X-Ray Reflectivity Study of Hafnium Silicate Thin Films Prepared by Thermal Chemical Vapor Deposition

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Scaling down of the device dimensions of advanced CMOS transistors is creating a demand for high-*k* gate dielectric thin films as potential replacements for the usual silicon dioxide (SiO_2) thin films. Therefore considerable efforts are being devoted to the development of high-quality high-*k* dielectric thin films such as Hf-silicate thin films. In this work, we have evaluated the structure of Hf-silicate thin films by the X-ray reflectivity (XRR) technique.

Hf-silicate thin films (4~5 nm) were deposited on 8” silicon wafers. XRR measurements were performed at the beam line BL16B2 in SPring-8. An X-ray wavelength of 1.3 Å was chosen by the Si(111) double crystal monochromator. The fitting simulations were conducted using Rigaku XRR software. The calculated thickness and the surface roughness were respectively compared with the obtained TEM and AFM experimental results.

An example of XRR profile is shown in Fig. 1. It was clarified from the TEM images that an interfacial layer is formed between the Hf-silicate thin film and the Si-substrate during film deposition. A fitting simulation was then performed with an interfacial layer added to the model parameters. The calculated film thickness and the surface roughness were in agreement with the corresponding TEM and AFM observations for all samples. Furthermore, we clarified that the interfacial layer between Hf-silicate and Si-substrate included the non-uniform Hf atoms in the vertical direction. It was found that the XRR experiment is a powerful method to obtain the microscopic structure of high-*k* gate dielectrics.

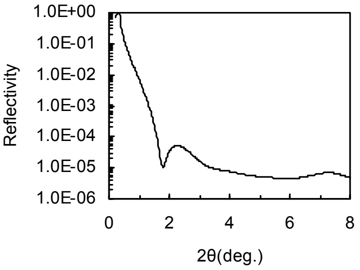

Fig.1 XRR curve obtained from Hf-silicate thin film grown on Si substrates

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Background

Scaling down of CMOS transistor devices

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Decrease of gate oxide (SiO_xN_y) thickness

Issue

Gate leakage current

To be required new materials

Replacing SiO_xN_y with a dielectric material with higher dielectric constant (high-*k*).

Capacitance between gate electrode and channel (C):

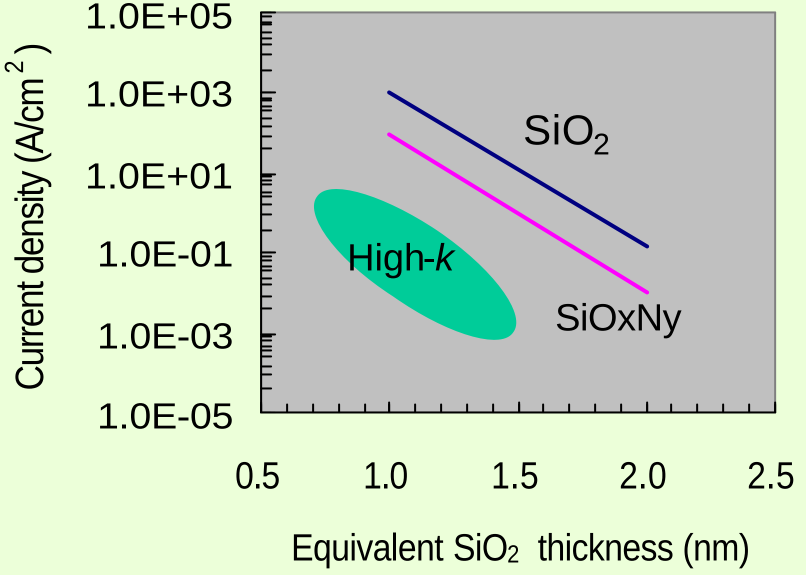
$$C = kA/d$$

k: dielectric constant, A: electrode area,
d: thickness of dielectric films

A → decrease ⇨ d → decrease

⇨ Increase of leakage current

Leakage current density vs. EOT



Ref. T. Ghani *et al*., Symp. on VLSI p.174, June 2000

Hafnium-silicate based dielectric materials

Among many candidates, Hf-silicate based dielectrics seem most promising following reasons:

