Study on Gate Stacks in Future Nano-Scaled CMOS using Hard X-Ray Photoelectron Spectroscopy

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Outline

- Introduction
  - Issues in gate stacks in future CMOS technology
- Chemical bonding states at high-k/Si and /Ge interfaces
  - $HfO_2/SiO_2/Si$, PrO_x/Ge, $LaAlO_3$/ALD-Al_2O_3/Ge, Pt/LA_2O_3/Si
- Electronic properties
  - Work function modulation and band offset of metal gates
  - Dielectric constant of suboxides
- Bonding states of nanostructures
  - Si nanodots
- Summary

New Materials and Structures for Future MOSFETs

- Increase in current drivability
- Suppression of short channel effects
- Suppression of power consumption
- Lowering of supply voltage

$$I_{Dsat} \uparrow \propto \mu \uparrow \frac{\varepsilon_{ox} \uparrow}{d_{ox} \downarrow} (V_G \downarrow - V_{th})^2$$

Gate Stack Engineering

High-k gate dielelectric: HfSiO, LaSiO, …

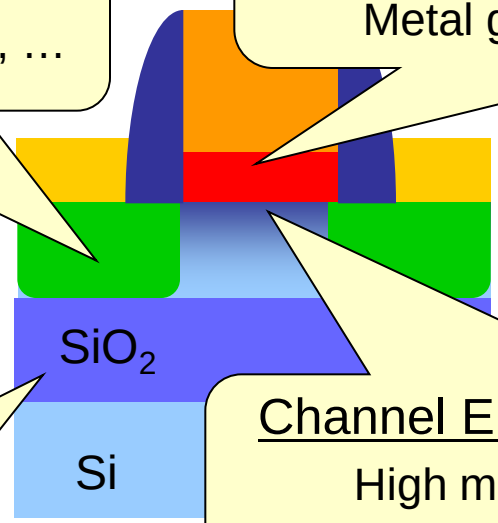
Metal gate electrode: TiSiN, TaSiN, …

I_{ON}, V_{th}, I_{leak}

Source/Drain Engineering

Schottky contact: PtSi, NiSi, …

I_{ON}, I_{leak}



I_{ON}, V_{th}

Substrate Engineering

SOI, SGOI, GOI, …

I_{ON}, V_{th}

Channel Engineering

High mobility channel: s-Si, Ge, III-V,…

3D channel: FinFET, Nanowire…

- New device engineering including new materials and new device structures become indispensable (technology boosters).
- Choices and variety of materials are spreading now and the control of interfaces becomes more and more important.

Gate dielectrics for the next generation CMOS

Requirement for gate dielectrics

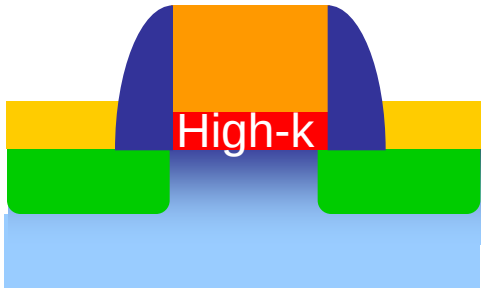
• High dielectric constant (High-k), Low leakage current, Low density of interface states, High reliability

$SiO_2 \rightarrow SiON \rightarrow HfSiON \rightarrow$ Rare-earth metal oxides (LaO_x, PrO_x,…)

• Formation of gate dielectrics on non-Si channels

strained-Si, SiGe, Ge, III-V …

Problems



➢ Reduction in dielectric constant

- Formation of interfacial reaction layers
- Diffusion of Si and Ge into high-k layers

➢ Increase in leakage current

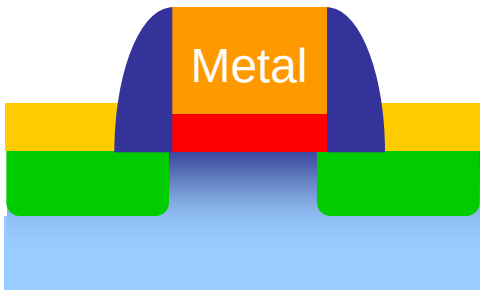
- Formation of defects in high-k (interfacial reaction and crystallization)

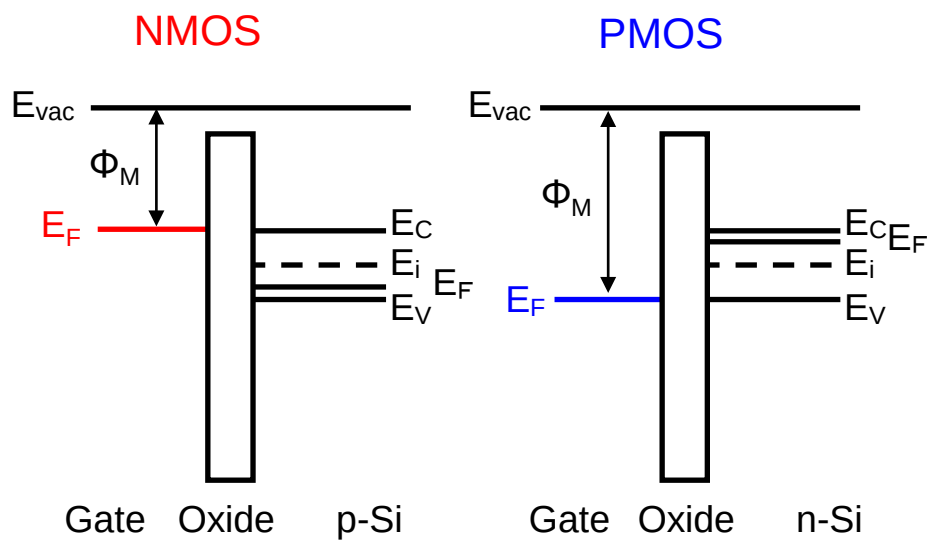
➢ Mobility degradation of MOSFETs

- Large interface state density

→ Control of interface properties of gate stacks is crucial.

Metal gate/high-k gate stacks for the next generation CMOS





Requirements for metal gates

- Control of work function
  For Si: 4.2 eV~5.2 eV
- Low resistivity
- Stability of metal/high-k interfaces

Problems

➢ Controllability of work function

- Fermi level pinning (defects formed by interfacial reaction)
- Stability of interfacial reaction (composition, crystalline phase, diffusion)

➢ Fluctuation of work function → Variability of device property such as V_{th}

- Compositional and crystalline phase uniformity, Solid-phase reaction

Requirements from CMOS technology

- Non-destructive characterization of buried interfaces in device structures
  - Wide variety of materials and multi-layered interfaces
  - Chemical bonding states of new materials such as rare-earth oxides
    - Depth-profiling of composition, chemical states, …
    - Formation of interfacial reaction layers
  - Electronic properties
    - Work function and work function modulation of metal gates on insulators
    - Dielectric constant of interfacial transition layers
- Microanalysis
  - Evaluation of variability
    - Spatial distribution of chemical and electronic properties
  - Local area analysis
    - Combination with various etching techniques/microbeam techniques
  - Characterization of nano-structures

Features of HAXPES

- High brilliance
- High excitation energy
  - Large inelastic mean free path of photoelectrons
  - Wide selectivity of core-spectra
- High energy resolution
- High spatial resolution

Long-term proposal at BL47XU of SPring-8

"Hard X-ray Photoelectron Spectroscopic Accurate Analysis of Next Generation Nano-Scale Devices for Post-Scaling Technology" (2005B0005-2008A0005)

Nagoya Univ.

Zaima, Ogawa, Sakai*, Nakatsuka, Kondo

Research management

Metal gate/high-k/Si(Ge) gate stack structure, Si nano-structures

Accurate analysis of depth profile of chemical bonding states

Development of post scaling technology

Tohoku Univ. & Musashi Inst. Tech.**

Hattori, Nohira, Tanaka

Development of analysis method for high-k/Si(Ge), metal nano-dots

JAXA

Hirose

Dielectric const. at interface

Tokyo Inst. Tech.

Iwai, Tsutsui, Kakushima

Preparation of high-k samples

Hiroshima Univ.

Miyazaki, Murakami

High-k insulators, Metal/high-k interface, Si nano-structure

Osaka Univ.

Setsuhara, Takenaka

Polymer thin-films, Ultra shallow junctions

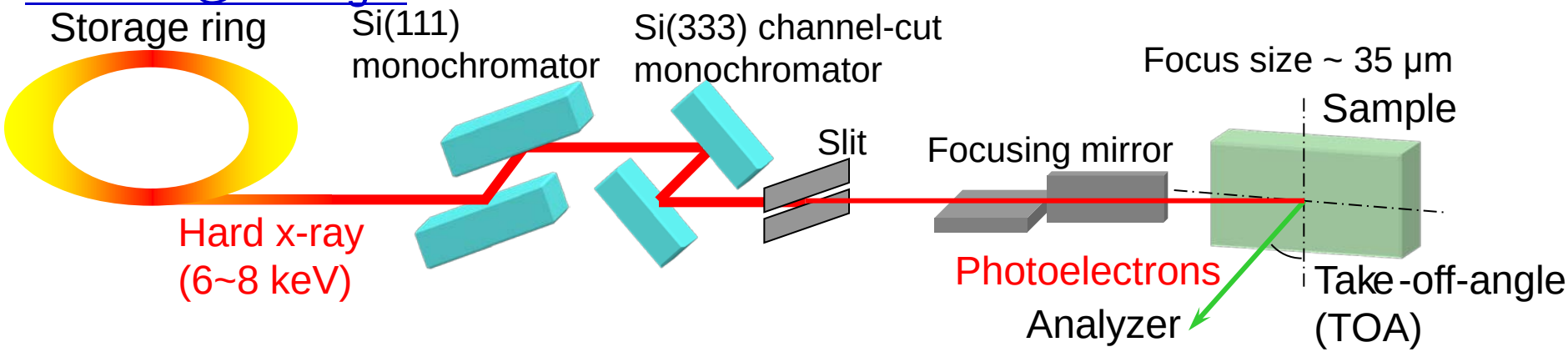
JASRI Ikenaga, Kobata, Kim, Son, Machida

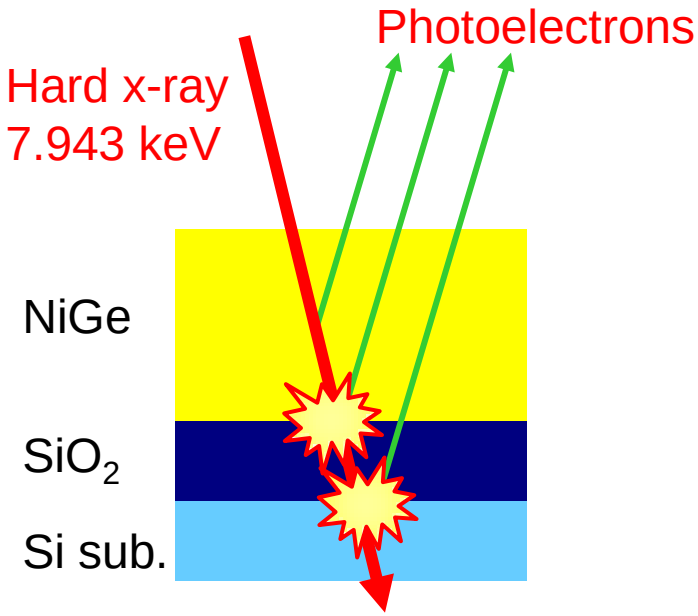
Development of analysis method, Support and advise

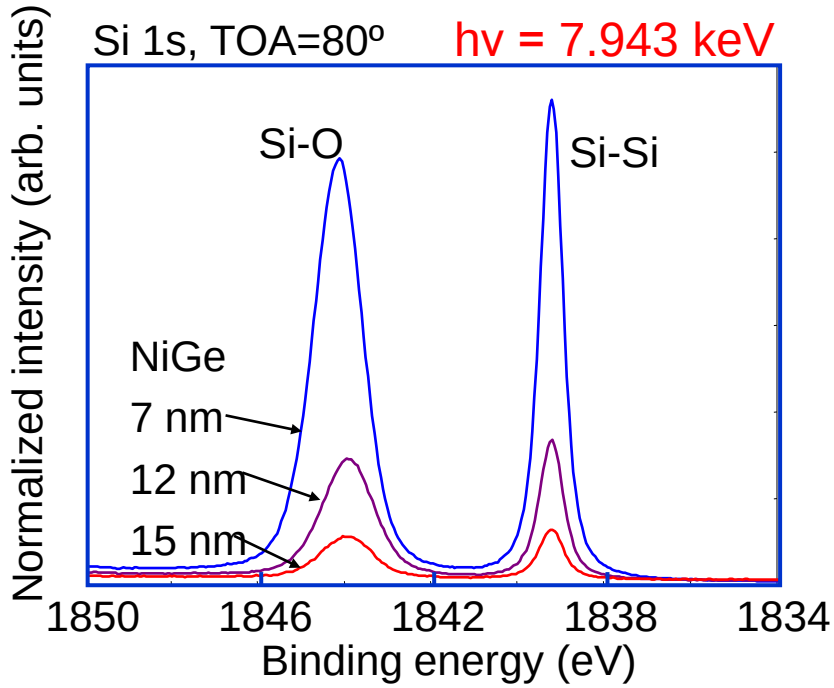
*Present affiliation: Osaka Univ. **Present name: Tokyo City Univ.

