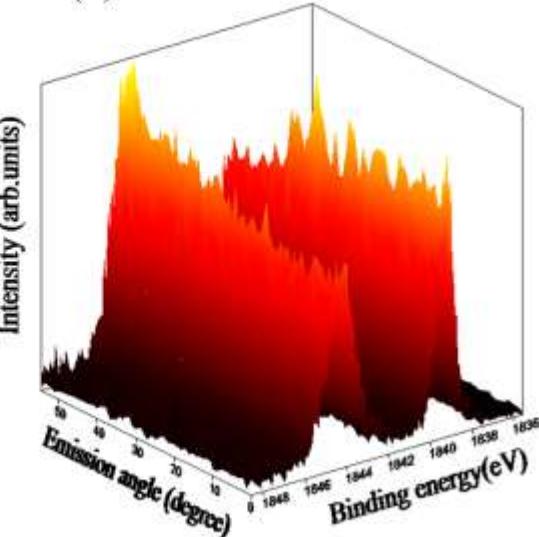
(a) Natural Oxide



(b) $t_{ox} = 4.1\text{nm}$

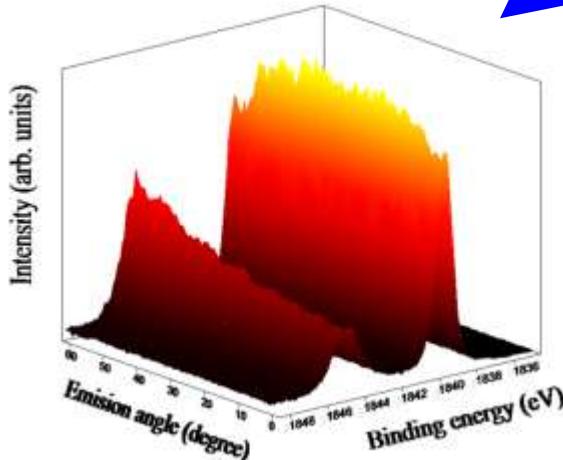


(c) $t_{ox} = 7.0\text{nm}$



azimuth angle in 110 direction.

Continuous rotation around azimuth axis
reduces the XPD modulation in substrate Si1s
intensity.



Evaluation of Attenuation Length and Thickness for SiO₂/Si by Sample Rotation

$$\frac{I_S}{I_O} = \frac{n_S L_S}{n_O L_O} \frac{1}{\exp(d / L_O \sin \theta)}$$

$$d = \ln \theta \left(\frac{n_S L_S I_O}{n_O L_O I_S} + \dots \right)$$

d : overlayer thickness

I_S : peak intensity of Si substrate

I_O : peak intensity of SiO₂ layer

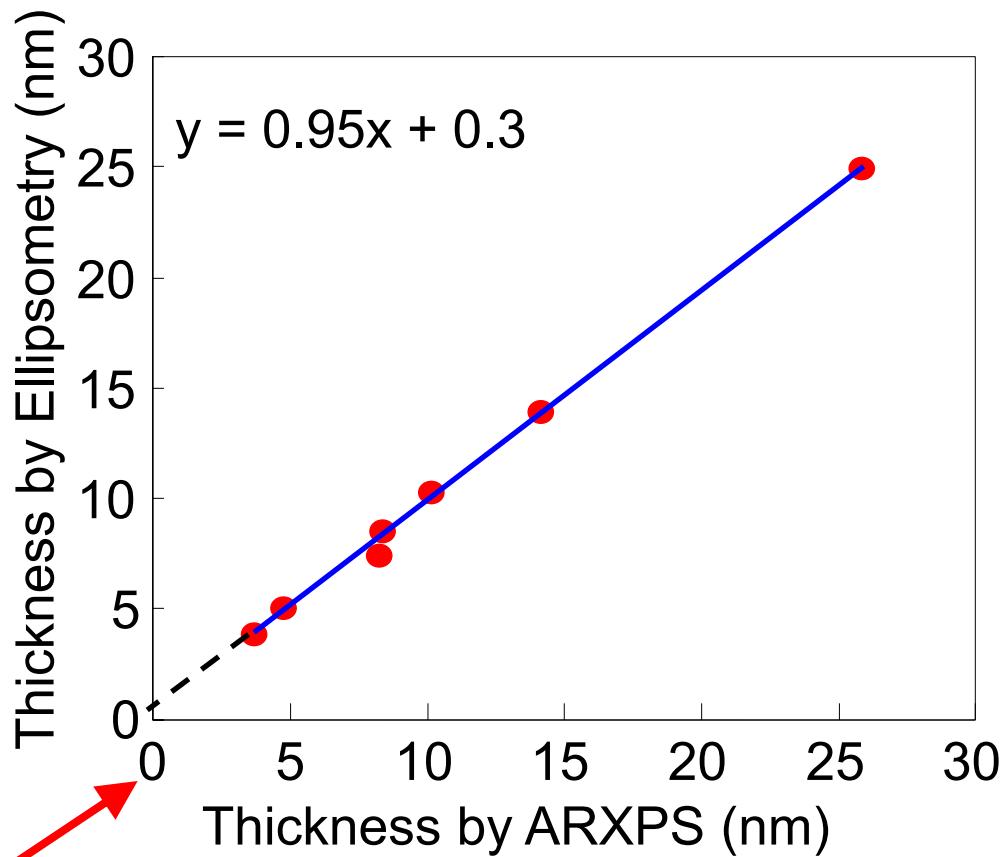
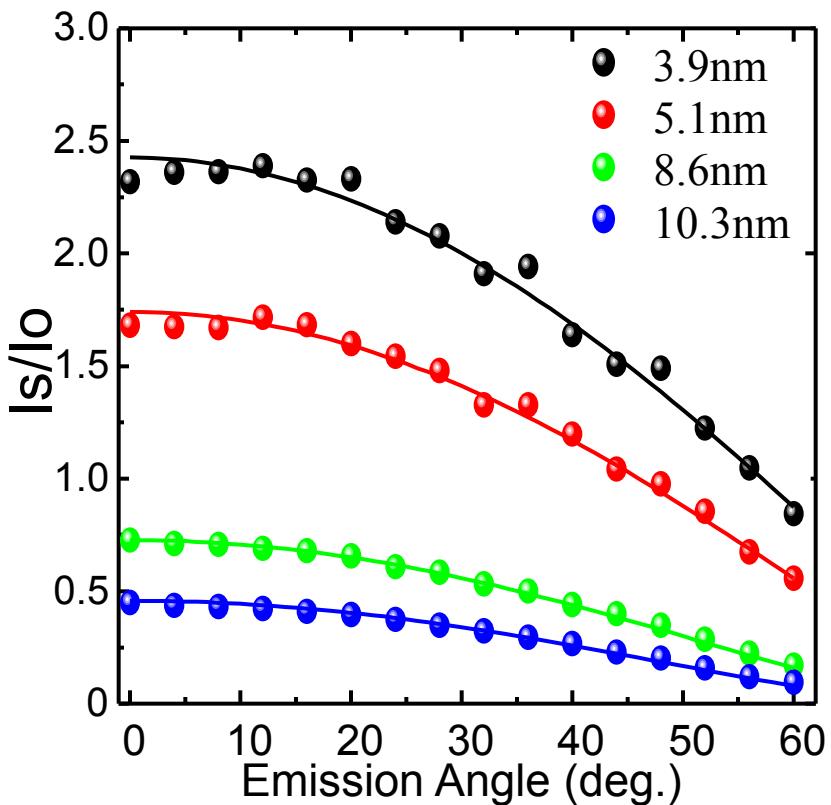
L_S : electron attenuation length in Si