(1) useful dielectric constant

(2) good thermal stability in contact with silicon

(3) high crystallization temperatures for some compositions

Candidates for high-*k* dielectric material

Material	Dielectric constant (*k*)	Band gap (eV)
Al_2O_3	9	8.7
Y_2O_3	15	5.6
La_2O_3	30	4.3
HfO_2	25	5.7
ZrO_2	25	7.8
$HfSi_xO_y$	5～20	5～7
$ZrSi_xO_y$	4～9	5～7

Ref.: R. M. Wallace, G. D. Wilk, Semicond. Int., 24, 227, 2001.

What is a problem for actual integration of Hf-silicate dielectric materials?

Control of interface structure and film quality

Objective:

To examine the structure of hafnium silicate grown on Si substrates by synchrotron x-ray reflectivity

Samples and experiments

Samples: as-deposited $HfSi_xO_y$ films grown on Si sub.

Deposition method: thermal chemical vapor deposition

No.	Deposition temperature (°C)
1	700
2	650

X-ray reflectivity measurements

◆at SPring-8 BL16B2 (Bending magnet)

◆X-ray wave length: 1.38 Å

Cross sectional TEM

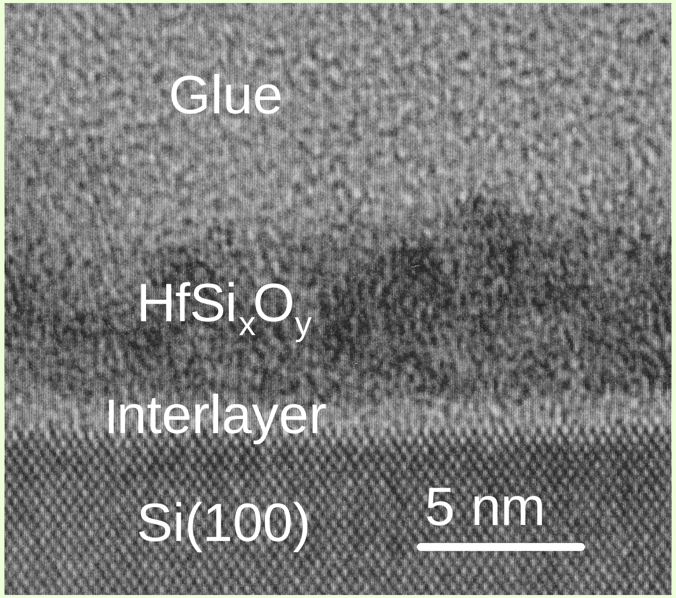
◆accelerating voltage: 200 kV

High-resolution Rutherford backscattering spectroscopy

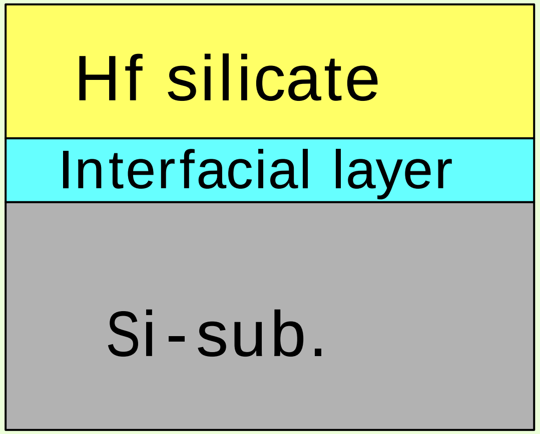
◆Ion beam energy: 450 keV He^+

Simulation model (1)