Non-destructive depth profiling by HAXPES

BL47XU@SPring 8





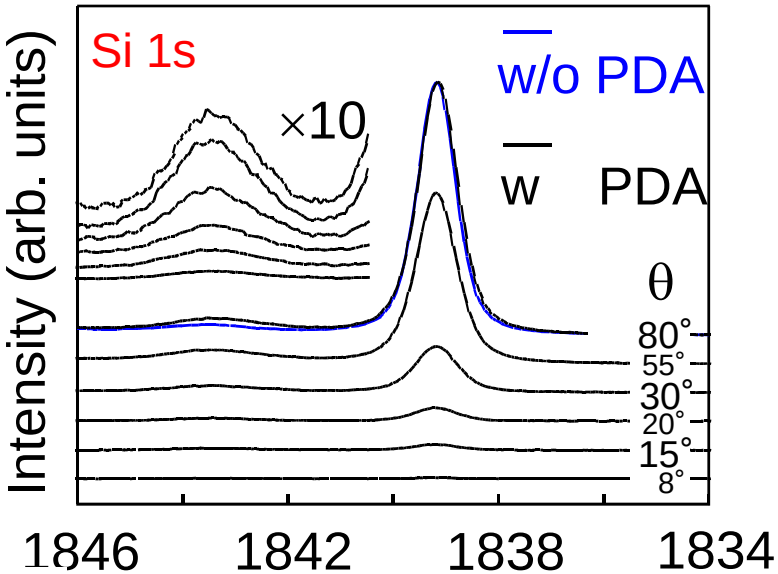


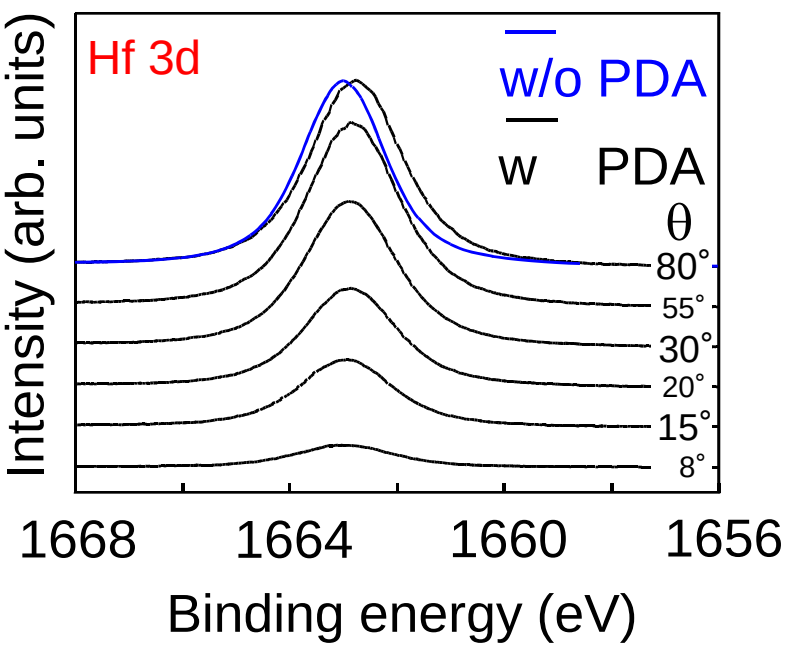
Detection of Si1s photoelectrons from Si substrate through NiGe(15nm)/SiO_2(12nm)

→ Analysis of buried interfaces

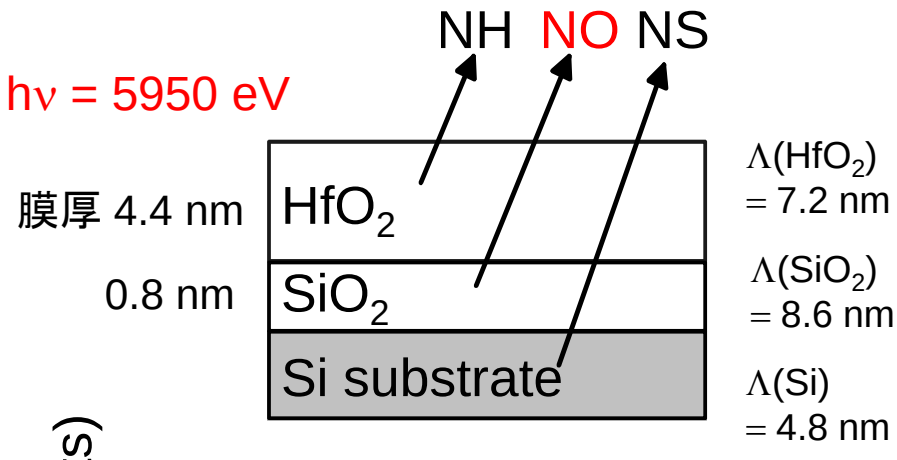
T. Hattori, H. Nohira, K. Azuma, K. W. Sakai, K. Nakajima, M. Suzuki, K. Kimura, Y. Sugita, E. Ikenaga, K. Kobayashi, Y. Takata, H. Kondo, and S. Zaima, Int. J. High Speed Electronics ***16*** *(2006) 353.*

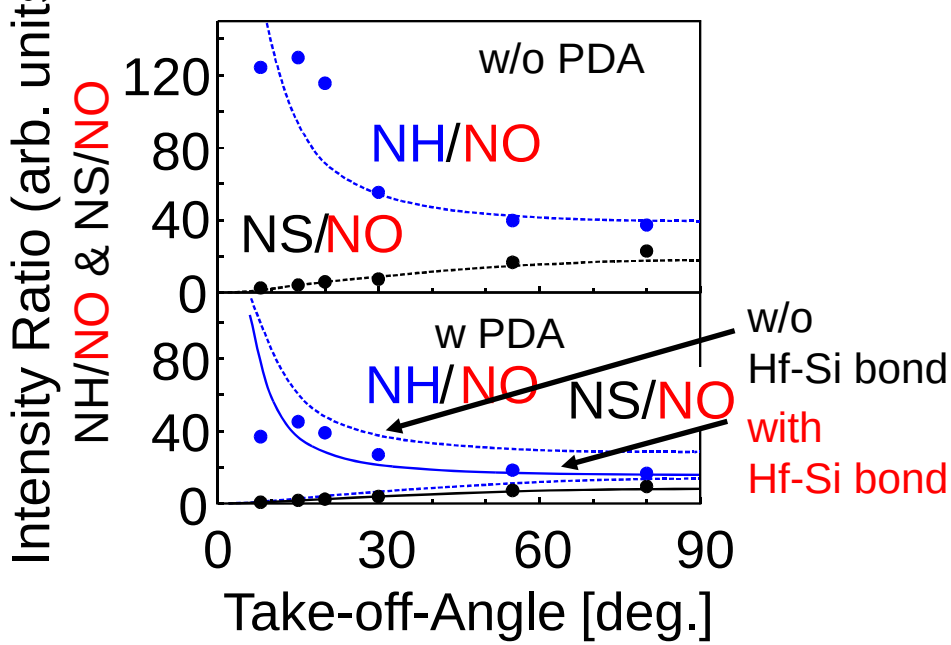
Hf-Si chemical bonding states at $HfO_2/SiO_2/Si$ interfaces





PDA: RTA in 1 atm. N_2 at 1000°C for 5 sec.



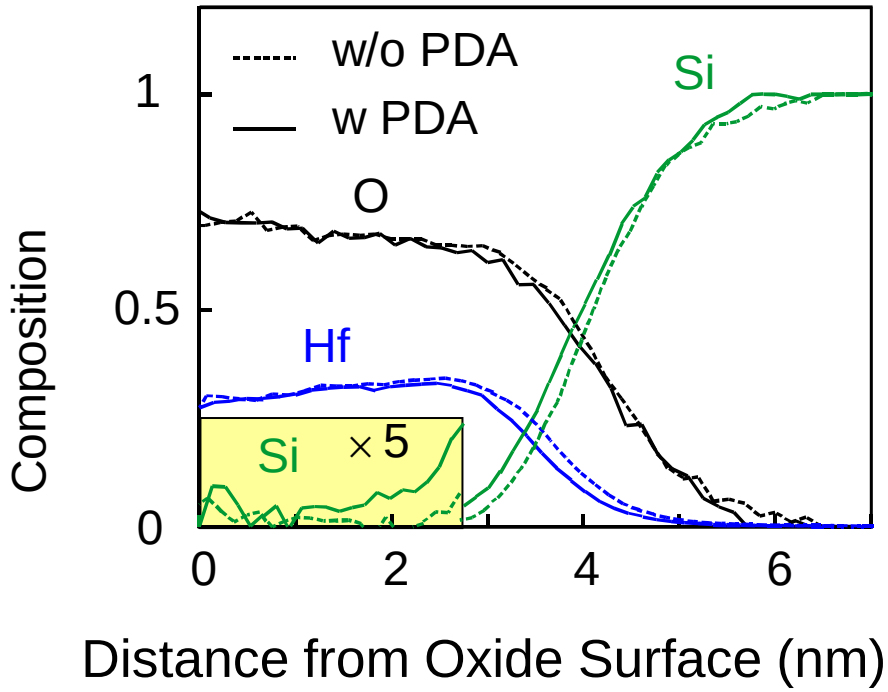


T. Hattori, H. Nohira, K. Azuma, K. W. Sakai, K. Nakajima, M. Suzuki, K. Kimura, Y. Sugita, E. Ikenaga, K. Kobayashi, Y. Takata, H. Kondo, and S. Zaima, Int. J. High Speed Electronics ***16*** *(2006) 353.*

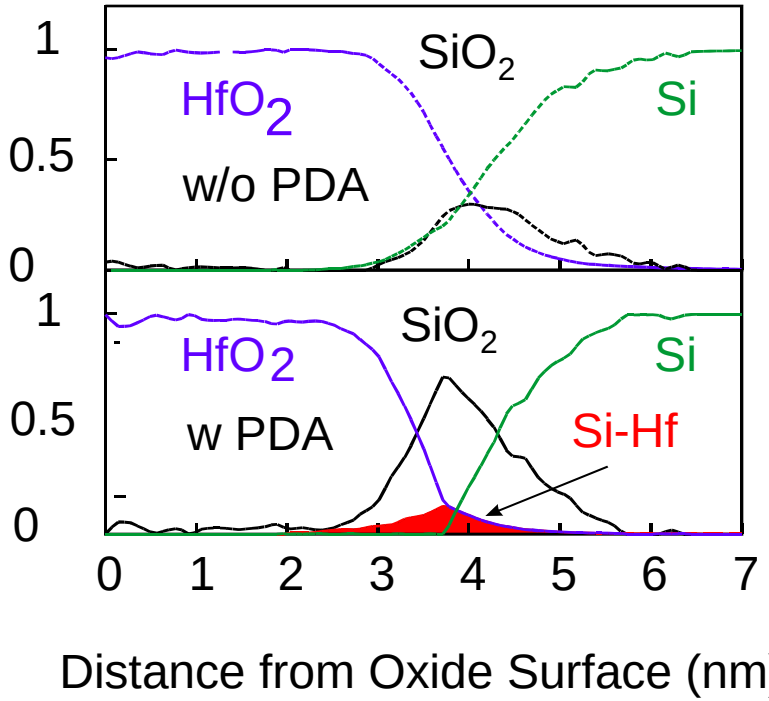
Depth profile of chemical bonding states at $HfO_2/SiO_2/Si$ interfaces

PDA: Annealing in 1 atm N_2 at 1000℃ for 5 min.

High-resolution RBS



Angle-resolved PES



Clarifying depth profiles of Hf-Si chemical bonding states at the buried interface region by the combination of HR-RBS performed by K. Kimura *et al*. (Kyoto Univ.) and HAXPS.

