XAFS study of Hafnium-based high-k ultra-thin films

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Introduction

Roadmap of transistor technology

(from ITRS2003)

		2003	2004	2005	2006	2007	2008	2009	2010	2012
Technology node (nm)	**Dev.**	**65**		**45**						
	Mass		**90**		**65**				**45**	
EOT (nm)		**2.2**	**2.1**	**2.1**	**1.9**	**1.6**	**1.5**	**1.4**	**1.3**	**1.2**
Gate Dielectric	**Dev.**	**Hf-based**					**La-based**			
	Mass	**SiON**			**Hf-based**					**La-based**

(Dev.=development, Mass=mass production)

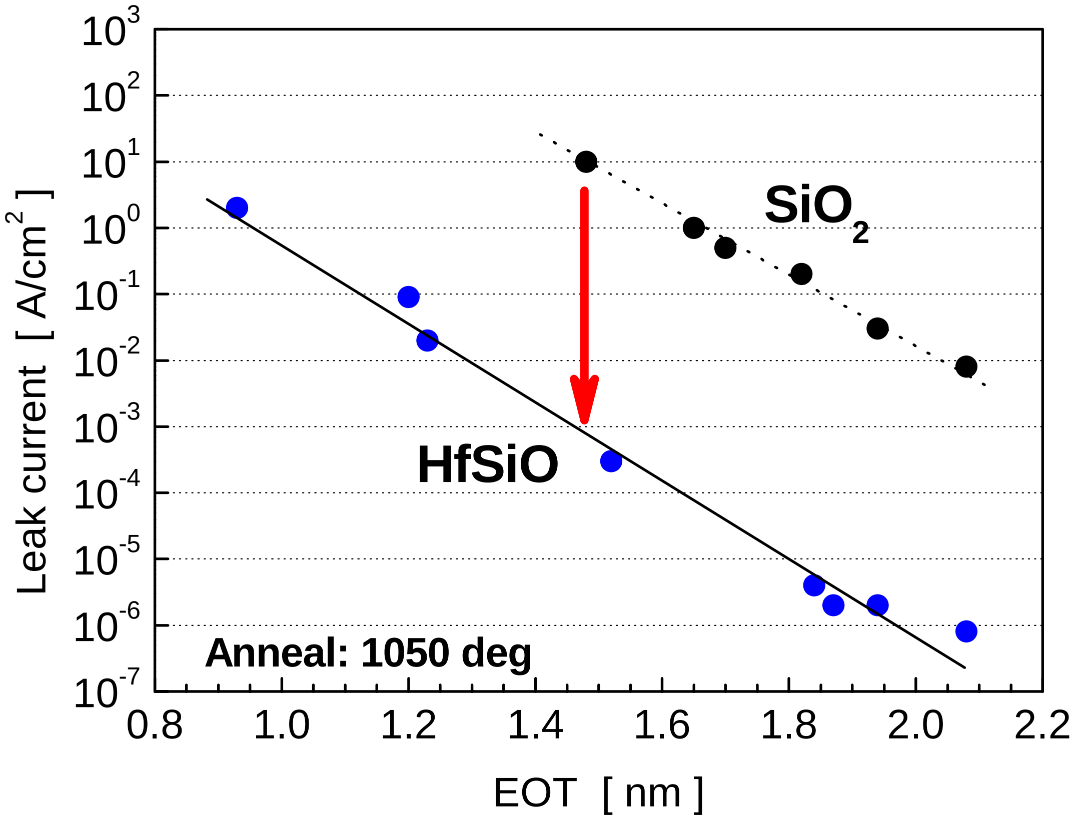
HfO_2 high dielectric constant （SiO_2 = 3.9 vs HfO_2 = 25)
good interface properties with Silicon
easy to fabricate amorphous films by PVD or CVD methods

Week point: crystallized at around 700℃ -> increase of leak current

Property of HfSiOx thin film

Adding Si to HfOx films is effective for keeping amorphous up to above 1000℃.

- EOT=0.9nm
- Reduction of leak currents by 4 orders.
- Stable at high temperature (~1050℃)



Objectives

However, the structures of the films with Si have not been fully studied.

It is quite important to know the structures of the films, in order to understand the mechanism of the suppressing crystallization and how much silicon we should add to the film for the purposes.

↓

We have applied XAFS analysis to investigate the difference of the local structure around Hf atoms between HfOx and HfSiOx films.

Challenging points: analysis of the films less than 10 nm!