Cross-sectional TEM image



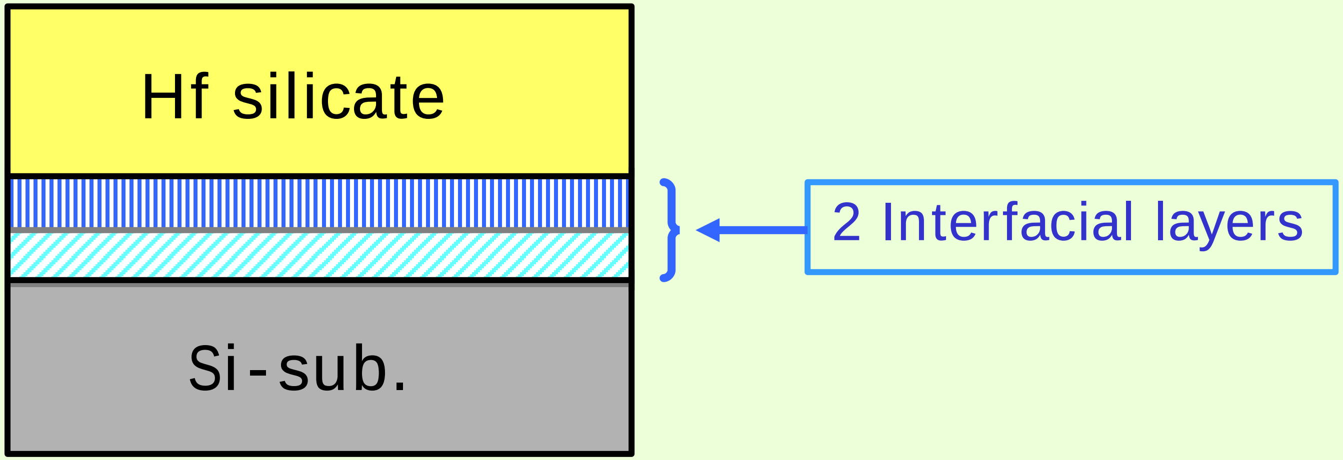
Model (1)
2 layers model



Calculated results of film thickness was NOT reasonable compared with TEM observation results.

Simulation model (2)