T. Hattori, H. Nohira, K. Azuma, K. W. Sakai, K. Nakajima, M. Suzuki, K. Kimura, Y. Sugita, E. Ikenaga, K. Kobayashi, Y. Takata, H. Kondo, and S. Zaima, Int. J. High Speed Electronics ***16*** *(2006) 353.*

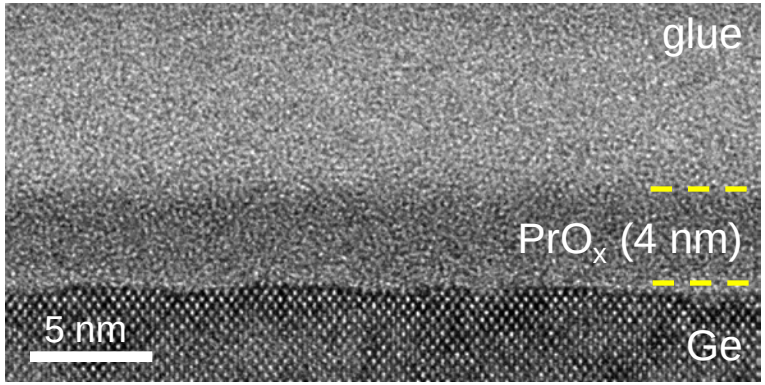
Interfacial reaction in PrO_x/Ge structures

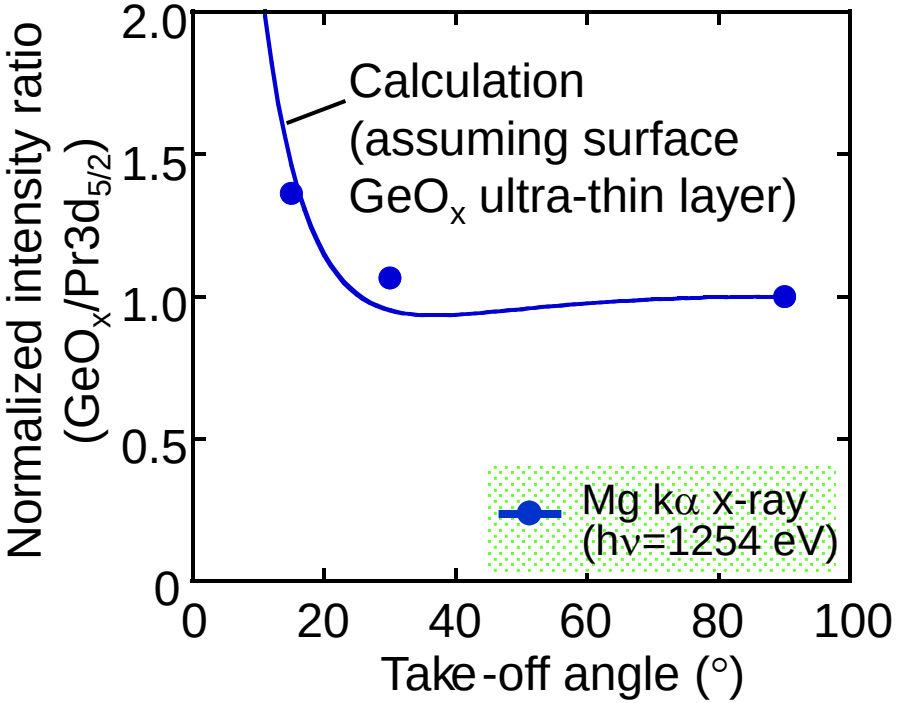
Interfacial reaction between rare earth oxides and Ge substrates

- ✓ Formation of low dielectric layers → Reduction in dielectric constant
- ✓ Diffusion of GeO into high-k layers from interfaces
  - → Increase in interface state density and leakage current
  - → Reduction in dielectric constant of high-k layers

Cross-sectional TEM image of PrO_x/Ge

Pulsed laser deposition:
In vacuum at 200°C





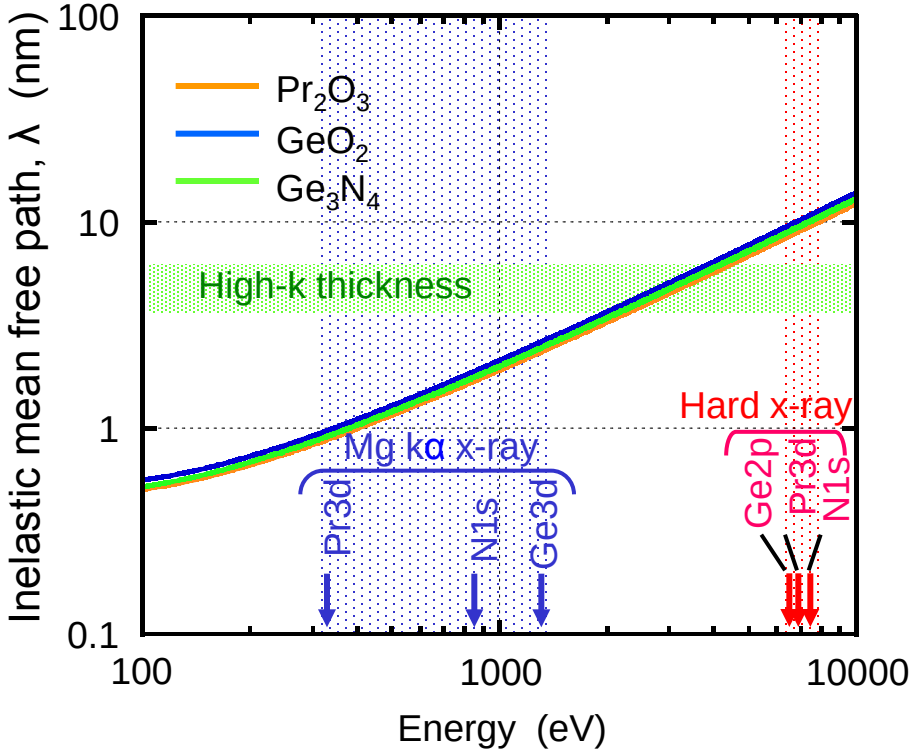
- ✓ No interfacial layer
- ✓ Dielectric constant: ε_r~8
  (Pr_2O_3: ε_r~24)

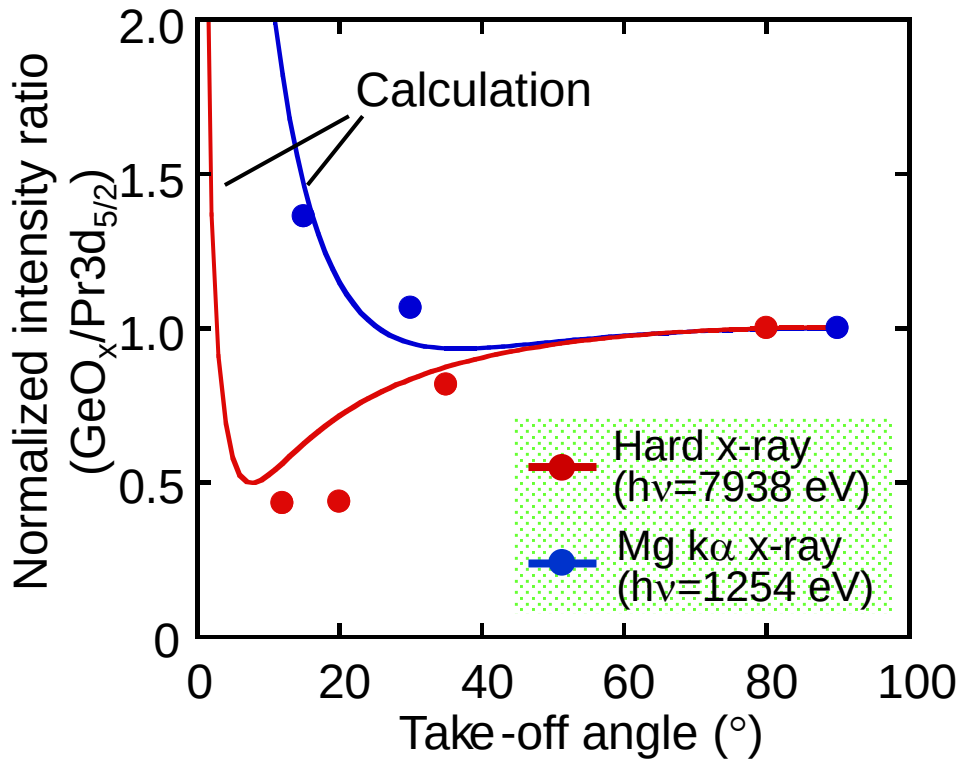
- ✓ Surface GeO_x ultra-thin layers

M. Sakashita, N. Kito, A. Sakai, H. Kondo, O. Nakatsuka, M. Ogawa and S. Zaima, Ext. Abst. of SSDM2007, pp. 330.

Angle resolved HAXPES and XPS analysis for PrO_x/Ge structures

✓ Depth profile analysis by using difference of inelastic mean free path of photoelectrons for conventional XPS and HAXPES.