Experimental

Samples： Hf(Si)Ox / Si(100)

- Process ： MOCVD
- Thickness ： 2 ～ 20 nm (confirmed by XRR)
- Composition ： Hf/Si=1/1 (confirmed by RBS)

- Standard ： HfO_2 crystal powder

XAFS experiments: at SPring-8 BL16B2 and BL16XU

- Si(311) / Si(111) double crystal monochromator
- Focusing & harmonics reduction: Rh-coated mirror (5 mrad)
- Detections: Electron yield method & Fluorescence method

  I_0 monitor ＝ 17 cm ionization chamber， $N_2$100%

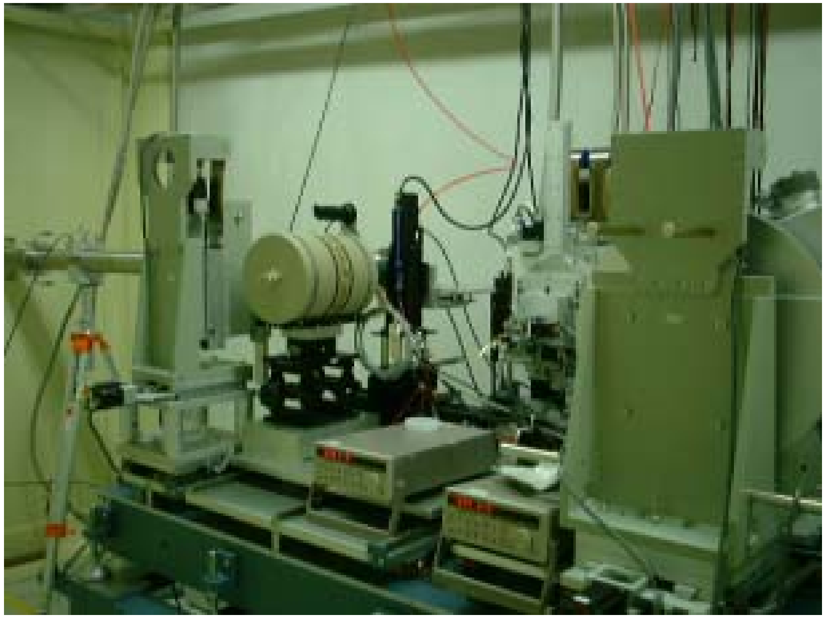
  EY = Teikoku denshi Co, He-flow type, HV = 1000V

  Fluorescence = IGLET pure-Ge single SSD / Rigaku spectrometer

Experimental Setup

Conversion Electron Yield detector

settled on the θ-2θ goniometer,
Inclined by 5 °

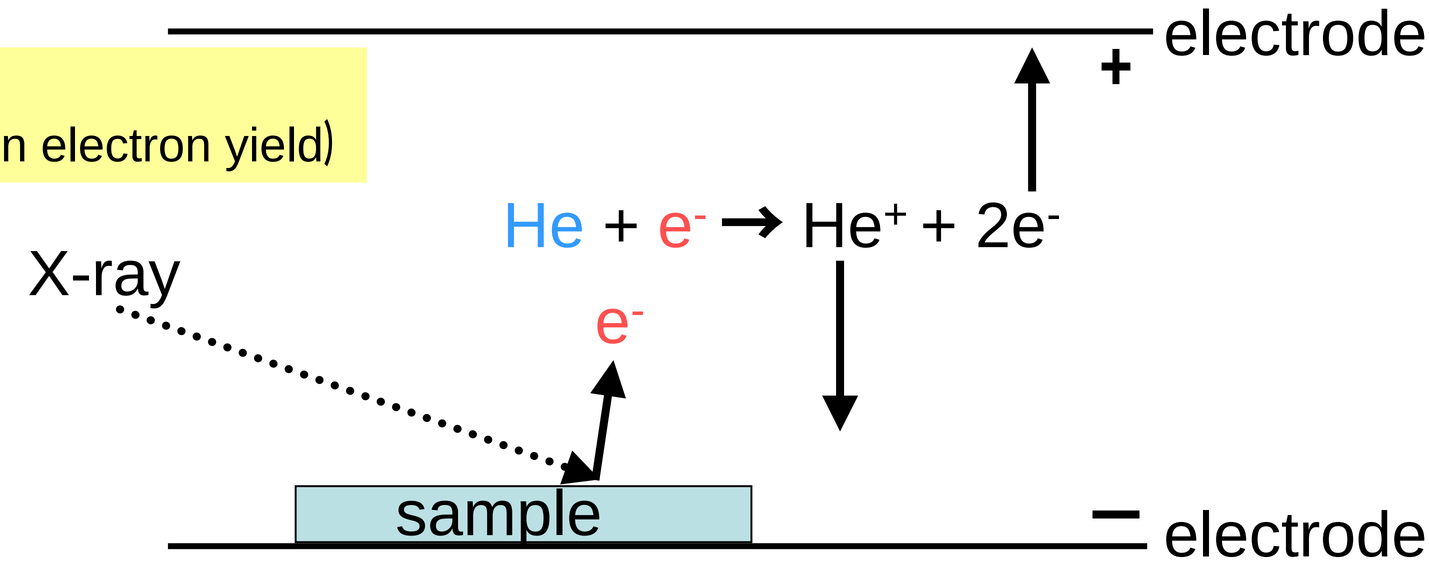


Fluorescence detection @BL16B2

Incident x-ray / sample / detector = 45 deg.
Sample / detector head = 5 cm

Principle of CEY

CEY
(conversion electron yield)