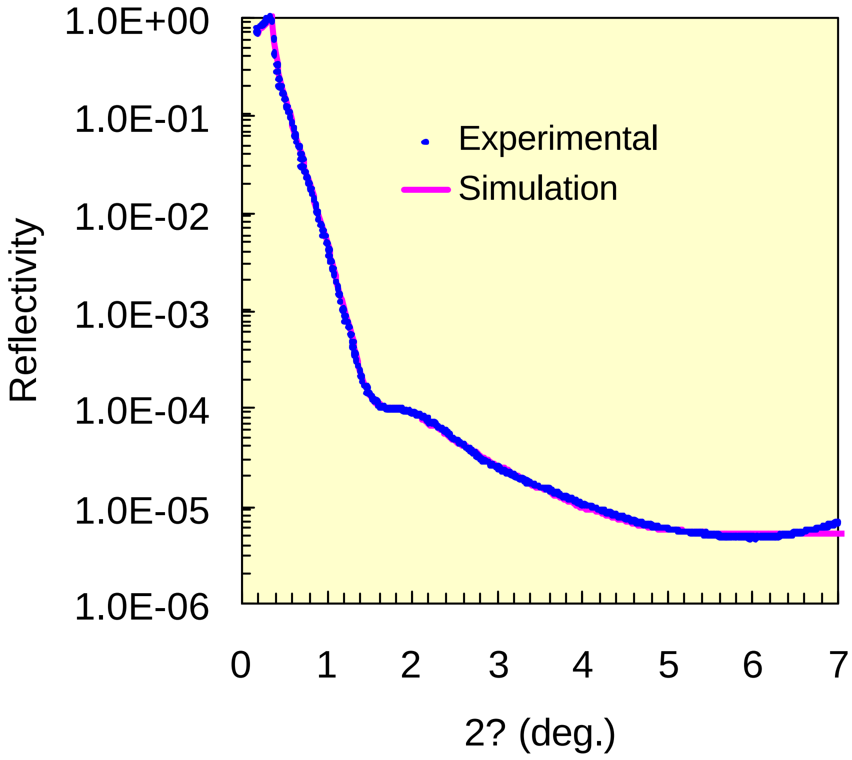
Model (2): 3 layers model



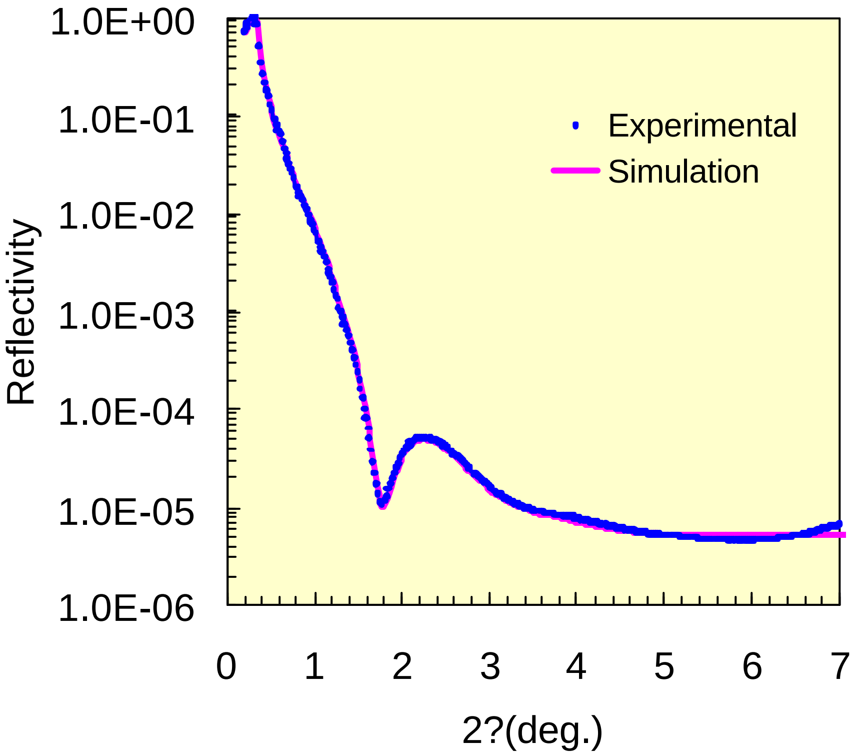
Closely fit experimental results

Measured and simulated XRR spectra of $HfSi_xO_y$ grown on Si substrate

Sample 1
(Deposition temp.: 700°C)



Sample 2
(Deposition temp.: 650°C)



Simulation Results

	Sample 1			Sample 2		
	Density (g/cm^3)	Thickness (nm)	Roughness (nm)	Density (g/cm^3)	Thickness (nm)	Roughness (nm)
HfSiO	4.8	5.2	1.6	4.5	4.4	1.0
Interfacial layer (HfSiO-side)	**2.4**	0.8	0.1	**2.6**	0.7	0.1
Interfacial layer (Si sub.-side)	**2.0**	0.5	0.1	**2.1**	0.6	0.1
Si sub.	2.3	—	0.2	2.3	—	0.2