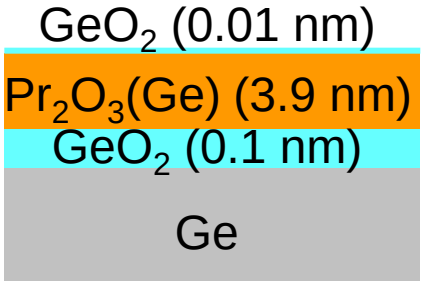
Insulator thickness: 4-8 nm

✓ Hard x-ray

λ : ~10 nm → Whole insulator layers

✓ Mg kα x-ray

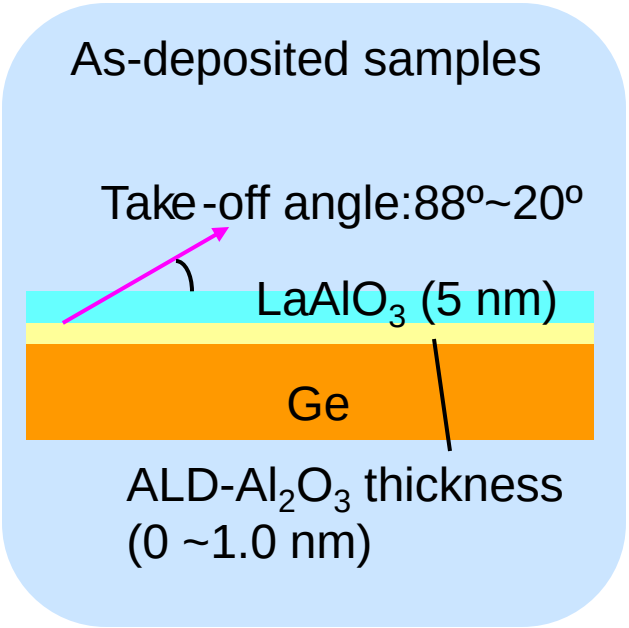
λ : 1~3 nm → Surface only

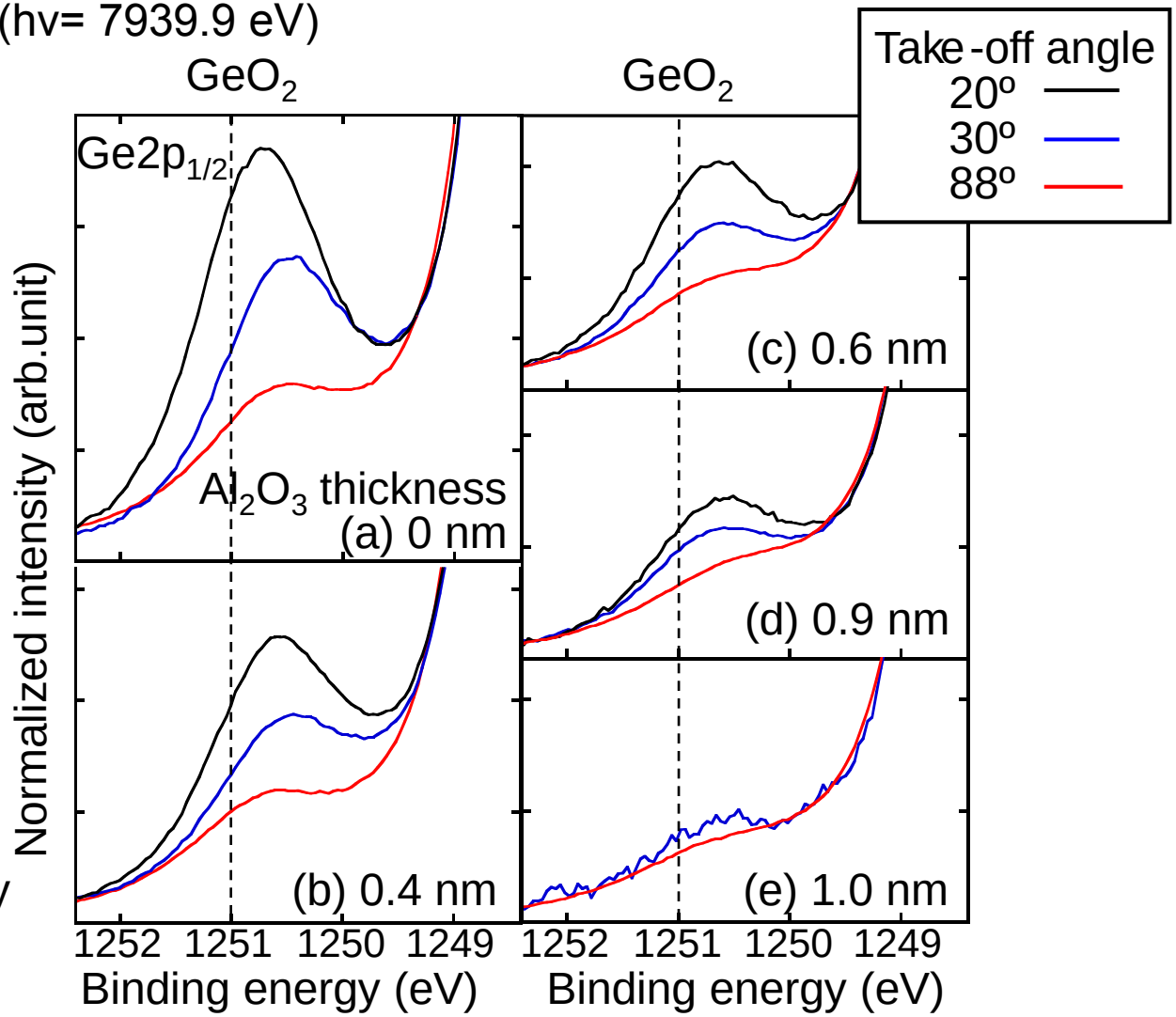


M. Sakashita, N. Kito, A. Sakai, H. Kondo, O. Nakatsuka, M. Ogawa and S. Zaima, Ext. Abstr. of SSDM2007, pp. 330.

ALD-Al_2O_3 thickness dependence of Ge oxide formation

ARXPS @SPring-8 BL47XU (hv= 7939.9 eV)





∗ Normalized by Ge^{0+} intensity

- ✓ Ge2p is analyzed because Ge3d and La5s peaks are overlapped.
- ✓ Ge oxidation is suppressed by ALD-Al_2O_3 with increasing Al_2O_3 thickness.

R. Kato, S. Kyogoku, M. Sakashita, H. Kondo, and S. Zaima, Jpn. J. Appl. Phys. ***48*** *(2009) 05DA04.*

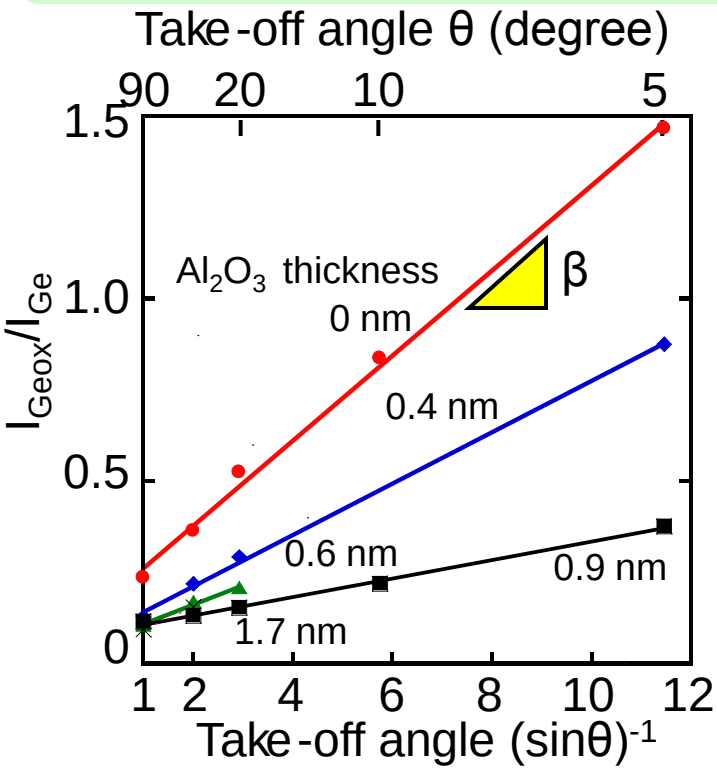
Evaluation of the amount of Ge oxide

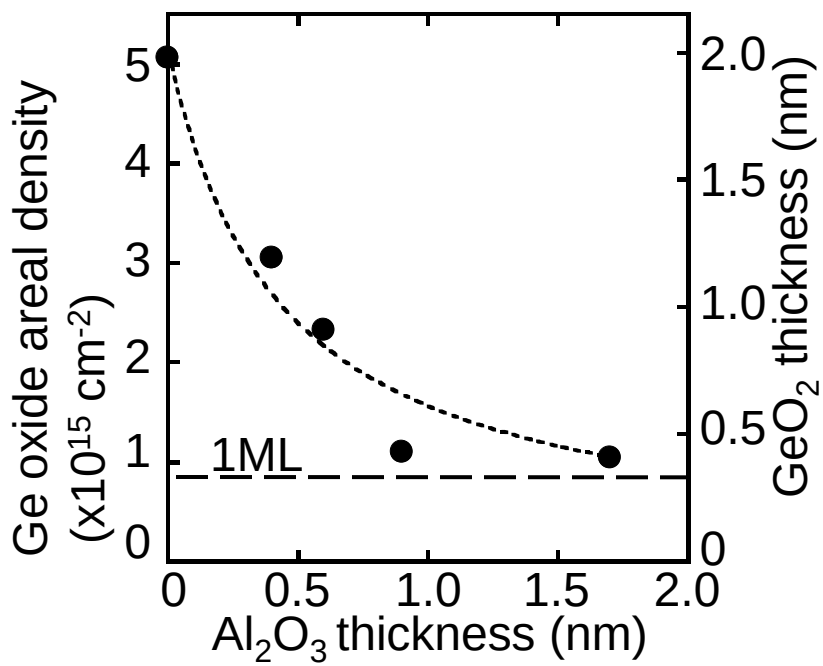
$$\frac{I_{GeOx}}{I_{Ge}} = \frac{X_{GeOx}}{X_{Ge}}\left[\exp\left(\frac{T_{GeOx}}{\lambda}\frac{1}{\sin\theta}\right)-1\right]$$

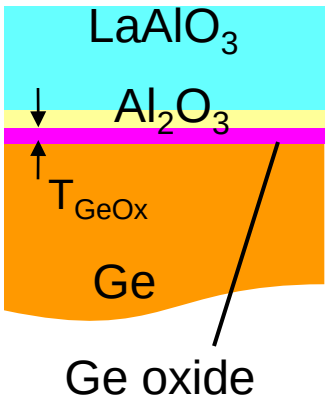
$$\approx \underbrace{\frac{X_{GeOx}T_{GeOx}}{X_{Ge}\lambda}}_{\text{Gradient: }\beta}\frac{1}{\sin\theta}$$

∗ Taylor expansion (large mean free path)

I_{GeOx} : Area intensity of Ge oxide
I_{Ge} : Area intensity of Ge^{0+}
X_{GeOx} : Density of Ge oxide
X_{Ge} : Density of Ge of substrate
T_{GeOx} : Ge oxide thikness
λ : Mean free path for Ge2p in Al_2O_3 (9.73 nm)
θ : Take-off angle (88° ~ 5°)
$X_{GeOx}T_{GeOx}$: Ge oxide surface density



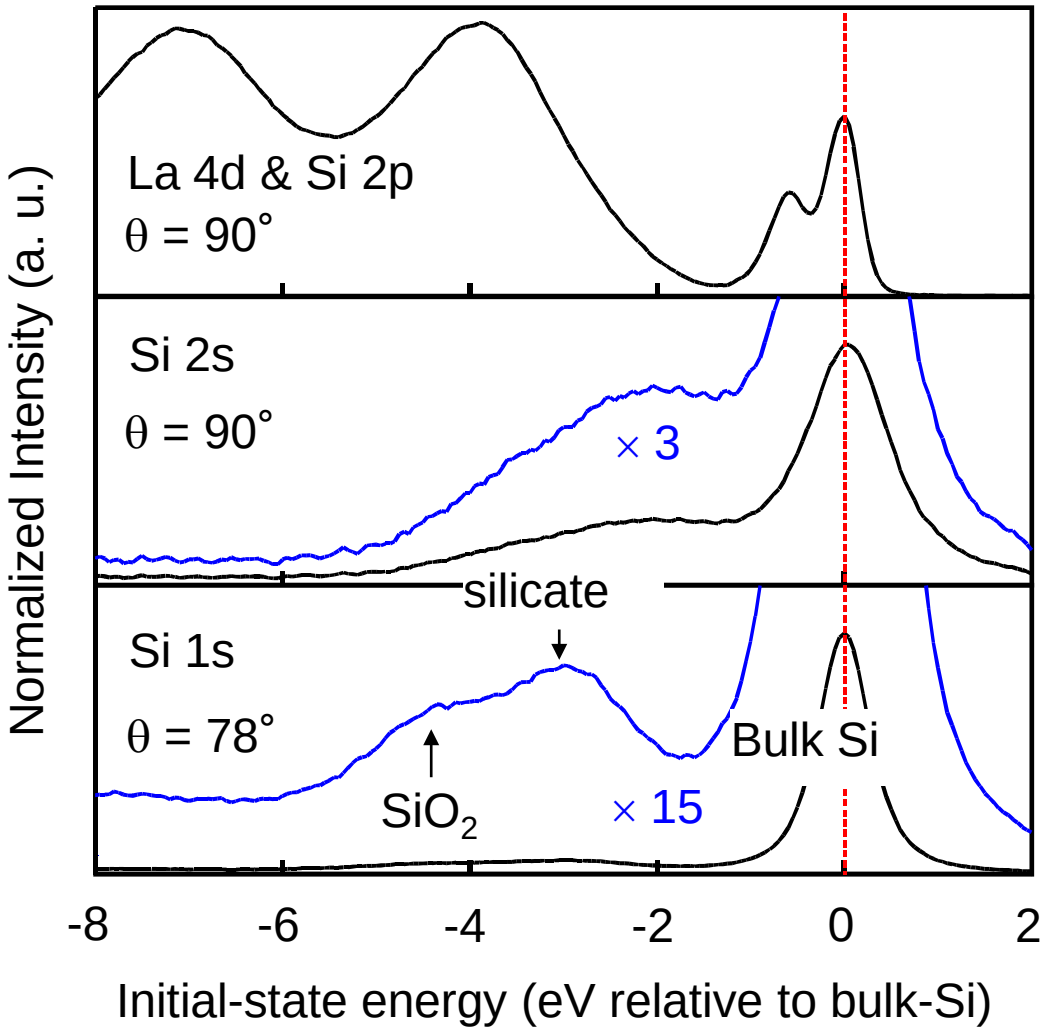




✓ Interfacial reaction between Ge and high-k layers are suppressed.
→ Formation of Ge oxide can be controlled in monolayer thickness.

R. Kato, S. Kyogoku, M. Sakashita, H. Kondo, and S. Zaima, Jpn. J. Appl. Phys. ***48*** *(2009) 05DA04.*

Detection of interfacial layers by XPS and HAXPES



Si2p spectrum overlaps with La 4d spectrum.