electrode +

$He + e^- \rightarrow He^+ + 2e^-$

X-ray

e^-

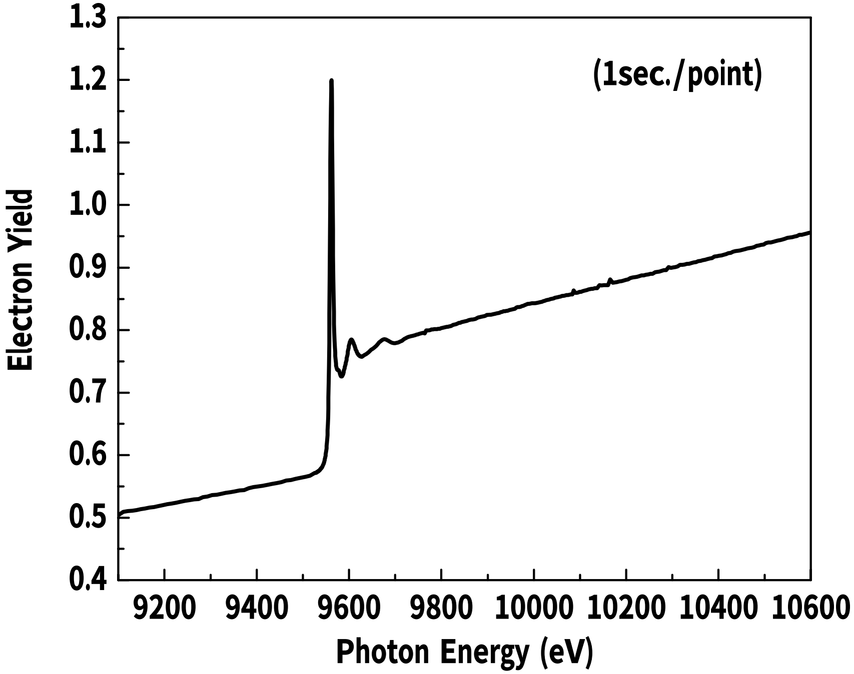
sample

− electrode

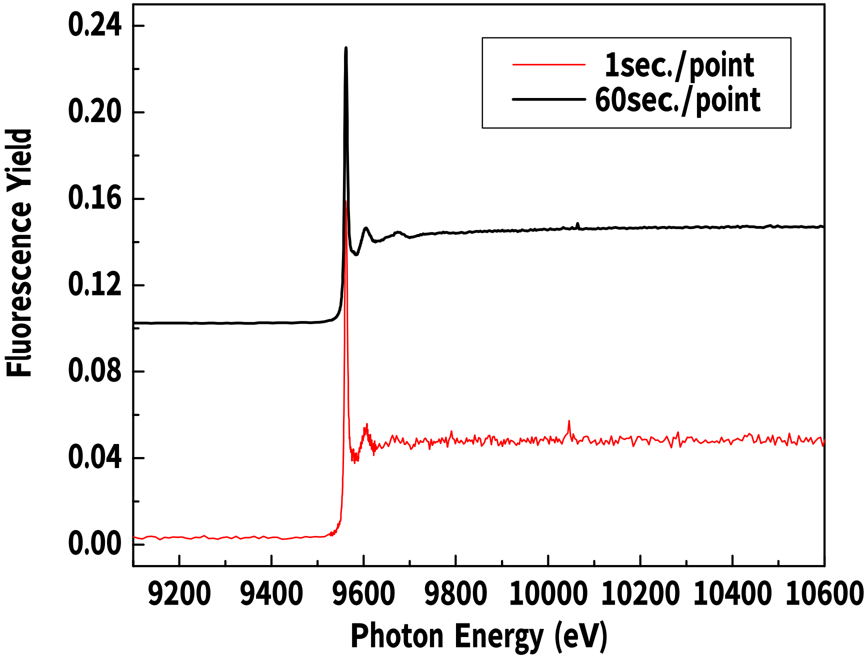
escape depth：
Auger electron, photo electron ∼ nm
secondary electron ∼ sub μm

Hf-L_3 spectra of a HfOx thin film

(CEY vs SSD-F)



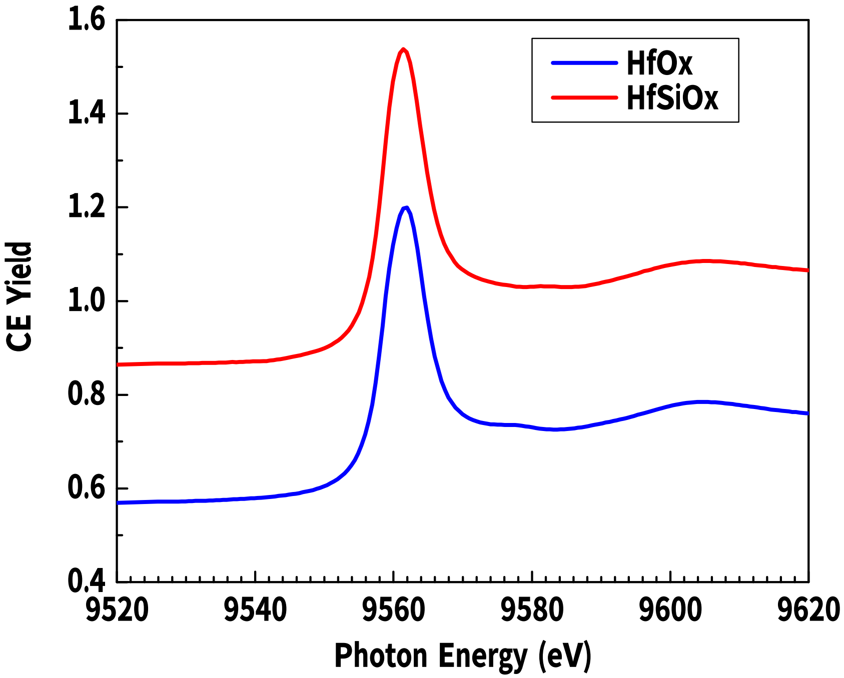
By Conversion Electron Yield method
(total measurement time = 40 min.)



