Characterization of high-k gate dielectric films by x-ray absorption fine structure analysis

ハフニウムシリケート膜のXAFSによる構造解析

Momoko Takemura

(Corporate Research & Development Center, Toshiba Corporation)

Contents

Authors

Momoko Takemura, Tsunehiro Ino, Hirobumi Ohmori, Hideyuki Yamazaki, Akira Nishiyama, and Shiro Takeno

XAFS experiment was performed as SPring-8 proposal No. C03B16B2-4012-N

Introduction 1 : The shrinking CMOS requires high-k materials

Shrinking CMOS devices' scale

∴Required channel length and gate-dielectric thickness to decrease

→Caused increase of gate leakage current and boron penetration

→Physical thickness (T) should be increased to prevent leakage current.

The introduction of high-k gate dielectric films to CMOS devices is urgently required.

$C = k\varepsilon_0 S/T$

Increasing $k\varepsilon_0$
(using high-k materials)
→ Increasing T

Requirements for a new gate dielectric film :

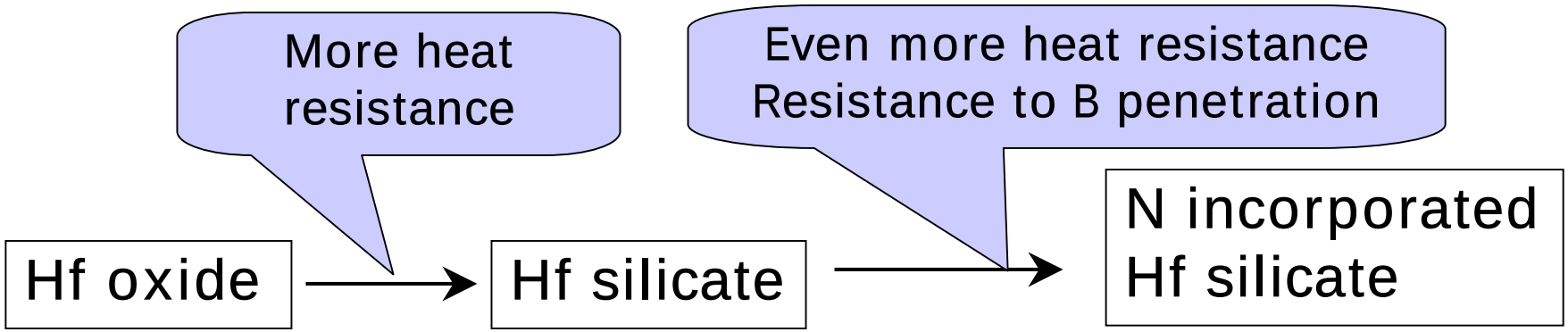
1) Large dielectric constant (k)
2) Enough barrier height
3) Minimum interface level, fixed charge,and traps in the film
4) The heat resistance of CMOS process
5) Reliability equal to SiON film

Introduction 2 : We paid special attention to N incorporated Hf silicate in high-k materials

N in HfSiON prevent:

the phase separation, micro-crystallization, and boron penetration

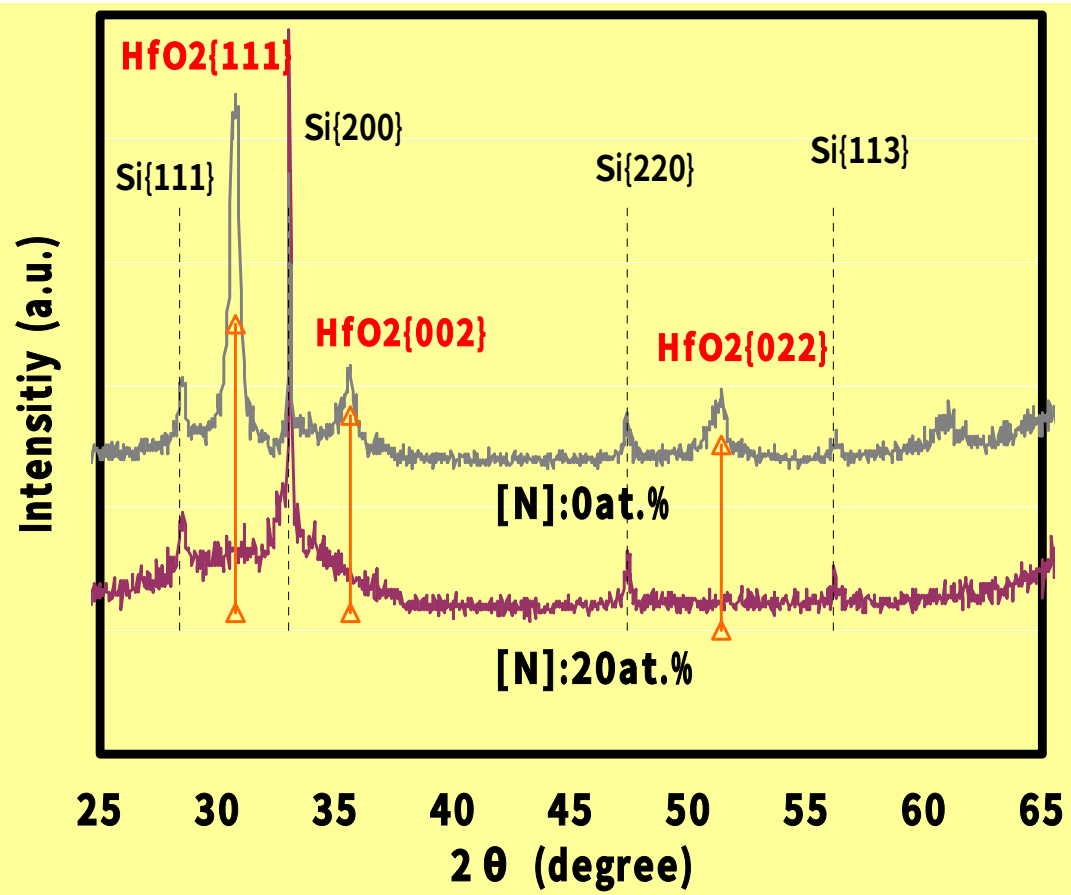
HfSiON is one of the most promising candidates for dielectric films for CMOS devices