L_O : electron attenuation length in SiO₂

n_S : atomic density of Si substrate

n_O : atomic density of SiO₂ layer

Evaluation of Attenuation Length and Thickness for SiO₂/Si by Sample Rotation



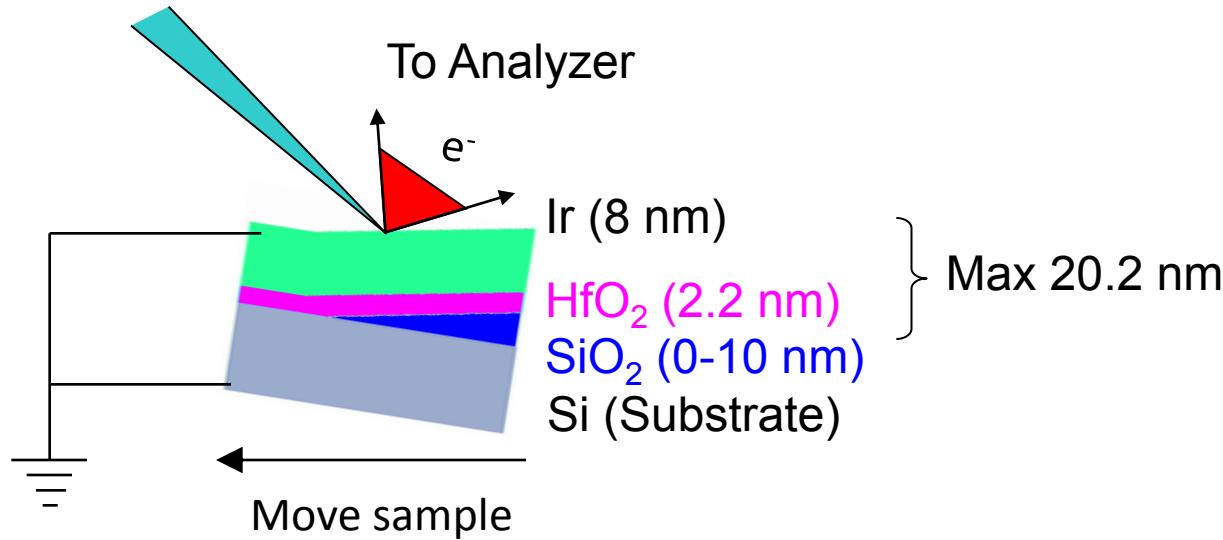
Estimated Attenuation Length
(5.6 ± 0.6) nm for Si
(7.0 ± 0.4) nm for SiO₂

IMFP from TPP2M
6.7 nm for Si and
8.1 nm for SiO₂

Practical EAL is less than IMFP by 7 ~ 32 %[1],
so that **good agreement**.

Application to a multilayer system

Ir(8nm)/HfO₂(2.2nm)/SiO₂ (0-10 nm)/Si(100)
wedged



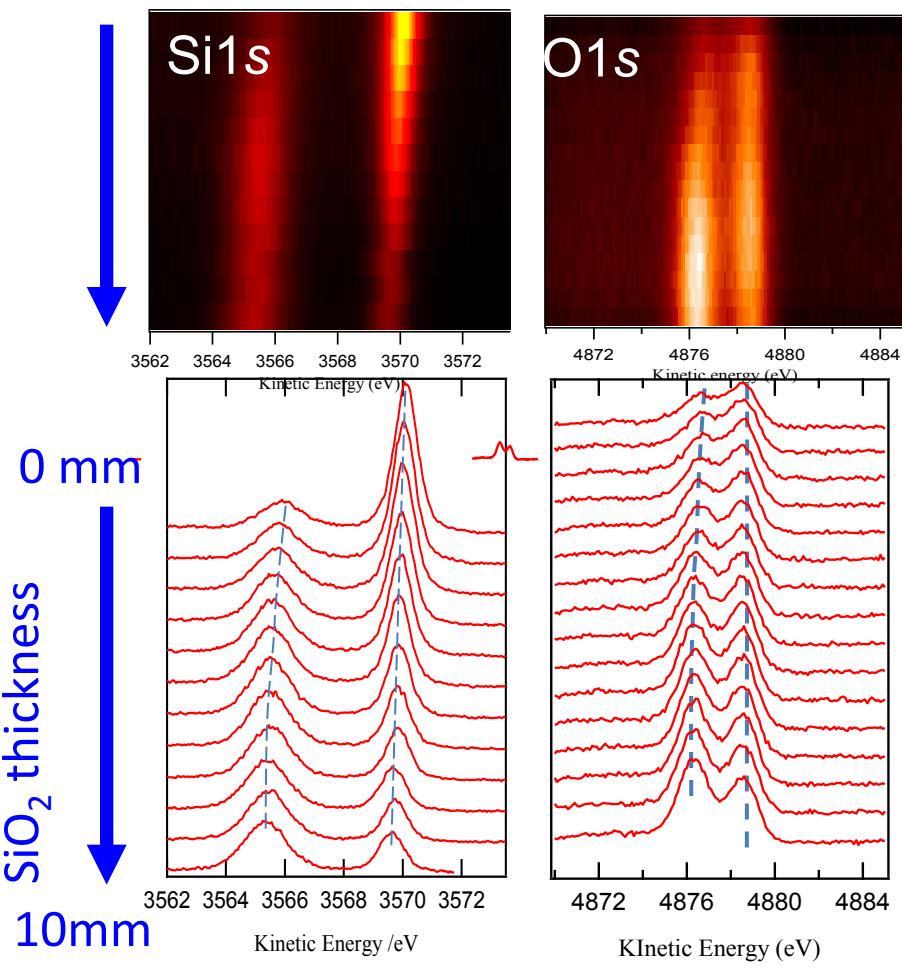
Ir(8 nm)/HfO₂ (2.2 nm)/thickness-graded SiO₂ (0-10 nm) /Si(100) sample
Y. Abe *et al.*, Jpn. J. Appl. Phys., Vol. 48, pp. 041201-1~6 (2009)

Can we monitor profiles buried layers and its interfaces under overlayer of 10 nm thickness?