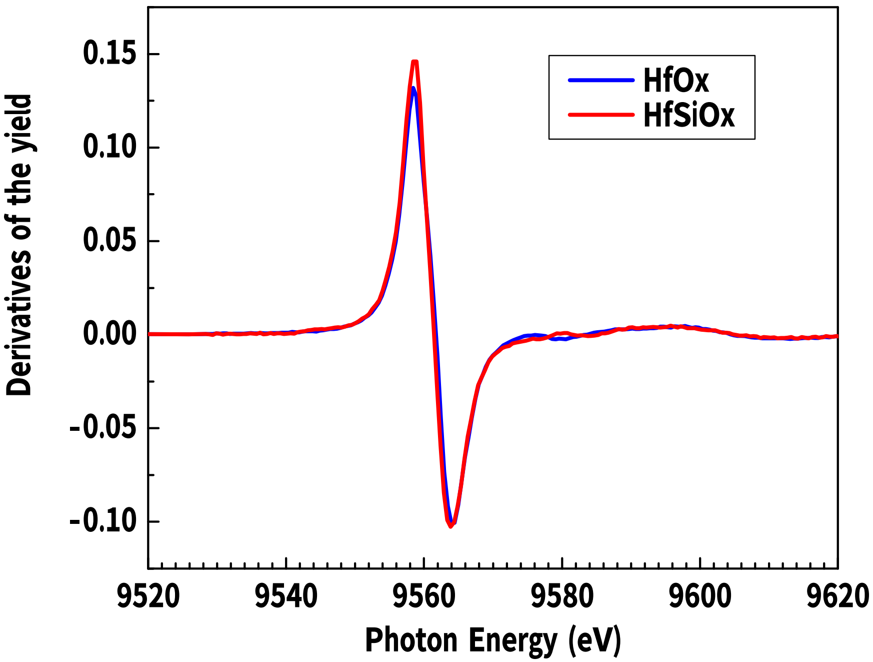
By Fluorescence Yield method
(total time = 40 min. / 6 hrs.)

Practical XAFS measurements of 10 nm thick film can be realized by CEY method.