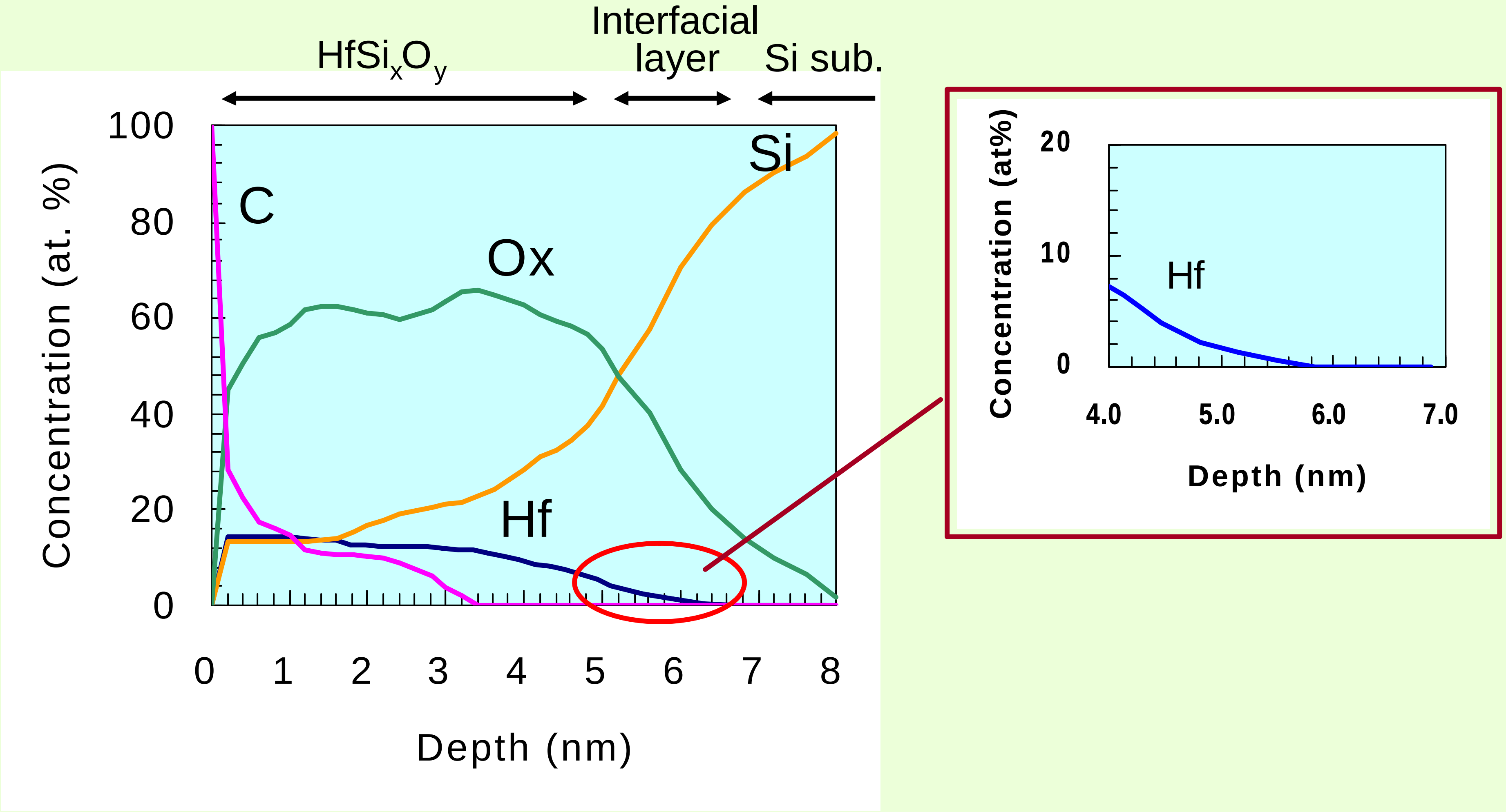
Density (ref. data) native oxide: 2.0-2.2 g/cm^3
thermal oxide: 2.1-2.2 g/cm^3

The calculated density of interlayer (HfSiO film side) is greater than that of SiO_2.

Interlayer (HfSiO film side) would include Hf atoms.

Crosscheck of XRR calculated result by HRBS

HRBS depth profiles obtained from sample 1



Conclusions

- Three-layer model including two interfacial layers produced good agreement with the experimental data.

- The interfacial layer between Hf-silicate film and Si substrate would include non-uniform Hf atoms in the vertical direction.