Ir(8 nm)/HfO₂(2.2 nm)/SiO₂ (0-10 nm)/Si(100):SR

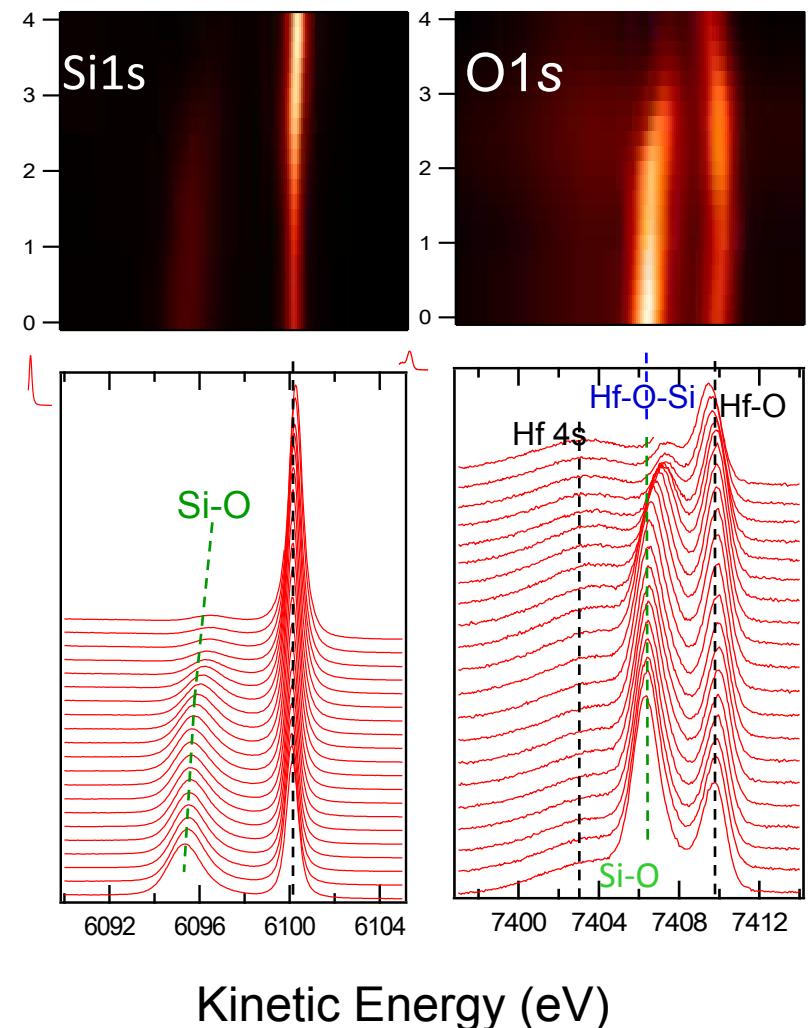
Laboratory

Scanning 200 mm step_

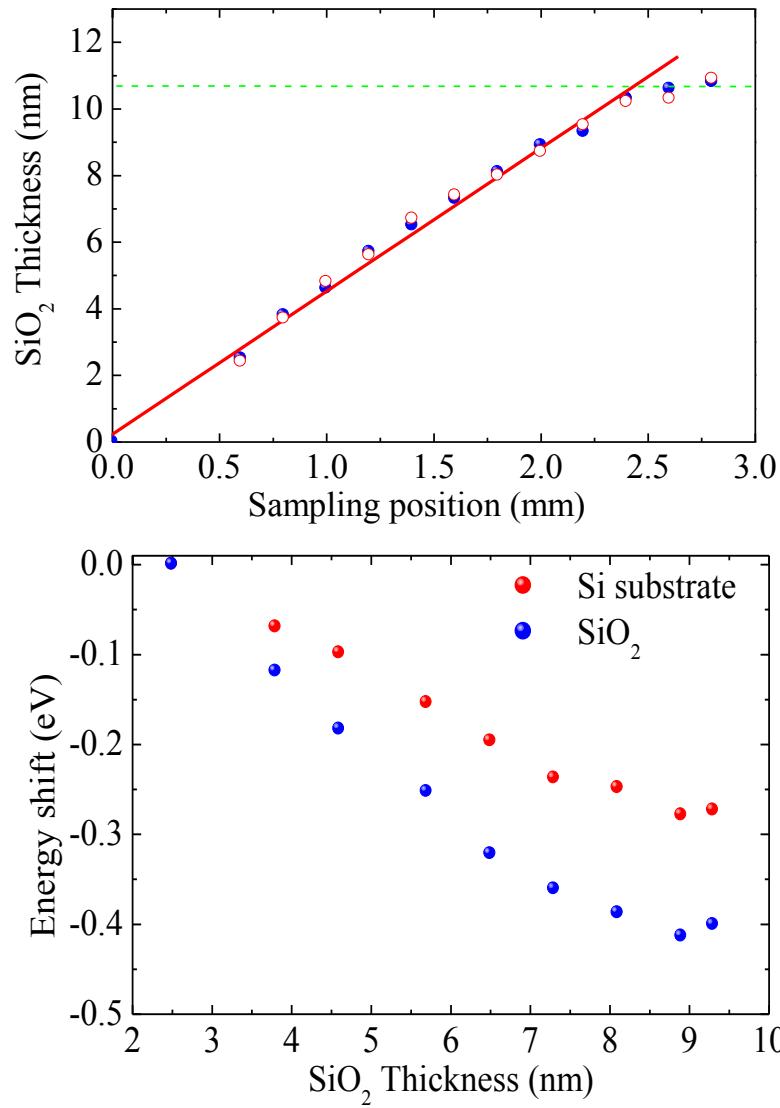
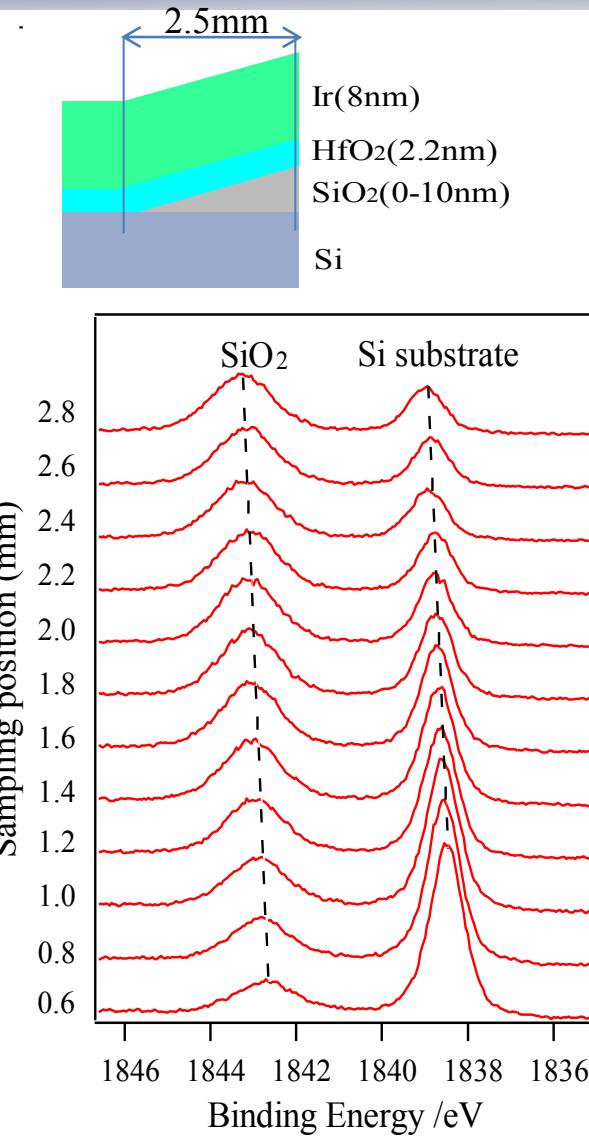


Beamline

Photon Energy=7.94 keV,
Pass Energy=200 eV
Slit: C 0.5, TOA=80°, Transmission mode



Charge at Ir(8nm)/HfO₂(2.2nm)/SiO₂ (0-10 nm)/Si(100)

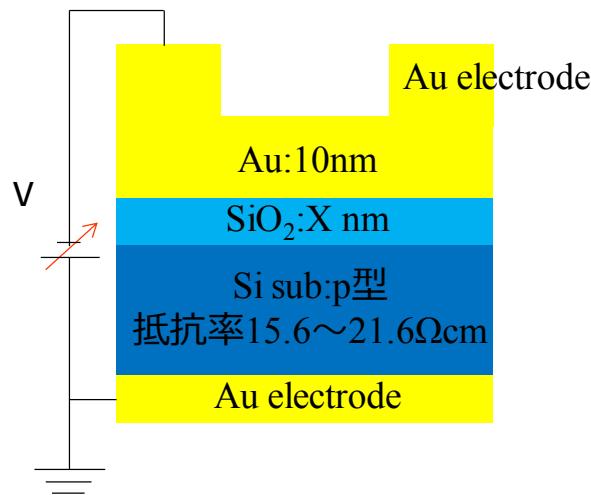


Effect of charge at HfO₂-SiO₂ interface on the Si1s peak positions is visible under the Ir overlayer of 8 nm thickness.