Hf-L_3 XANES of Hf(Si)Ox



Hf-L_3 XANES of Hf(Si)Ox thin films

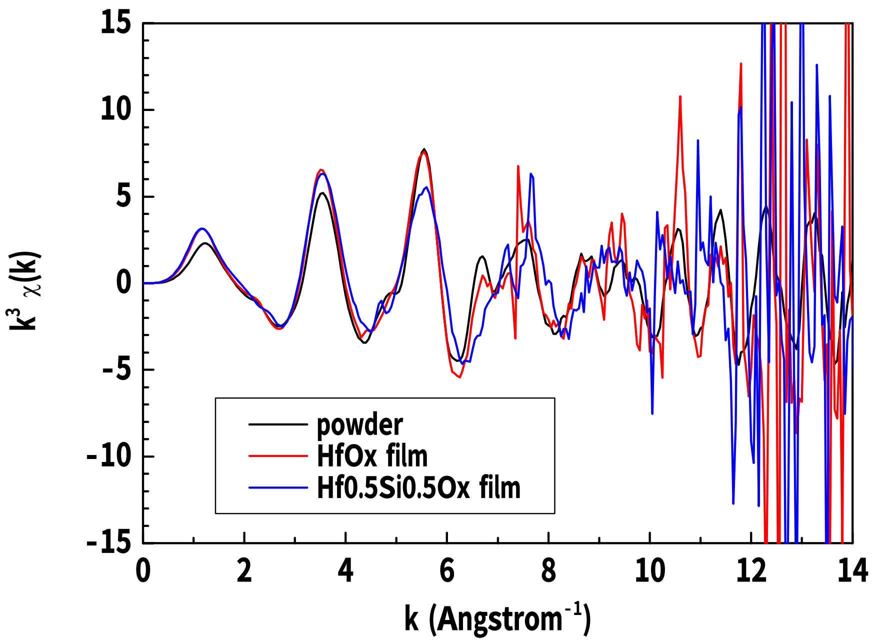


Derivatives of the XANES

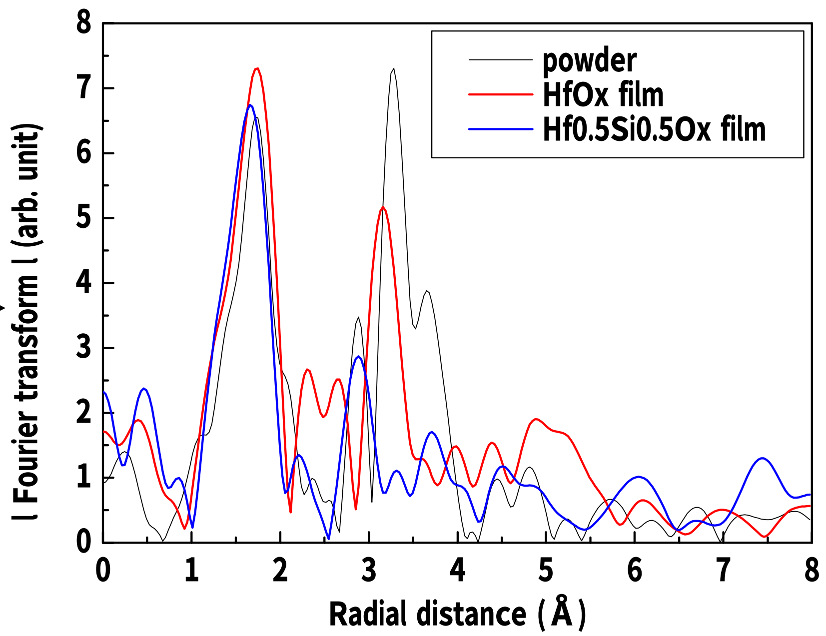
No difference in the absorption energy and other features

→ The valence of Hf atoms does not change when adding Si atoms to the film.

EXAFS analysis



EXAFS function $k^3 \chi(k)$



Fourier transform of $k^3 \chi(k)$

- Up to k ~ 12 of EXAFS functions can be used for the analysis.
- Signal of the 2nd coordination shell is quite weak for the HfSiOx film.

Results of curve fitting

Sample	Hf - O			Hf (- Hf*)		
	r	n	DW	r	n	DW
Powder	0.212 nm	6.8	0.107	0.339 nm	5.5	0.061
HfOx film	0.211 nm	6.9	0.090	0.339 nm	4.5	0.064
$Hf_{0.5}Si_{0.5}Ox$ film	0.211 nm	6.6	0.112	0.305 nm	2.3	0.073

r = distance, n = coordination number, DW = Debey-Waller factor

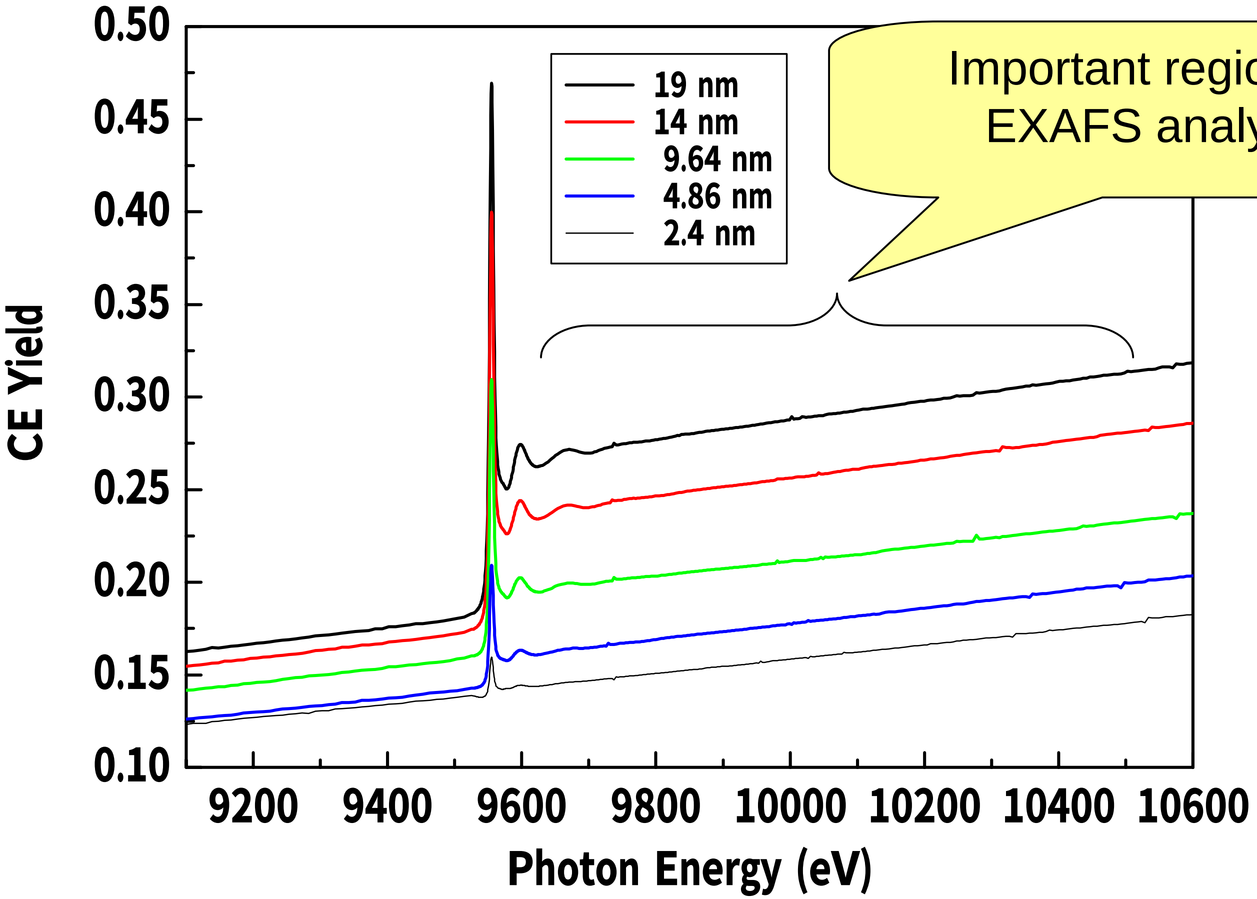
Fitting parameter: values from the powder result were used.