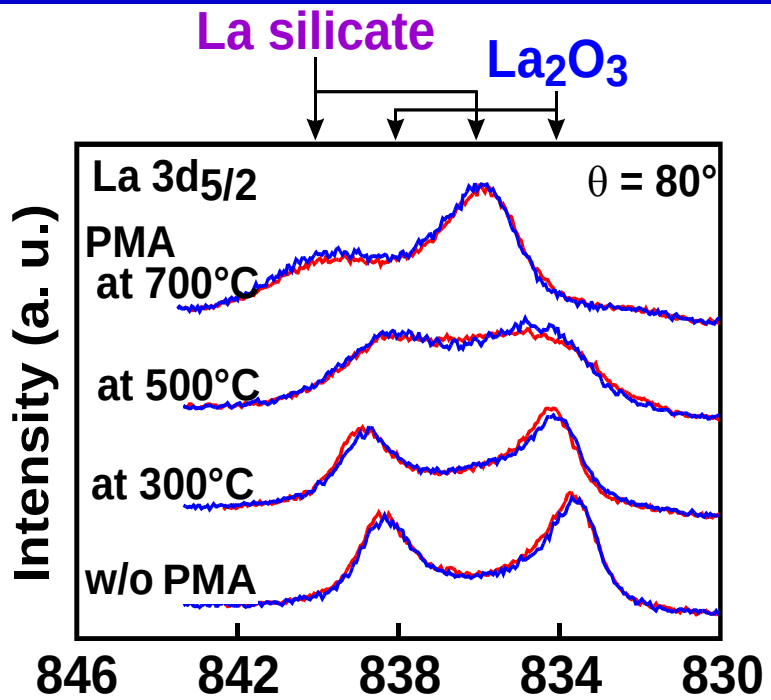
FWHM of Si2s spectrum is not small enough for the detection of interfacial layers.

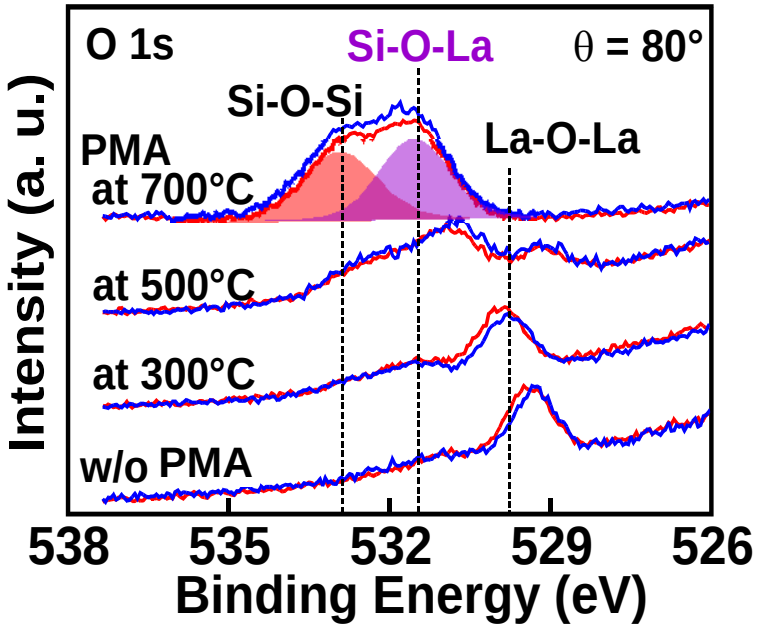
FWHM of Si1s spectrum is small enough for the detection of interfacial layers.

We can detect detail chemical structures of interfacial transition layers by measuring Si1s core-spectra by HAXPES.

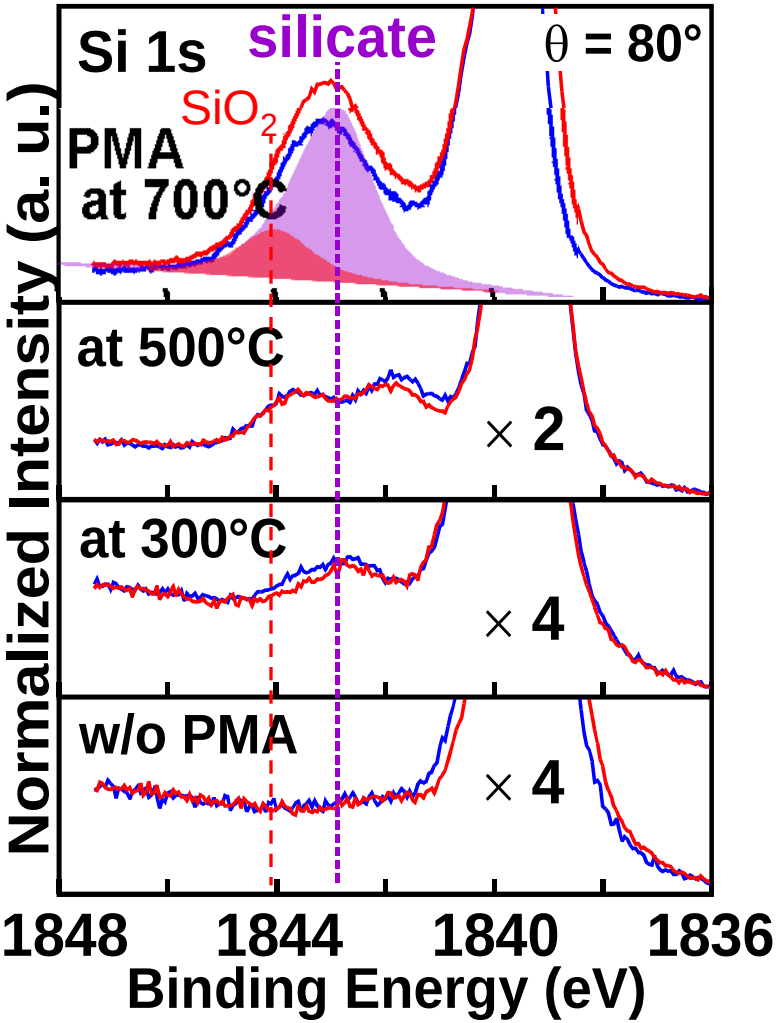
H. Nohira, T. Shiraishi, K. Takahashi, T. Hattori, I. Kashiwagi, C. Ohshima, S. Ohmi, H. Iwai, S. Joumori, K. Nakajima, M. Suzuki, K. Kimura, Appl. Surf. Sci. ***234*** *(2004) 493.*

Annealing temperature dependence of $Pt/La_2O_3/Si$ structures





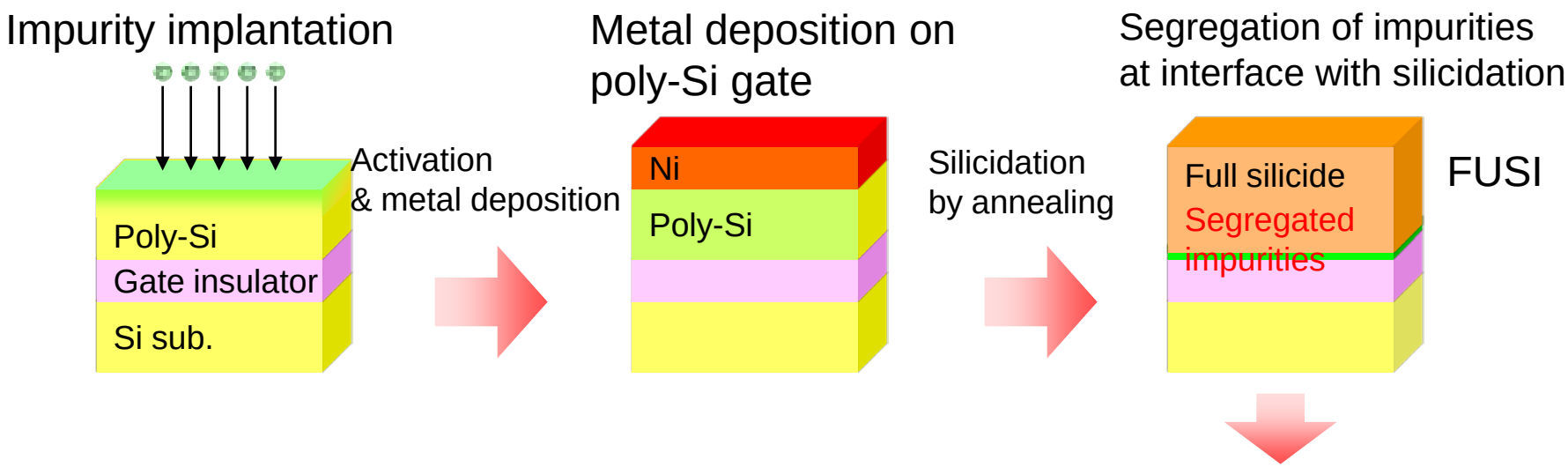
(Deposited at 300°C and RT)



La-O-Si bonds increase with increasing PMA temperature.

H. Nohira et al., Appl. Surf. Sci. ***234*** *(2004) 493.*

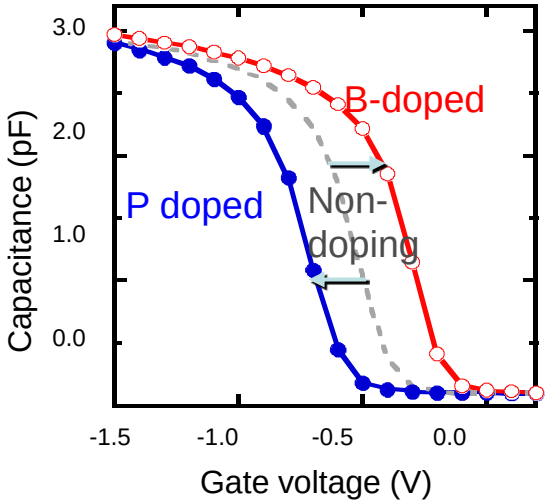
Control of work function at $NiSi_x/SiO_2$ interface by impurity segregation



Threshold voltage shifts with segregation of impurities at the interface.

- ✓ Change of work functions of metal gates
- ✓ Different modulation behavior between B and P

Small ← Work function → Large



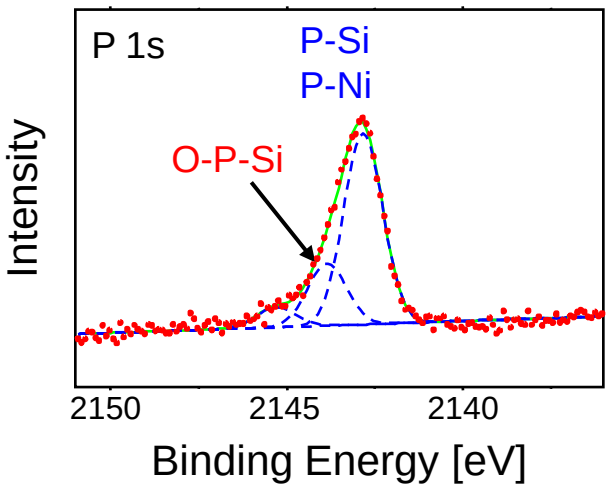
Why is the work function changed?

→ HAXPES observation of chemical bonding states at $NiSi_x/Si$ interfaces

TOSHIBA
Leading Innovation >>>

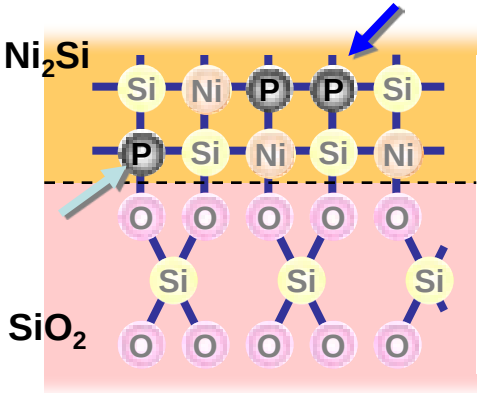
(by courtesy of Dr. Yoshiki, TOSHIBA)

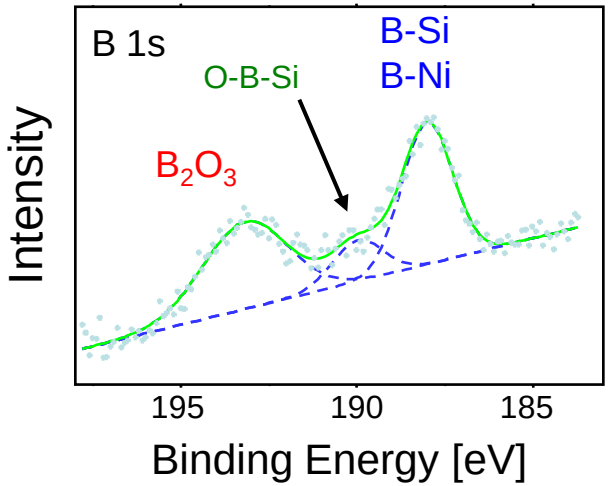
Estimation of impurity segregation from chemical bonding states



HAX-PES[1)]