Operand observation

Si1s HXPS in MOS under Bias Application

Au(10nm)/SiO₂(3.6 nm)/p-Si/Au

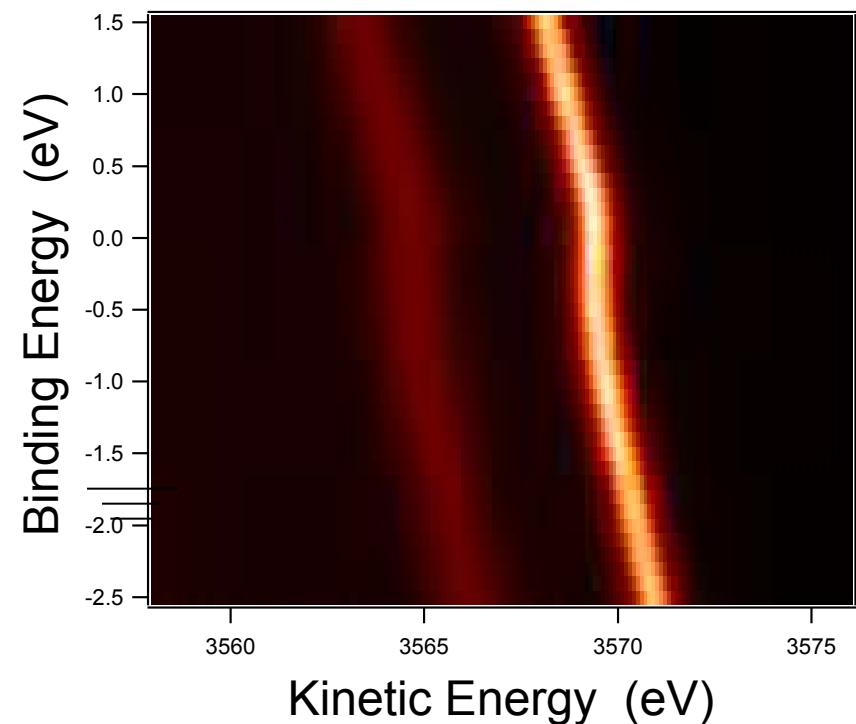
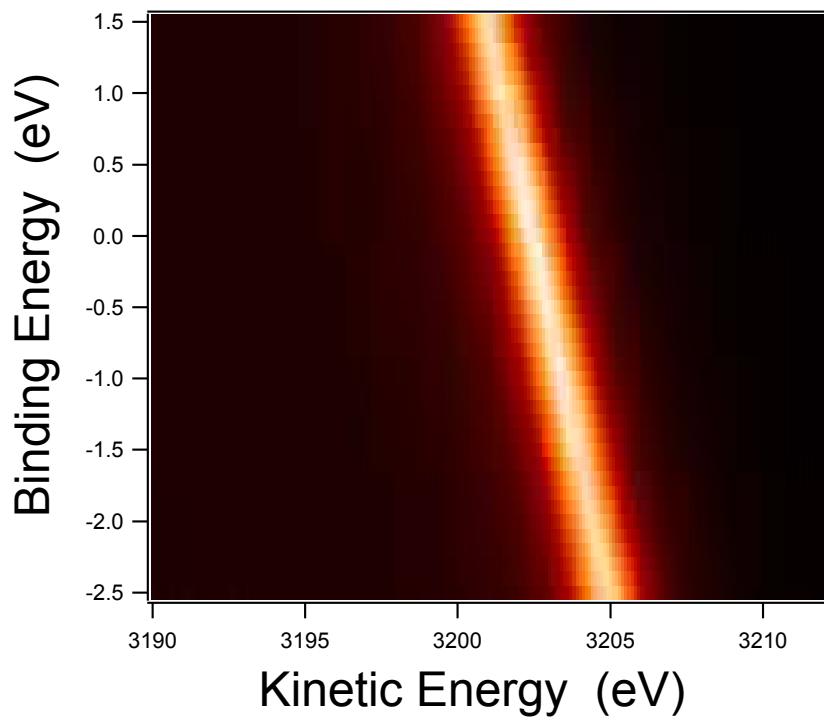


Crka(Ef5408.46eV),

PE=200eV, Slit:C08

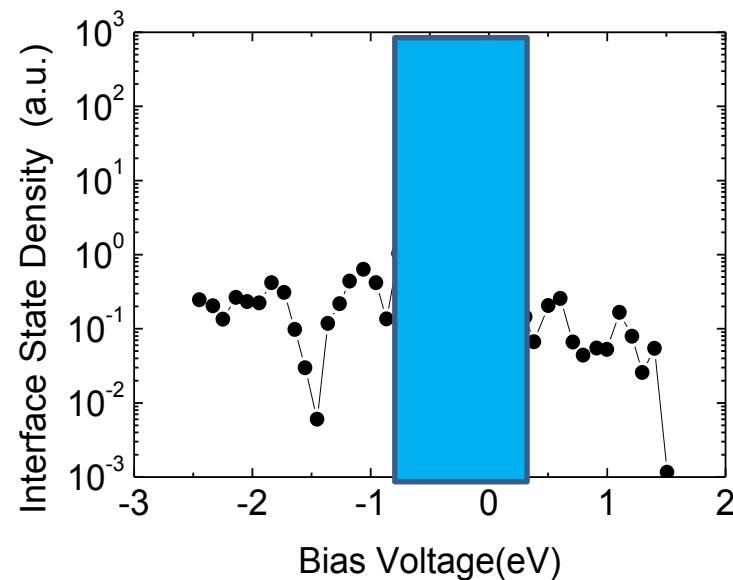
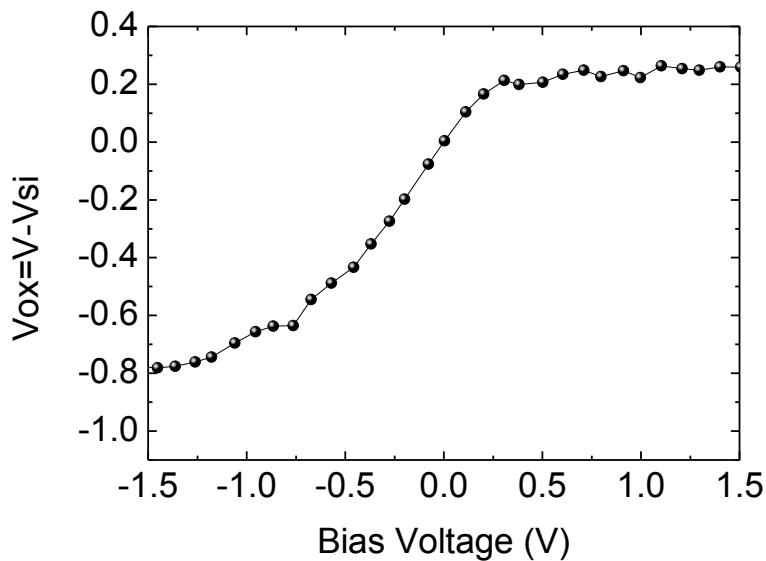
TOA=85deg, Bias Voltage step100mV