*Hf-O-Si model was tried at the fitting of the HfSiOx, however, the model gave us a worse fitting result.

It is confirmed that the HfSiOx film is completely amorphous.
(having quite few Hf-O-Hf configurations)

Hf-L_3 spectra of HfOx thin films

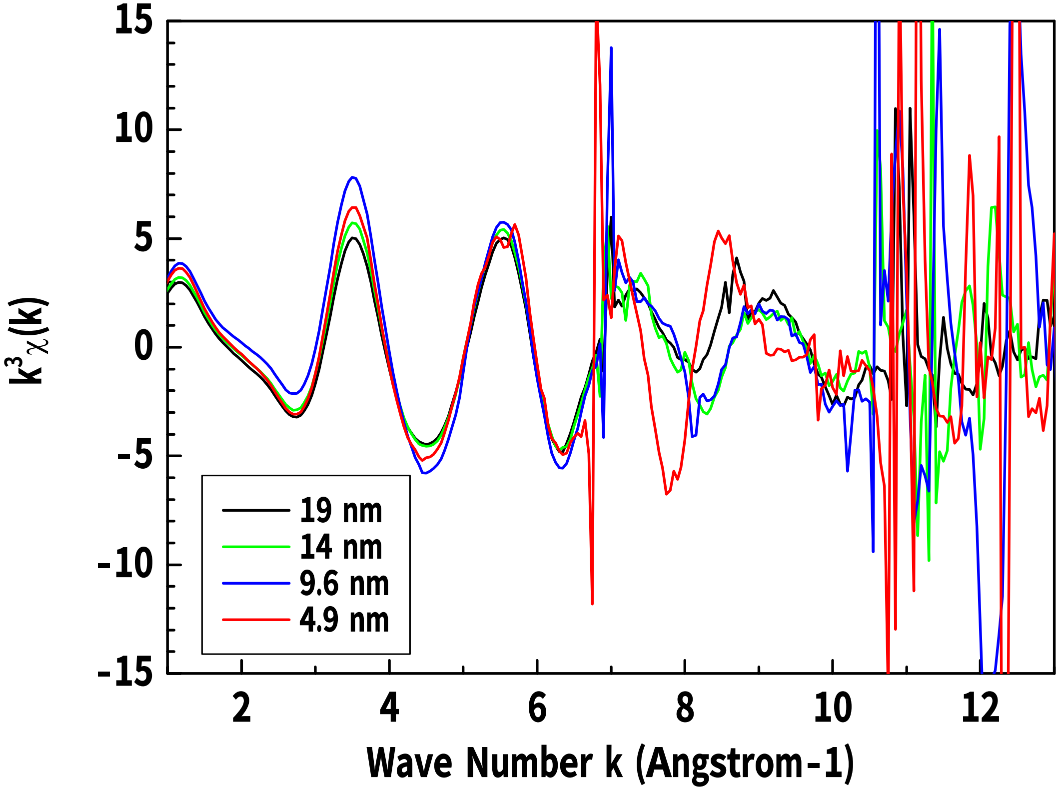
thickness effect



Important region for EXAFS analysis

No apparent beat can be observed in the spectra of the films less than 5 nm.