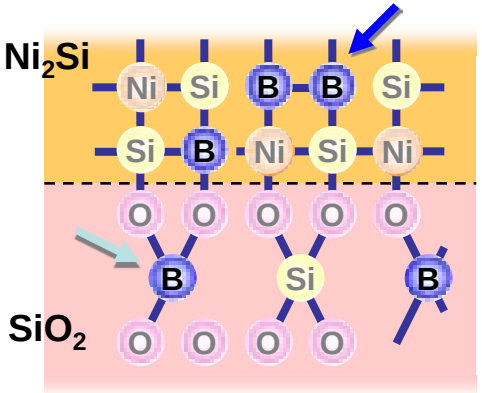
P and As segregate from interface to electrode





Backside XPS[2)]

B segregates from electrode to insulator



Different segregation position of impurities at interface regions → Different modulation behavior of work functions

Y. Tsuchiya, M. Yoshiki, J. Koga, A. Nishiyama, M. Koyama, M. Ogawa, and S. Zaima, Jpn. J. Appl. Phys. ***47*** *(2008) 8321.*
Y. Tsuchiya, M. Yoshiki, A. Kinoshita, M. Koyama, J. Koga, M. Ogawa, and S. Zaima, J. Appl. Phys. ***102****, 104504 (2007).*

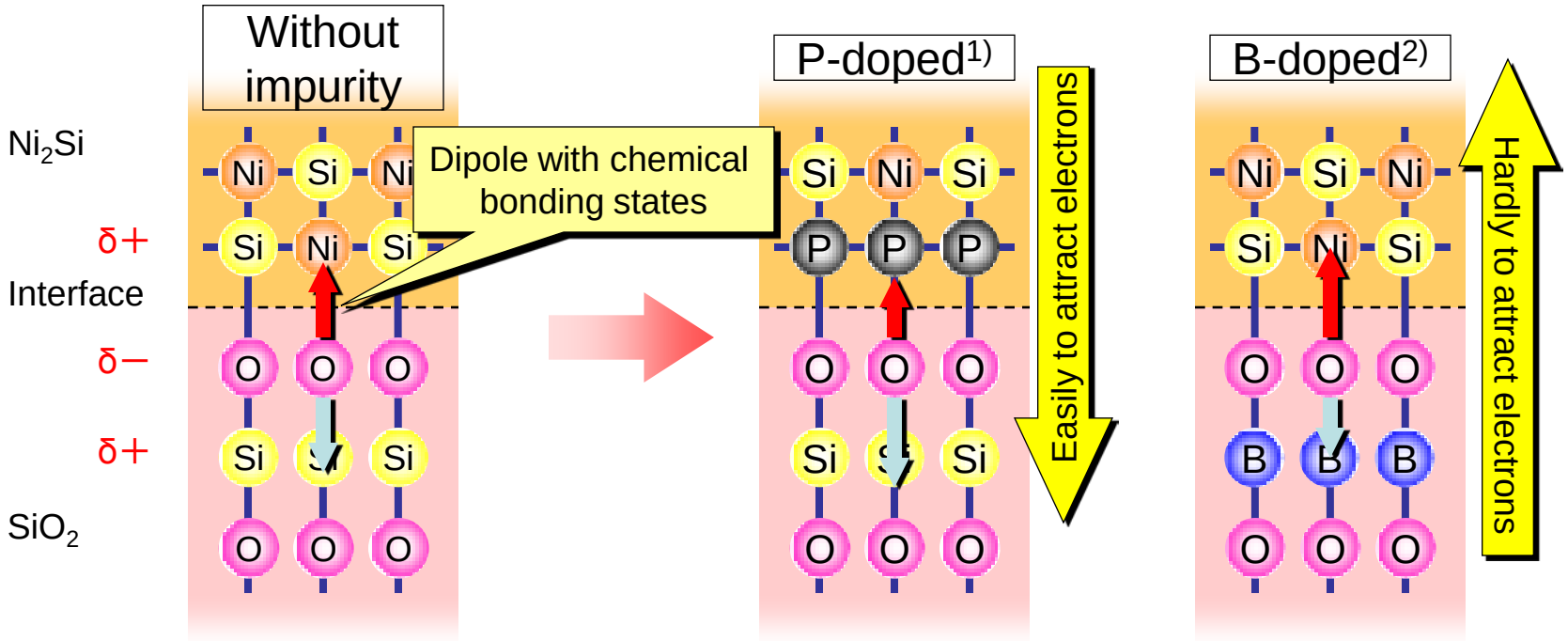
Dependence of interface dipole on impurity segregation

■ Qualitative estimation of interface dipole by electronegativity

Electronegativity: The ability of an atom to attract electrons towards itself.

Pauling electronegativity

B	O	Si	P	Ni	As
2.04	3.44	1.90	2.19	1.91	2.18



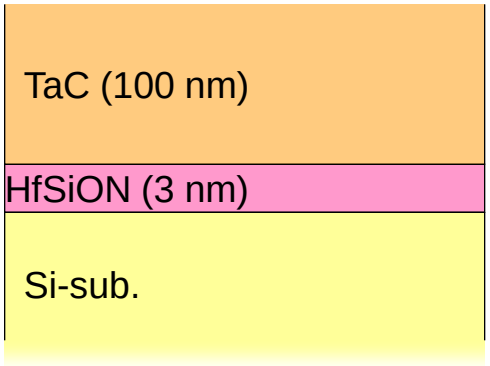
Direction of interface dipole depends on impurity position at the interface region.

→ Direction of work function modulation can be controlled.

Y. Tsuchiya, M. Yoshiki, J. Koga, A. Nishiyama, M. Koyama, M. Ogawa, and S. Zaima, Jpn. J. Appl. Phys. ***47*** *(2008) 8321.*
Y. Tsuchiya, M. Yoshiki, A. Kinoshita, M. Koyama, J. Koga, M. Ogawa, and S. Zaima, J. Appl. Phys. ***102****, 104504 (2007).*

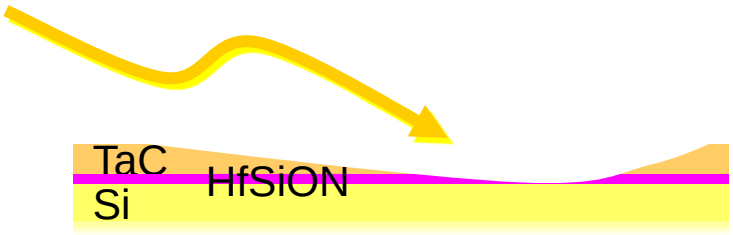
Spatial resolved HAXPES for TaC/HfSiON/Si structure

■ Annealing condition dependence of flat band voltage shifts in TaC/HfSiON/Si samples



Two MIS samples with different annealing condition

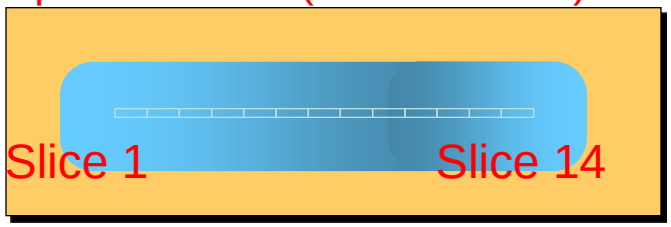
- Different behavior of flat band voltage shift
  ⇒ Difference of energy band offset ?
- Too thick even for HAXPES measurement
  ⇒ *Ex-situ* etching before measurement



Gradient etching by Ar ion sputtering

→ Spatial resolved mode of HAXPES

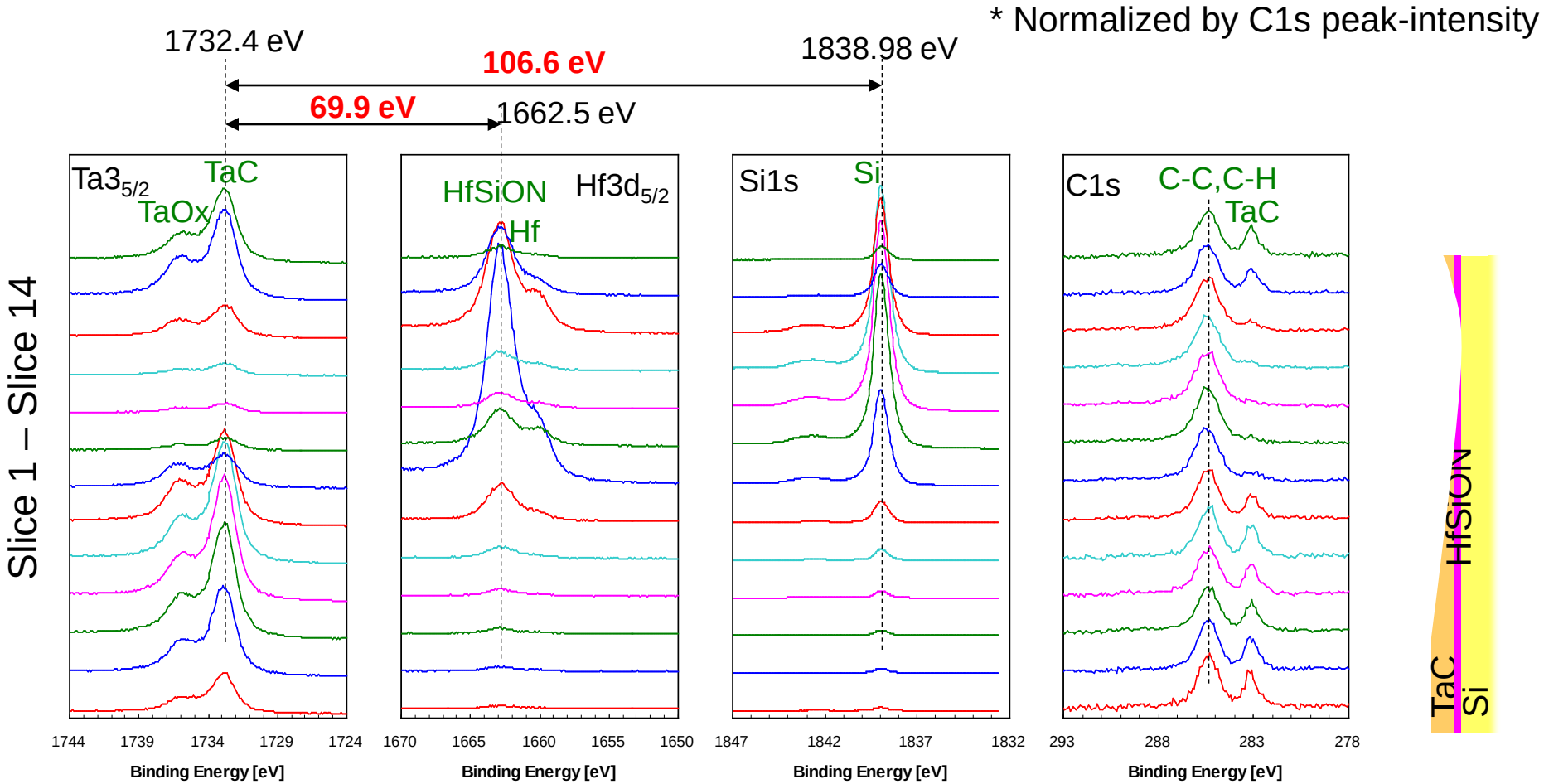
Sputtered area (4 mm x 1 mm)



Analyzed area (3.6 mm x 0.1 mm)

(by courtesy of Dr. Yoshiki, TOSHIBA)

Spatial resolved HAXPES for TaC/HfSiON/Si sample A



- Simultaneous measurement of spectra from electrode surface to Si substrate by spatial resolved HAXPES
- Observed chemical bonding states of Hf: HfSiON and Hf metal
  ⇒ Reduction of HfSiON by TaC interface or/and sputtering for etching