Collaboration with Toray Research Center,
A.Yasui, S. Ogawa, and M. Miyata,



Si1s HXPS in MOS under Bias Application

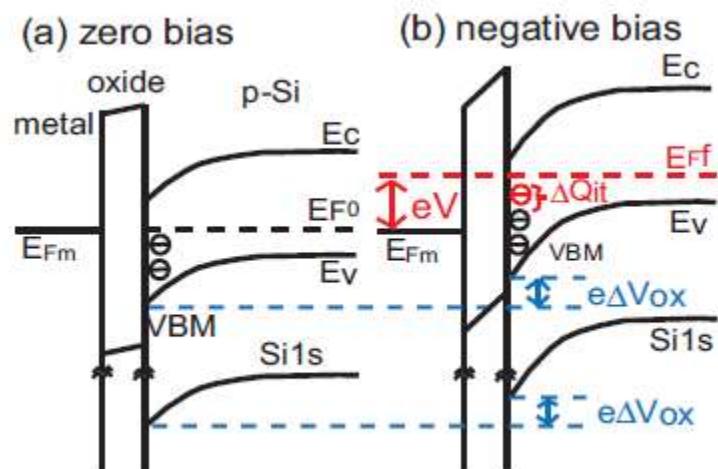
Au(10nm)/SiO₂(3.6 nm)/p-Si/Au



$$|\Delta V| = \left(\frac{e}{C_{ox}}\right) \left\{ \int_0^{E_f} \rho_i(E) dE - \int_0^{E_{f0}} \rho_i(E) dE \right\}$$

$$\rho(E_f) = \left(\frac{C_{ox}/e}{e}\right) \left(\frac{d\Delta V}{dE} \right)$$

$$= \left(\frac{C_{ox}}{e^2}\right) \left\{ \left(\frac{d\Delta V}{dV} \right) \left(\frac{1}{1 - \frac{d\Delta V}{dV}} \right) \right\}$$



Summary

- Laboratory type Angle Resolved HXPS system was developed , and evaluated to be a promising tool for the investigation of bulk and thin solid film materials.
- XPD 2D pattern of Si 1s is obtained within ca. 24 hrs.
- Sample rotation ARXPS is useful method to average (or reduce) the XPD modulation effect.
- 25nm deep is accessible by the laboratory system.
- Buried layer profiling is feasible.
- Operand observation of a MOS structure demonstrated.
- Ambient pressure HXPES is our next target.

Activities in HiSOR

Toward bulk sensitive high resolution spectroscopy at very low energy excitations.

Due to its high **bulk sensitivity**, it is expected to be complementally to HXPES.

(in case of materials with gap, it is clear. Not so clear in case of metal due to scattering channel by single particle excitations.)

High-resolution PES with tunable synchrotron radiation to study electronic structure of solids from VUV to hard X-ray

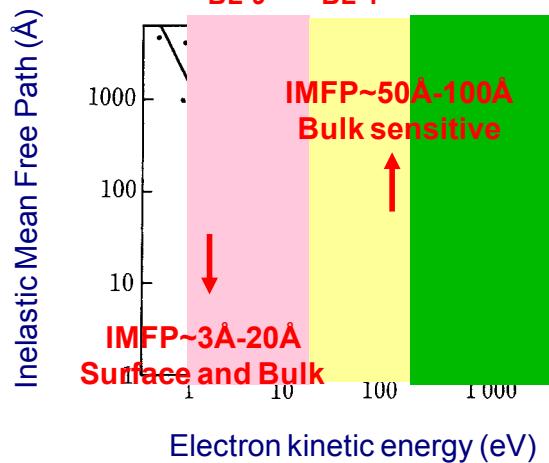


HiSOR
(700MeV compact storage ring)

VUV and Soft X-ray



Collaboration



SPring-8
(8GeV, 3rd generation ring)

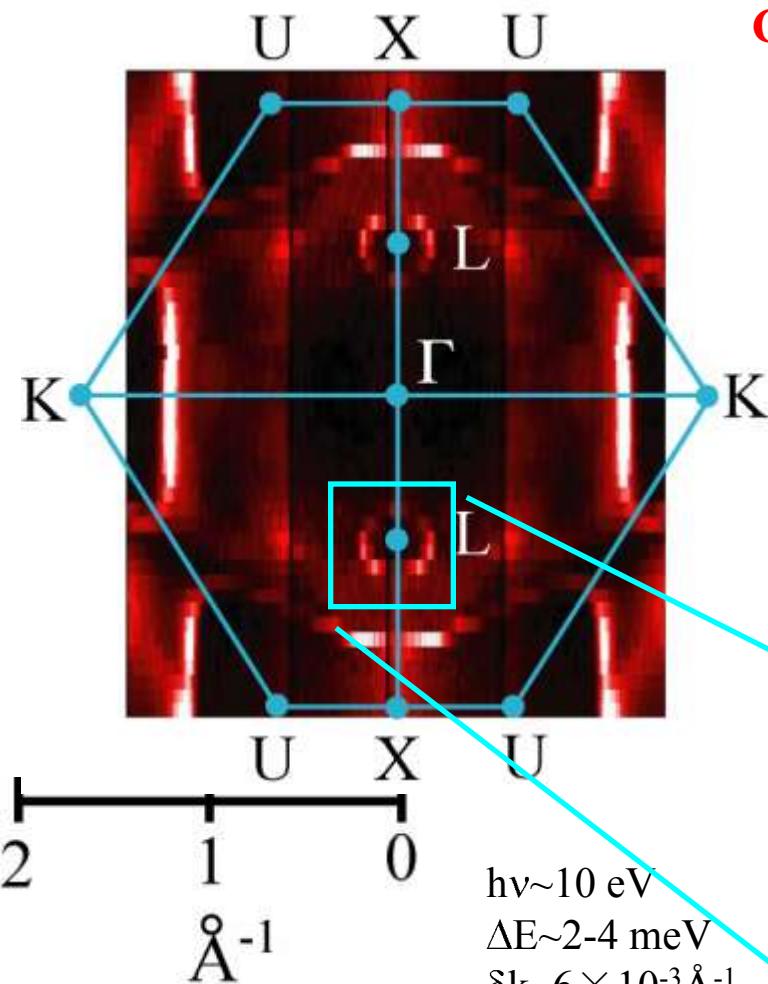
Soft and Hard X-ray



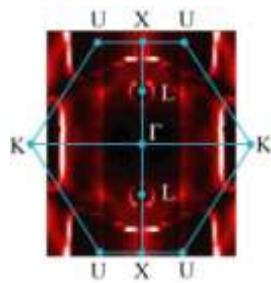
High-resolution PES with tunable photon energy in the wide range



A schematic view Fermi surface size



Cu(110) $h\nu=92 \text{ eV}$ HiSOR BL-1



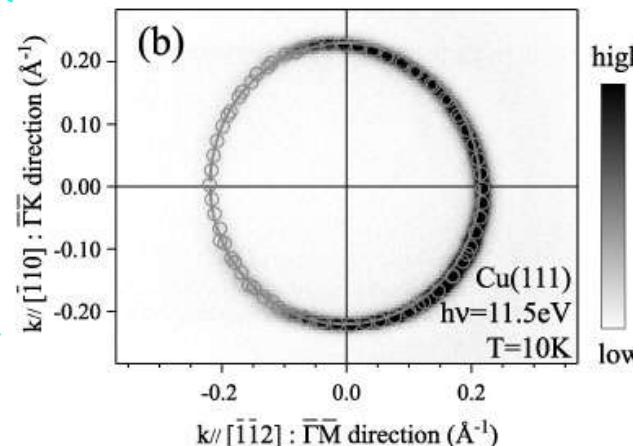
$h\nu \sim 100 \text{ eV}$
 $\Delta E \sim 20-40 \text{ meV}$
 $\delta k \sim 2 \times 10^{-2} \text{\AA}^{-1}$
Photon
 $k \sim 5 \times 10^{-2} \text{\AA}^{-1}$



$E_K \sim 1,000 \text{ eV}$
 $\Delta E \sim 200-400 \text{ meV}$
 $\delta k \sim 8 \times 10^{-2} \text{\AA}^{-1}$
Photon
 $k \sim 5 \times 10^{-1} \text{\AA}^{-1}$