EXAFS functions of ultra-thin films



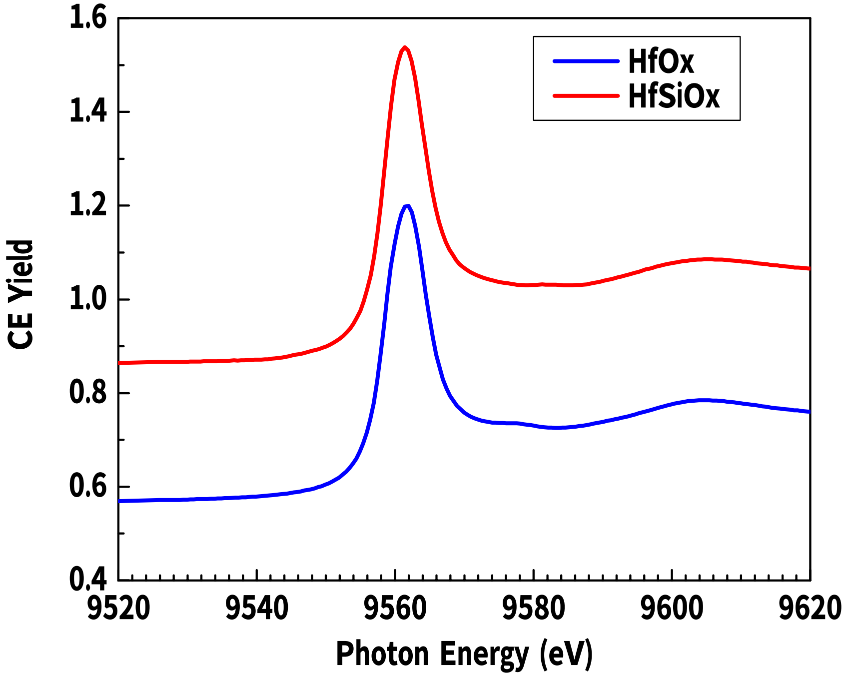
EXAFS functions

The EXAFS function of 4.9nm films is completely different from those of thicker films above k > 7.

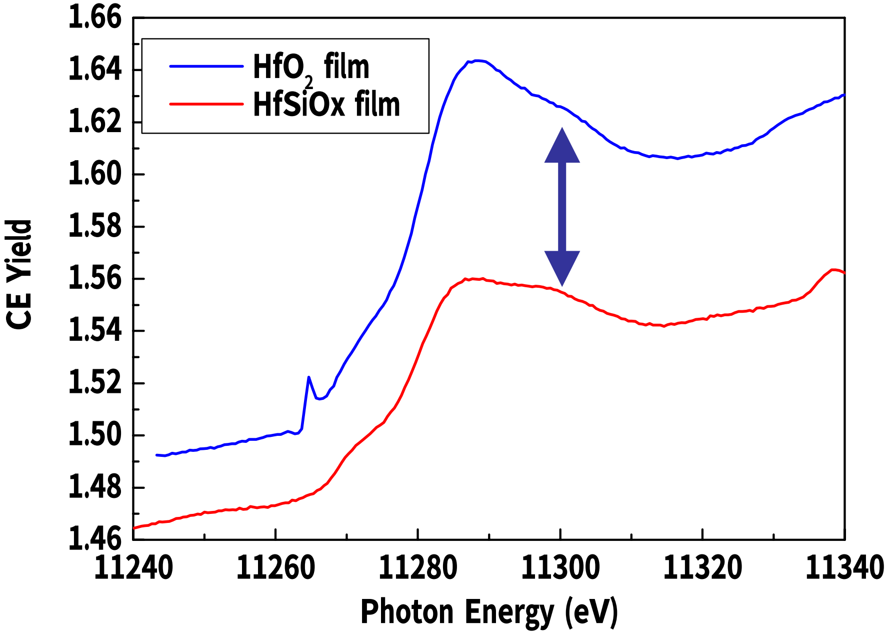
We confirmed that more than 10 nm of film thickness is necessary to get appropriate structural information from EXAFS analysis.

Hf-L_1 XANES of Hf(Si)Ox

by CEY method



Hf-L_3 edge



Hf L_1 edge

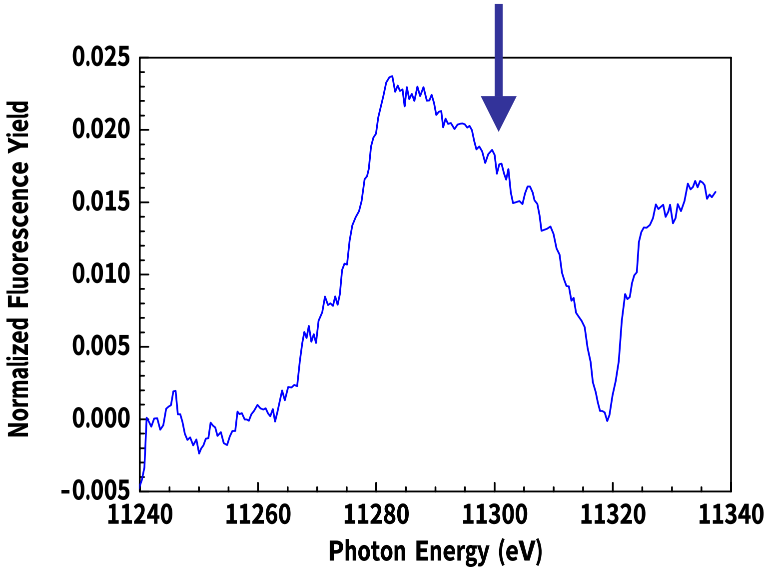
No difference in the Hf-L_3 edge

HfSiOx shows a new shoulder peak at 11300 eV.