TOSHIBA
Leading Innovation >>>

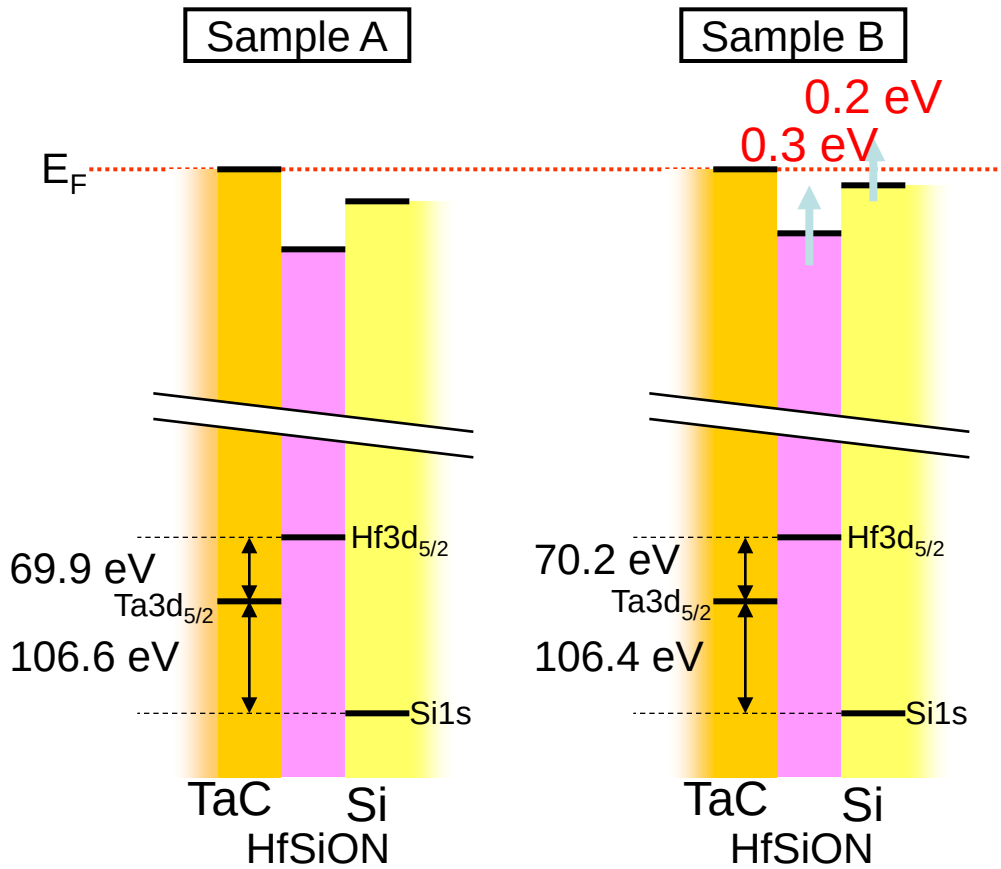
(by courtesy of Dr. Yoshiki, TOSHIBA)

Comparison of energy band alignment estimated by HAXPES

■ Relative comparison of valence band offset

Peak energy of photoelectron (eV)

peak	Sample A	Sample B
$Ta3d_{5/2}$ (TaC)	1732.4	1732.5
$Hf3d_{5/2}$ (HfSiON)	1662.5	1662.3
Si1s (Si-sub.)	1838.98	1838.90

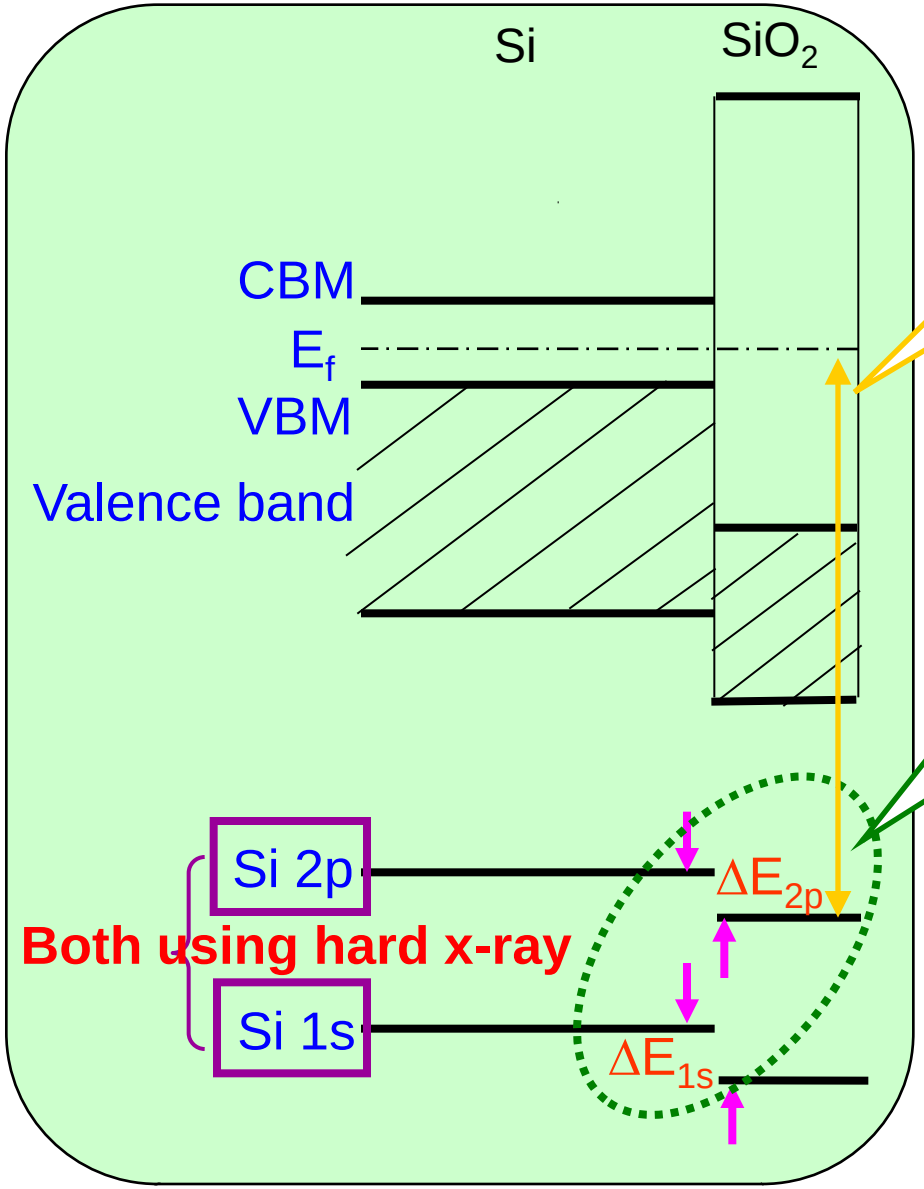


Valence-band-maxima of HfSiON and Si for that of TaC increase in sample B.

⇒ Corresponding to increase in the effective work function

(by courtesy of Dr. Yoshiki, TOSHIBA)

Novel technique for relative chemical shift measurement by HAXPES



Conventional technique

Relative chemical shift

$$\Delta E_{1s} - \Delta E_{2p} = \delta\Delta E_{chem}$$

Intrinsic factor !

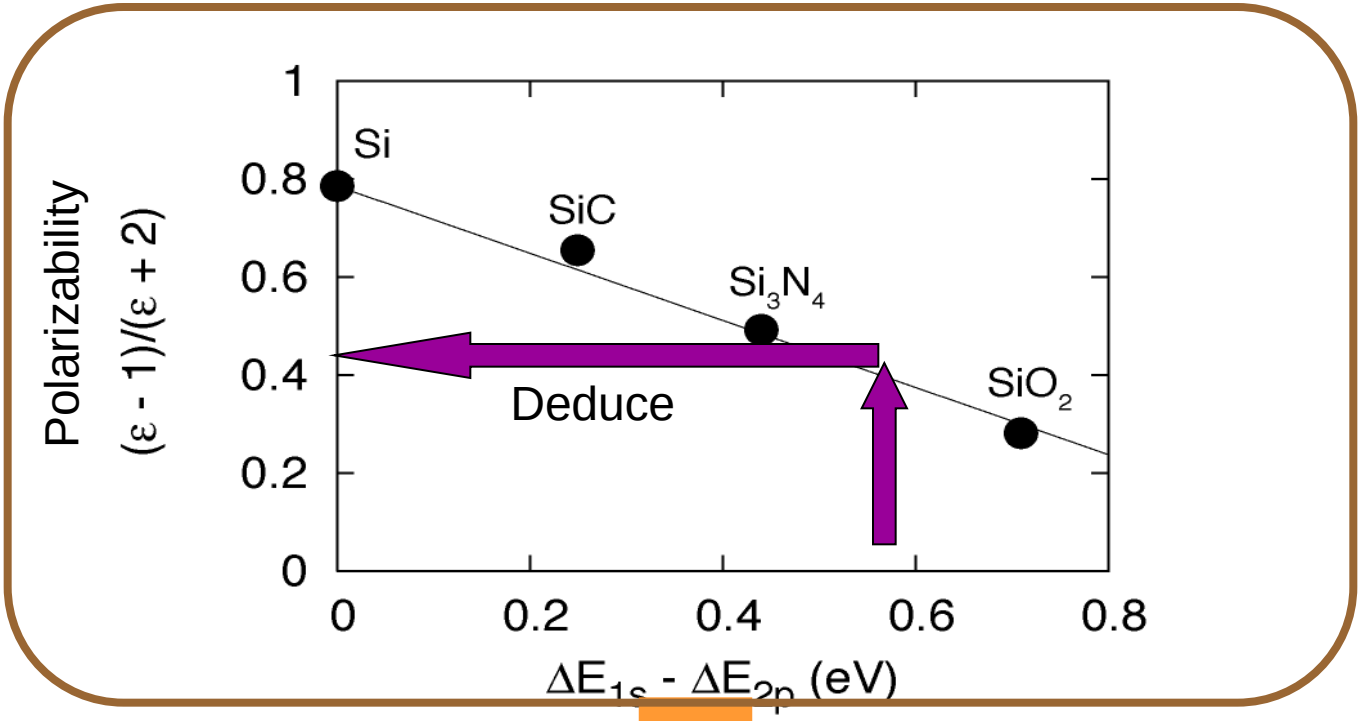
Intrinsic nature of Si chemical bonds can be extracted from $\Delta E_{1s} - \Delta E_{2p}$.

✓ HAXPES realizes measurement of Si1s core spectrum !

K. Hirose, M. Kihara, D. Kobayashi, H. Okamoto, S. Shinagawa, H. Nohira, E. Ikenaga, M. Higuchi, A. Teramoto, S. Sugawa, T. Ohmi, and T. Hattori, Appl. Phys. Lett. ***89,*** *154103 (2006).*

Deduction of dielectric constant from difference of core-level energy

$\Delta E_{1s} - \Delta E_{2p}$ is an excellent indicator for the optical dielectric constant ε of the Si atom in Si compounds



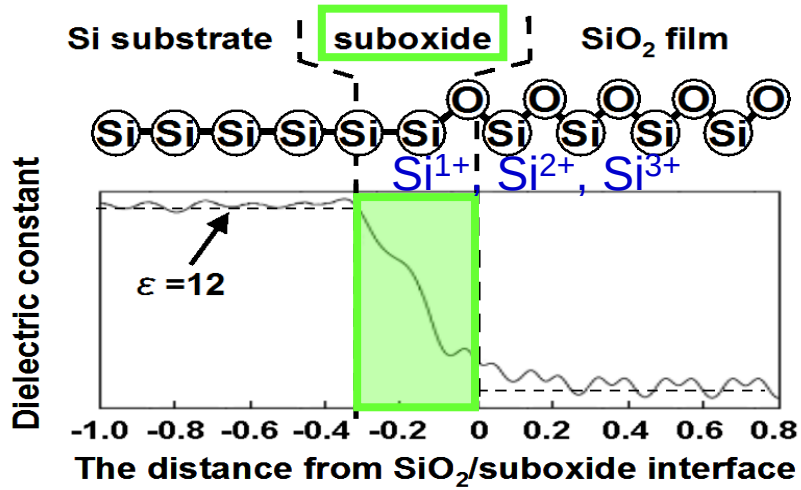
1. We will measure ΔE_{1s} - ΔE_{2p} for suboxide at SiO_2/Si.
2. Then we will deduce ε for suboxide from the measured ΔE_{1s} - ΔE_{2p} values using this correlation.