$E_K = 10,000 \text{ eV}$
 $\Delta E > 50 \text{ meV}$
 $\delta k \sim 2 \times 10^{-1} \text{\AA}^{-1}$
Photon
 $k \sim 5 \text{\AA}^{-1}$

Shockley State
Surface derived state



Cu(111)
 $h\nu \sim 11.5 \text{ eV}$
HiSOR BL-9

Acknowledgements

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Experimental results shown in this presentation are due
to collaborations with,

E. Ikenaga

JASRI/Spring-8

Igor Pis

Charles University

Y. Abe and N. Miyata

AIST

H. Nohira

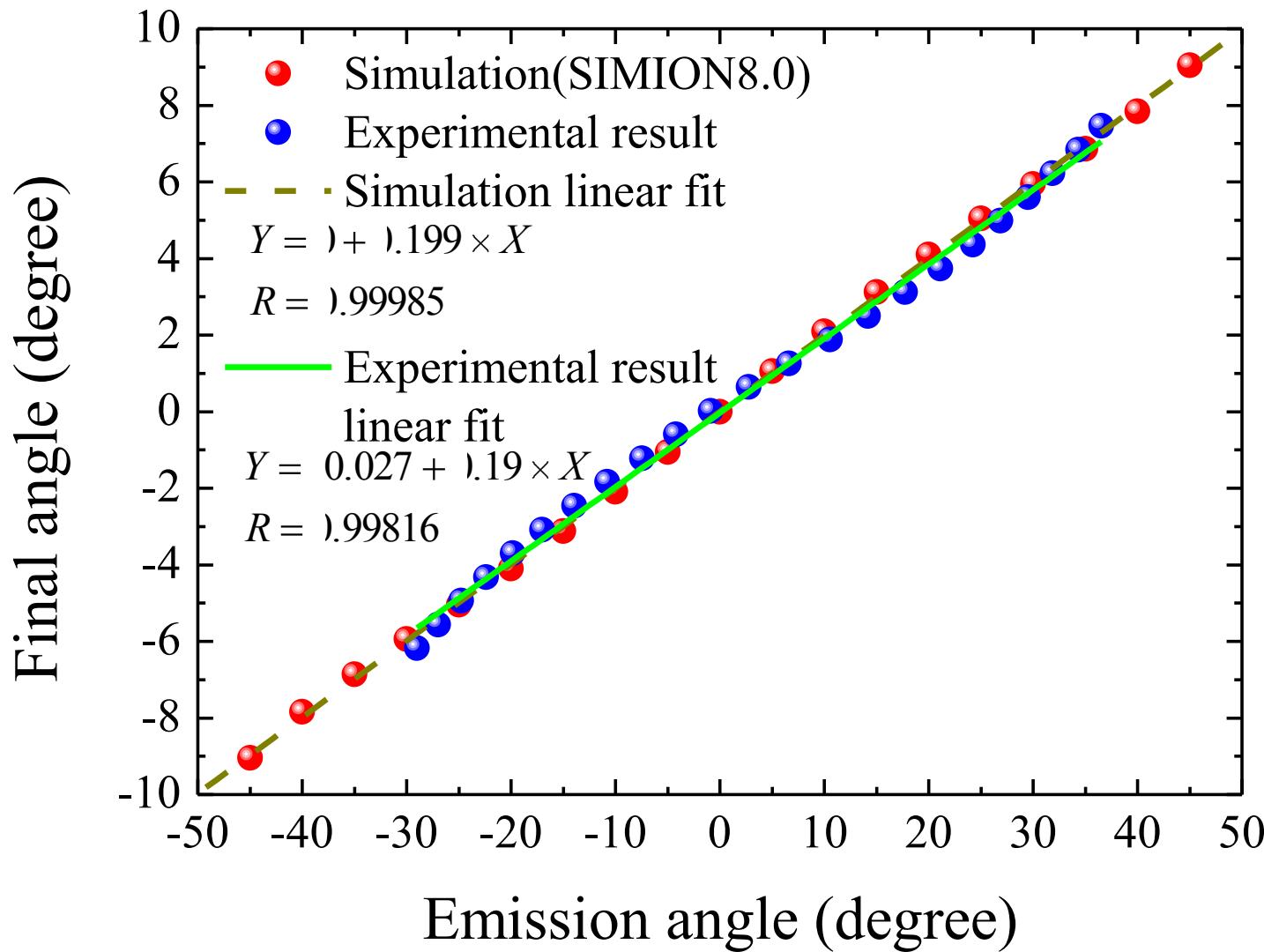
Tokyo City University

A. Yasui, S. Ogawa,
and M. Miyata

Toray Research Center

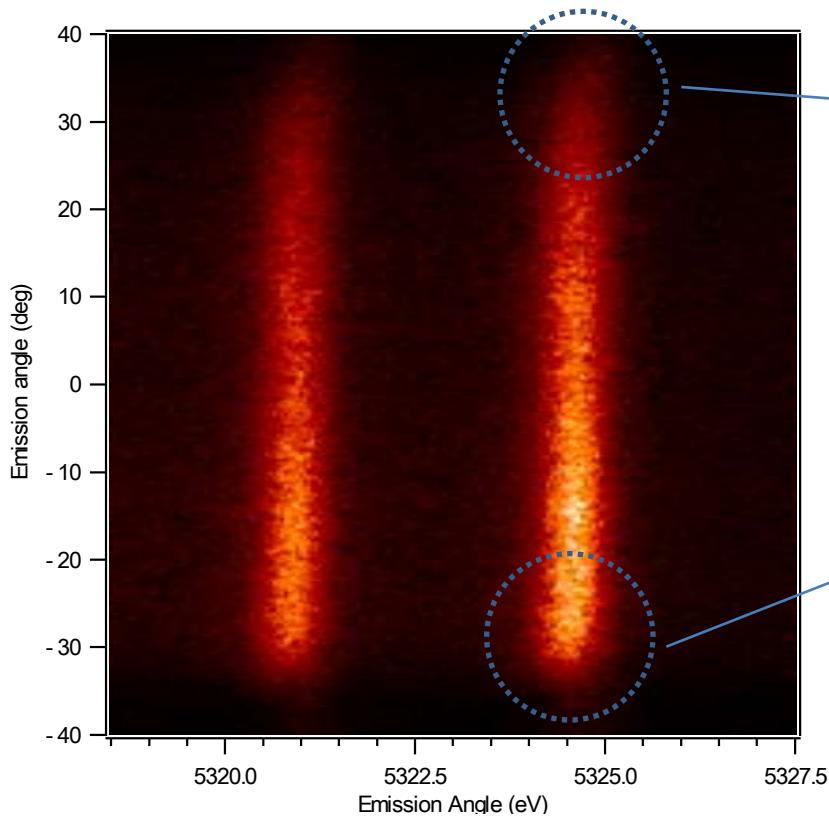
We are grateful to them.