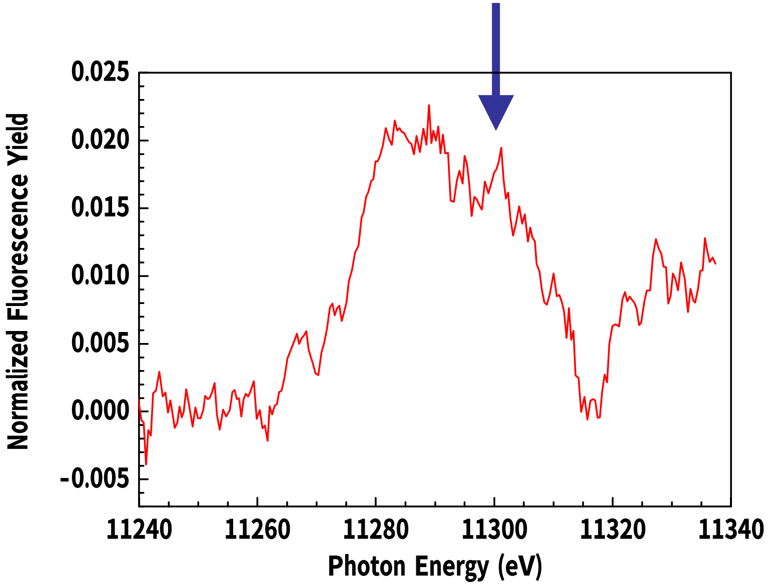
→ can be used as a footprint of Hafnium-silicate

Hf-L_1 XANES of Hf(Si)Ox (2)

by fluorescence method @BL16XU



HfOx (10nm) /Si



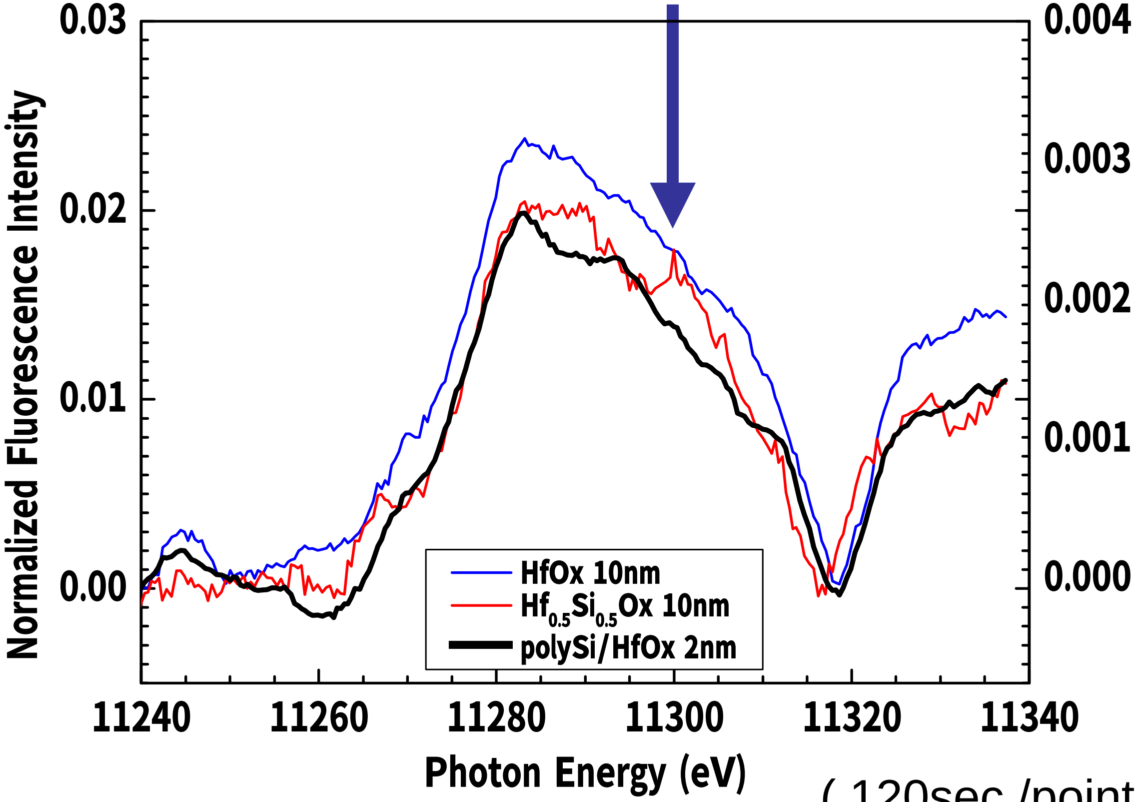
$Hf_{0.5}Si_{0.5}Ox$ (10nm) /Si

(20 sec/point -> total time = 1.1 hr)

The shoulder peak at 11300 eV is apparent in the spectrum of HfSiOx by the fluorescence method, even in bad S/N ratio.

Hf-L1 XANES of HfSiOx (3)

2 nm film under polySi electrode



The 2 nm HfOx film under poly-Si electrode does not show the shoulder peak.

(120sec./point -> total time = 6.7 hr)

We found that formation of Hf-O-Si is negligibly small after polySi electrode fabrication process.

Conclusions

- We showed CEY method is quite effective for the study of the thin films, however the thickness limit is around 10 nm.

- The valence of Hafnium atoms does not change when adding Silicon atoms to the film.

- HfOx thin film should contain some amount of amorphous phase, as its Hf-Hf signal in the EXAFS is smaller than that of the crystal powder. We confirm that HfSiOx thin film is completely amorphous.

- HfSiOx shows an extra absorption at 11300 eV, above its Hf-L_1 edge, which is not seen in HfOx. This extra absorption might be used to investigate whether an ultra-thin film of HfSiOx has Hf-O-Si configuration in it.