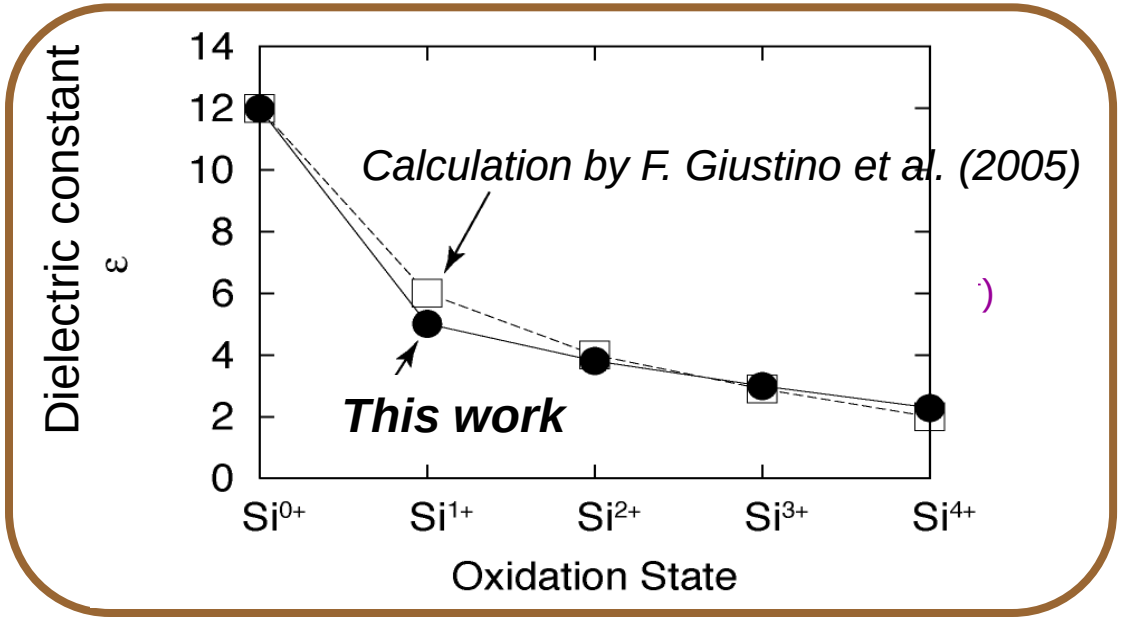
K. Hirose, M. Kihara, D. Kobayashi, H. Okamoto, S. Shinagawa, H. Nohira, E. Ikenaga, M. Higuchi, A. Teramoto, S. Sugawa, T. Ohmi, and T. Hattori, Appl. Phys. Lett. ***89,*** *154103 (2006).*

Deduction of local dielectric constant ε of suboxide from ΔE_{1s}- ΔE_{2p}

Measured $\Delta E_{1s} - \Delta E_{2p}$ for Si^{1+}, Si^{2+}, Si^{3+}

Deduction



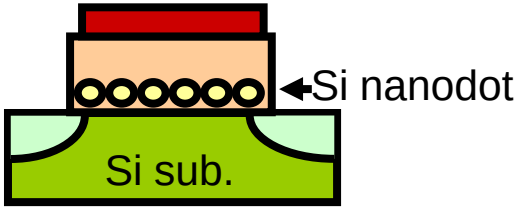


Estimation of dielectric constant at interface region by HAXPES

K. Hirose, M. Kihara, D. Kobayashi, H. Okamoto, S. Shinagawa, H. Nohira, E. Ikenaga, M. Higuchi, A. Teramoto, S. Sugawa, T. Ohmi, and T. Hattori, Appl. Phys. Lett. ***89,*** *154103 (2006).*

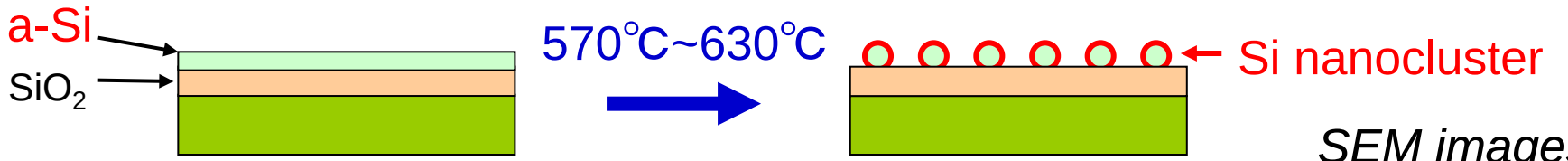
Si nanodot structures for quantum dot memory

✓ Analysis of crystalline structures of Si nanodot by HAXPES

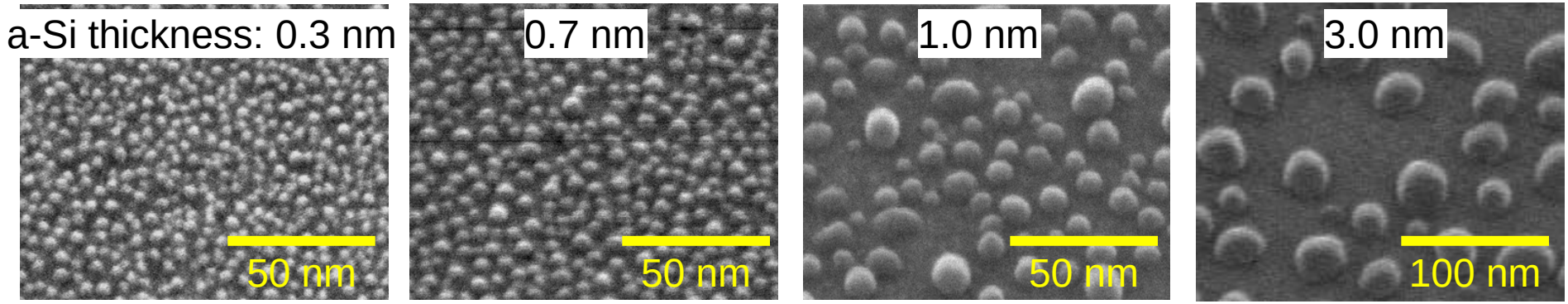


Quantum dot memory

■ Formation of ultra-high-density Si nanodots from amorphous a Si thin-layer



SEM images



Density: 3.1×10^{12} cm^{-2}	2.1×10^{12} cm^{-2}	4.1×10^{11} cm^{-2}	4.2×10^{10}cm^{-2}
Diameter: 4.9 ± 0.6 nm	6.0 ± 0.9 nm	9.0 ± 3.1 nm	27 ± 7 nm

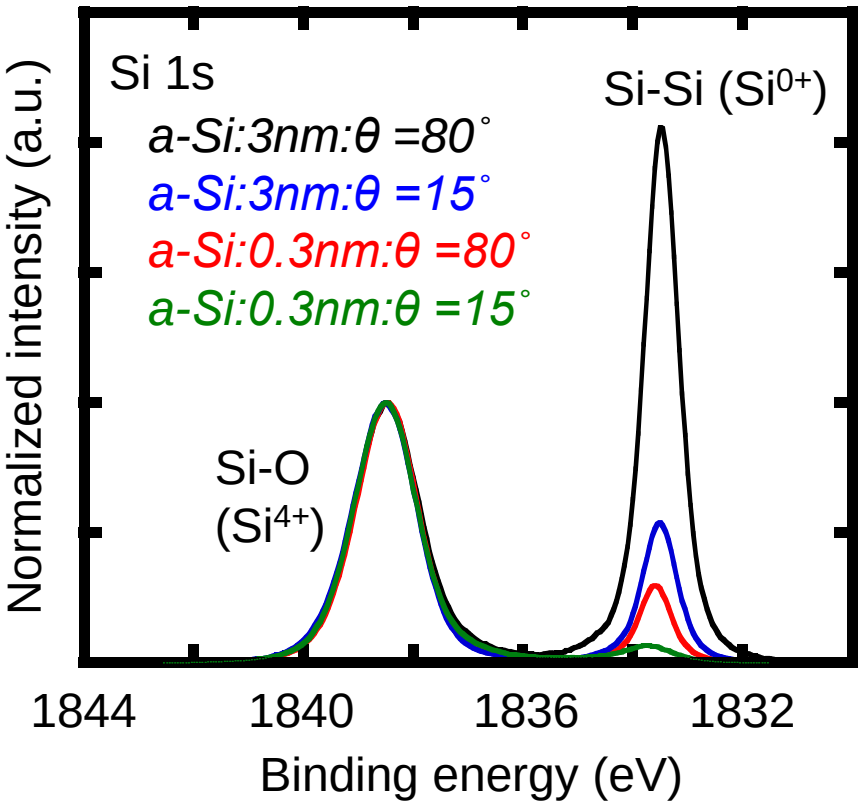
- a-Si thickness ~0.3 nm ・・・ We cannot observe by using conventional XRD or XPS.
- Si nanodots with amorphous structure (3~5 nm) ・・・ We cannot observe by TEM.

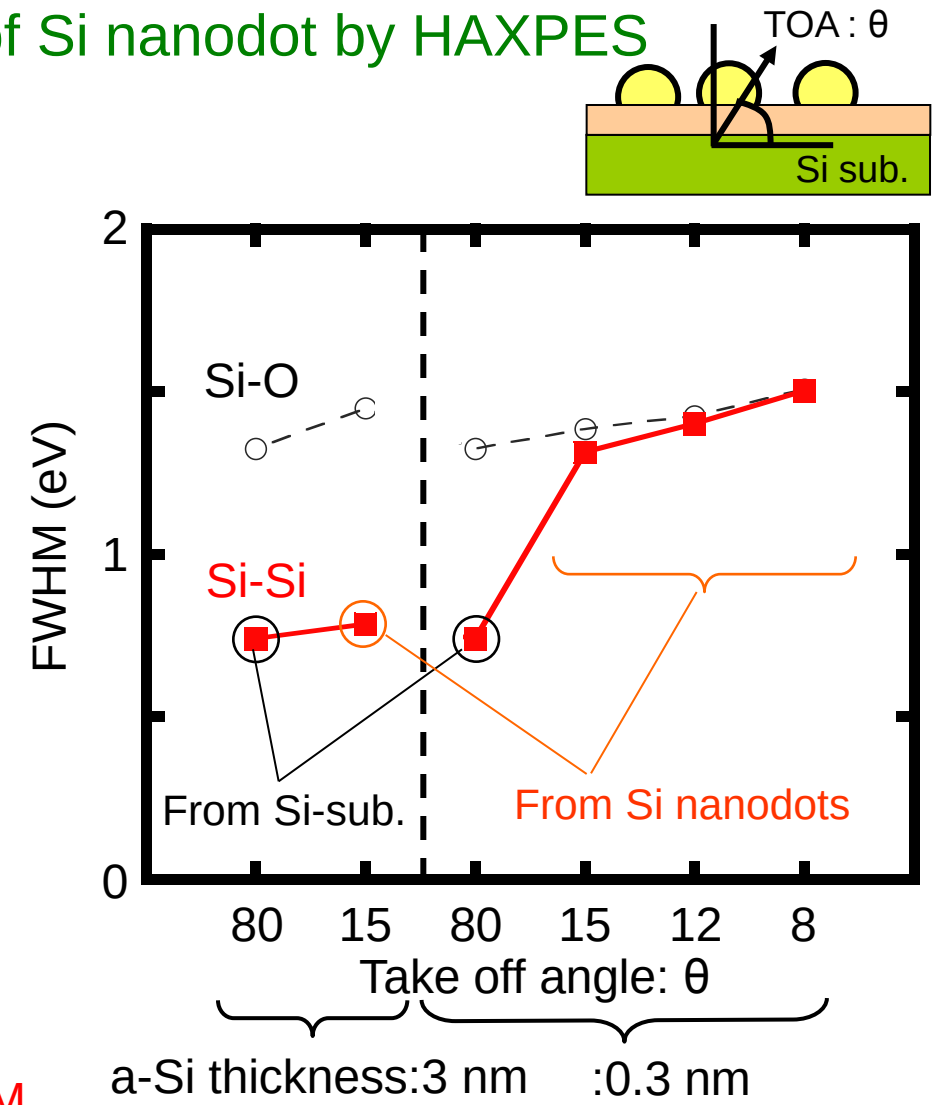
*H. Kondo, T. Ueyama, E. Ikenaga, K. Kobayashi, A. Sakai, M. Ogawa, and S. Zaima, Thin Solid Films **517**, 297 (2008).*

Dependence of Si1s spectra from Si nanoclusters on a-Si thickness

✓ Analysis of crystalline structures of Si nanodot by HAXPES

Angle resolved HAXPES
[SPring-8・BL47XU (hν = 7948.2 eV)]





a-Si thickness=0.3 nm: Increase in FWHM

→ Amorphous structure: Variation of Si-Si bond-angles and bond-lengths

H. Kondo, T. Ueyama, E. Ikenaga, K. Kobayashi, A. Sakai, M. Ogawa, and S. Zaima, Thin Solid Films ***517****, 297 (2008).*

Summary

HAXPES analysis for nano-scale multi-layered structures for Si ULSI devises

- Analysis of composition and chemical bonding states
  - ✓ Non-destructive analysis:

    Direct observation of buried interfaces in metal/high-k/Si(Ge) structures
  - ✓ Observation of deep core-levels:

    Avoiding overlap of core-levels among various elements (eg. LaO_x/Ge)
- Evaluation of electronic states
  - ✓ Work function of metal gates on high-k gate dielectrics
  - ✓ Deduction of local dielectric constant by chemical shift measurements
- Analysis of nano-structures for new-generation electric devices
  - ✓ Microstructures: Chemical bonding states of nano-dots

HAXPES contributes to the technology of nano-sclae Si devises for controlling interface structures and electronic properties.

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