角度保存の評価

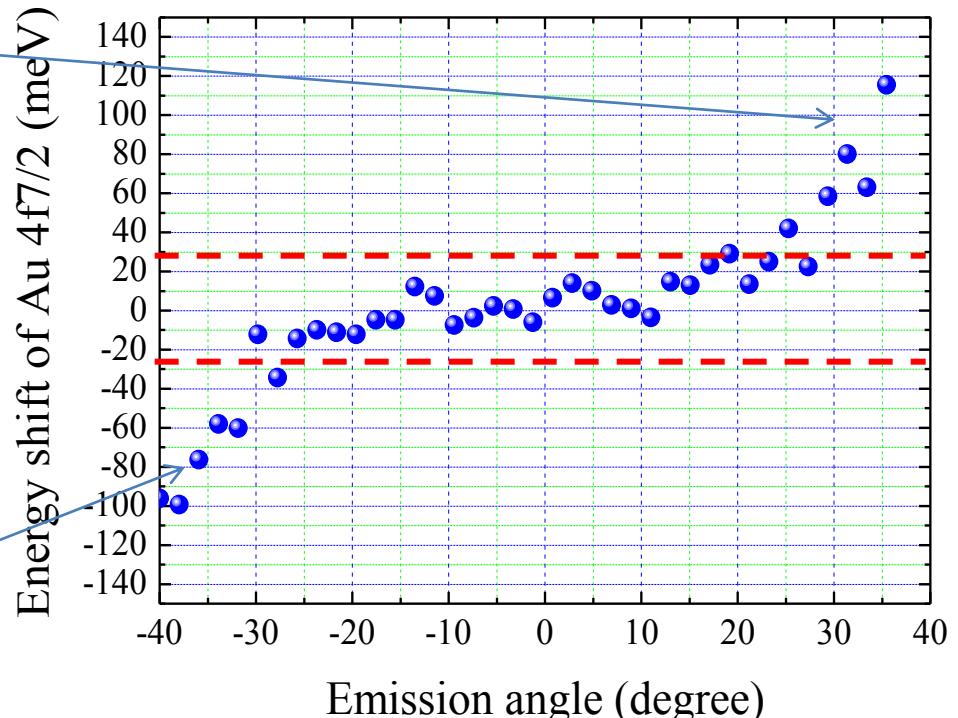


Lab-HXPES systemの評価-取込立体角と色収差-

2D detector Image of
Au 4f (5.32 keV)



New mesh: 100 mesh
Lens mode: angular
PE=200eV,Slit:C0.8mm,10Sweep
Energy step 50meV, Frame3(0.2s)
Beam Size100um(25W:CrK α)



Emission angle ± 30 deg: Energy shift ± 30 meV

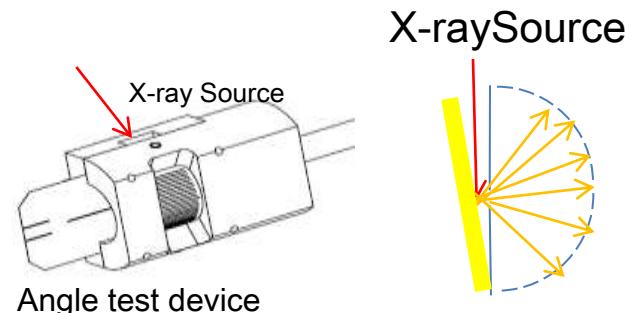
Emission angle ± 30 deg以上になると色収差が大きくなる。

対物レンズの有無による取込立体角評価(放射光)

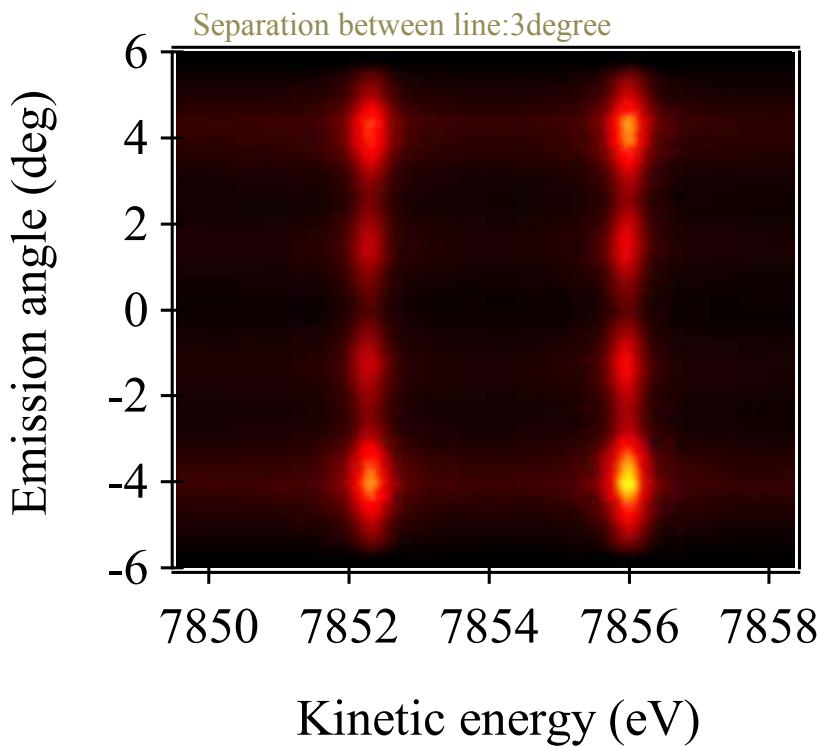
BL47XU

TOA80deg, Ep=200eV, Slit:C0.5

励起エネルギー : 7939.6eV



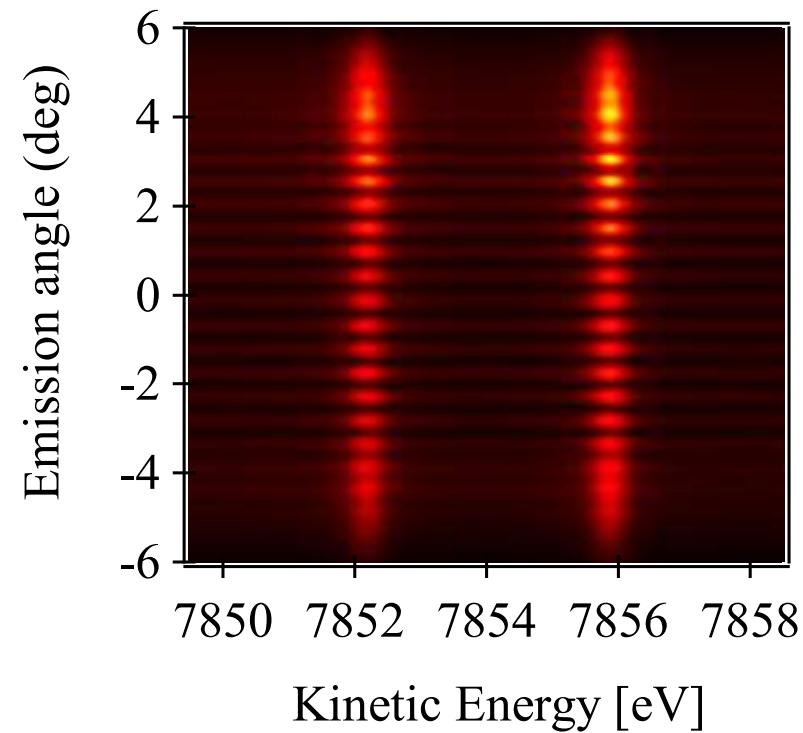
Without Objective Lens



約 5 倍



With Objective Lens

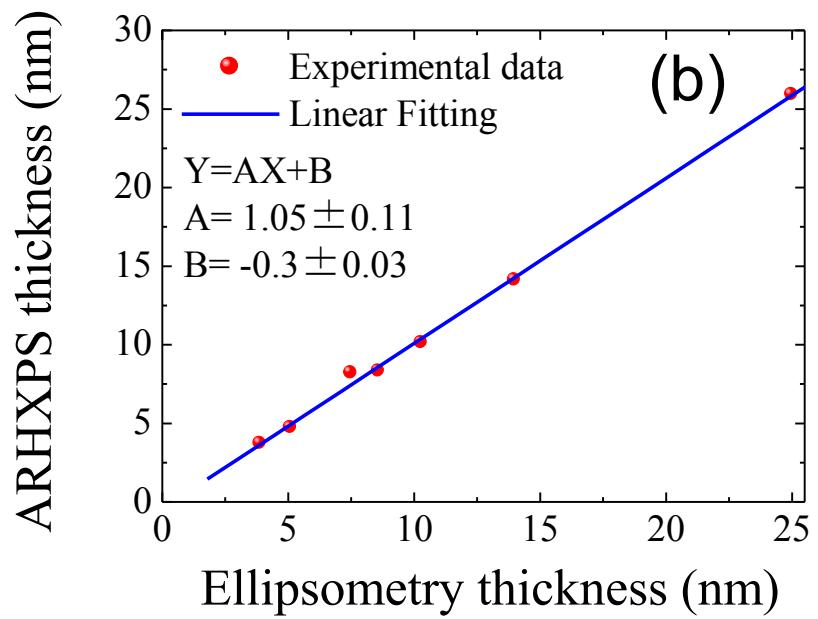
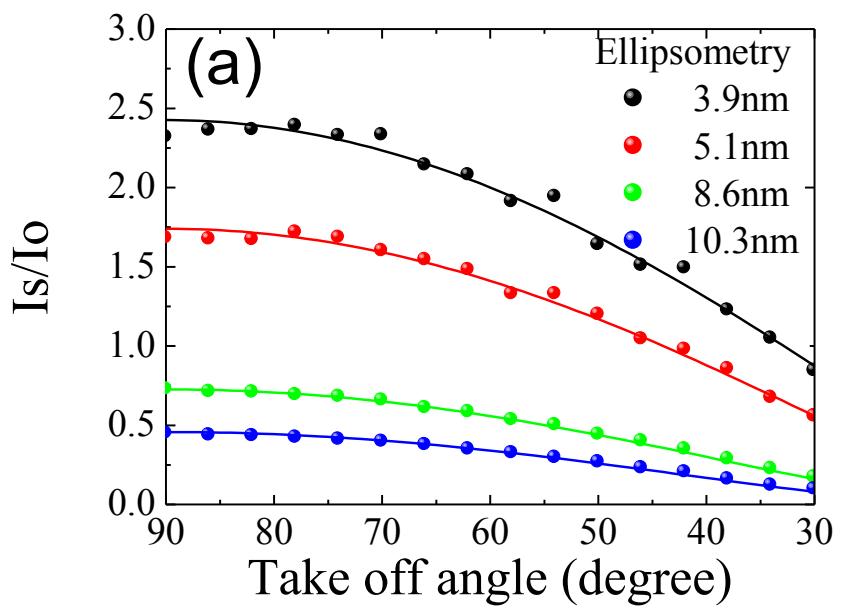


取込立体角 $\pm 6^\circ$ から $\pm 66^\circ$ に拡大！

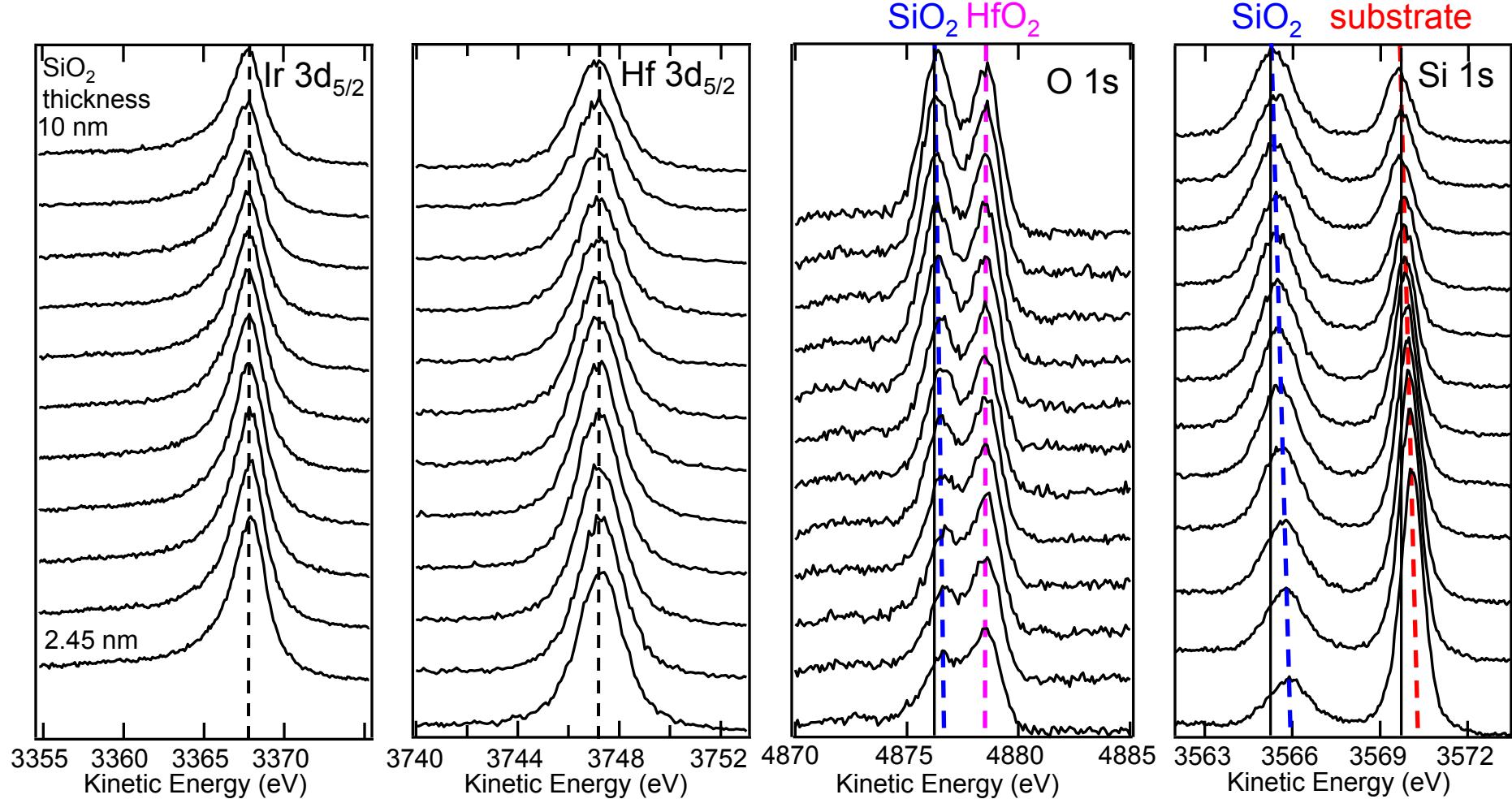
Oxide thickness determination in $\text{SiO}_2/\text{Si}(001)$

$$\frac{I_s}{I_o} = \frac{n_s \Lambda_s}{n_o \Lambda_o} \exp \left[-\frac{d}{\Lambda_o \sin \theta} \right]$$

L_o , attenuation lengths in SiO_2
 L_s , attenuation lengths in Si substrate
 d , oxide thickness
 n_o , density of Si atoms in SiO_2
 n_s , density of Si atoms in the Si substrate



Ir(8nm)/HfO₂(2.2nm)/SiO₂ (0-10 nm)/Si(100)



- The Si 1s photoelectrons from the substrate at kinetic energy of 3569 eV are still observed **through 20 nm thickness overayers**.
- The **peak shifts** of SiO₂ in O 1s spectra and both SiO₂ and Si in Si 1s spectra were observed, due to the change of the thickness of multilayer.