1) M.Koike et al., Extended Abst. Solid State Devices and Materials, 52 (2003).

In this Study

Our purpose is to elucidate the role of N in the microstructure for these characteristics by EXAFS for Hf L_{III} using high-brilliance x-ray beam at SPring-8



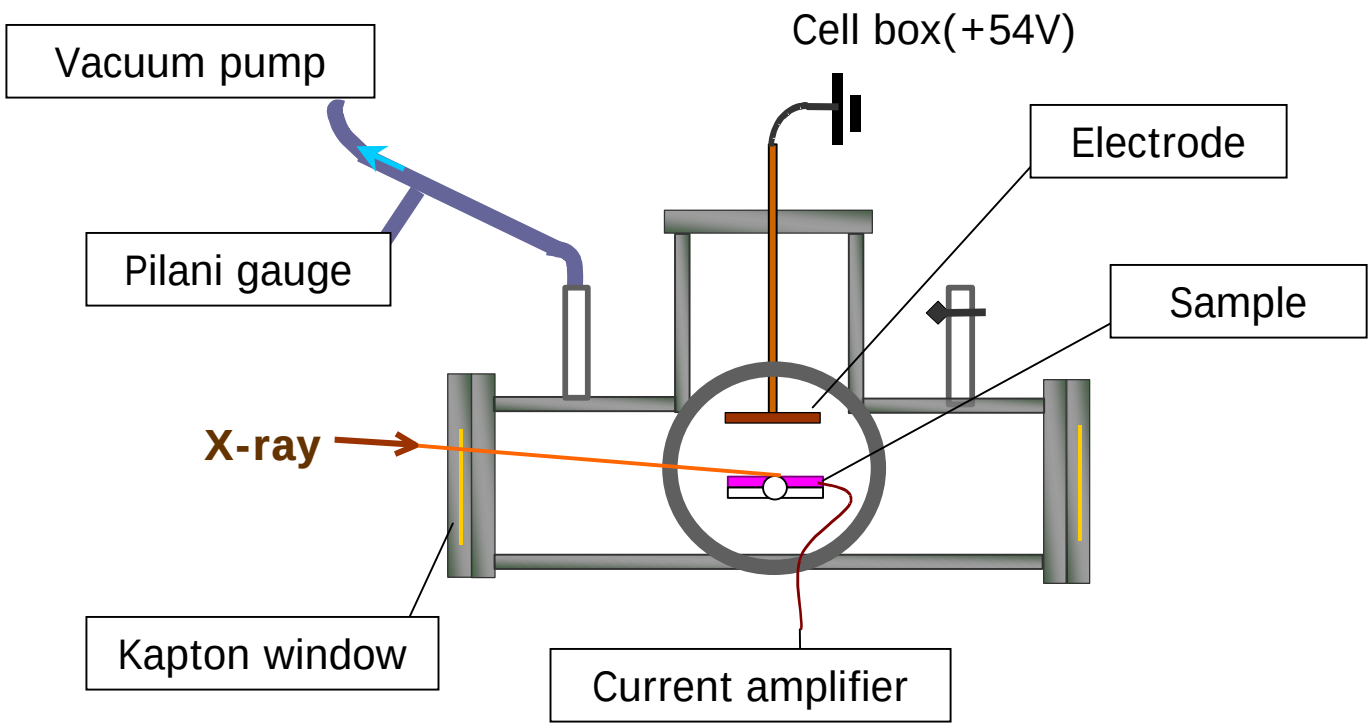
←Hf silicate without N grows HfO2 crystal when it is annealed at 1065℃.

←Hf silicate with N = 20 at% or more does not grow HfO2 crystal when it is annealed at 1065℃.

XAFS experiment

Hf L_{III} edge = 9565 eV (at SPring-8 BL16B2, SUN BEAM)
Energy range: 9300-10700eV, Monochromator: Si(311)
Step:0.0025-0.005deg., Counting time: 1 or 2 sec/point,
Incident angle: 5 degrees, Beam size : 0.4(V) x 2.0(W) mm

Vacuum cell for TEY detection



Samples

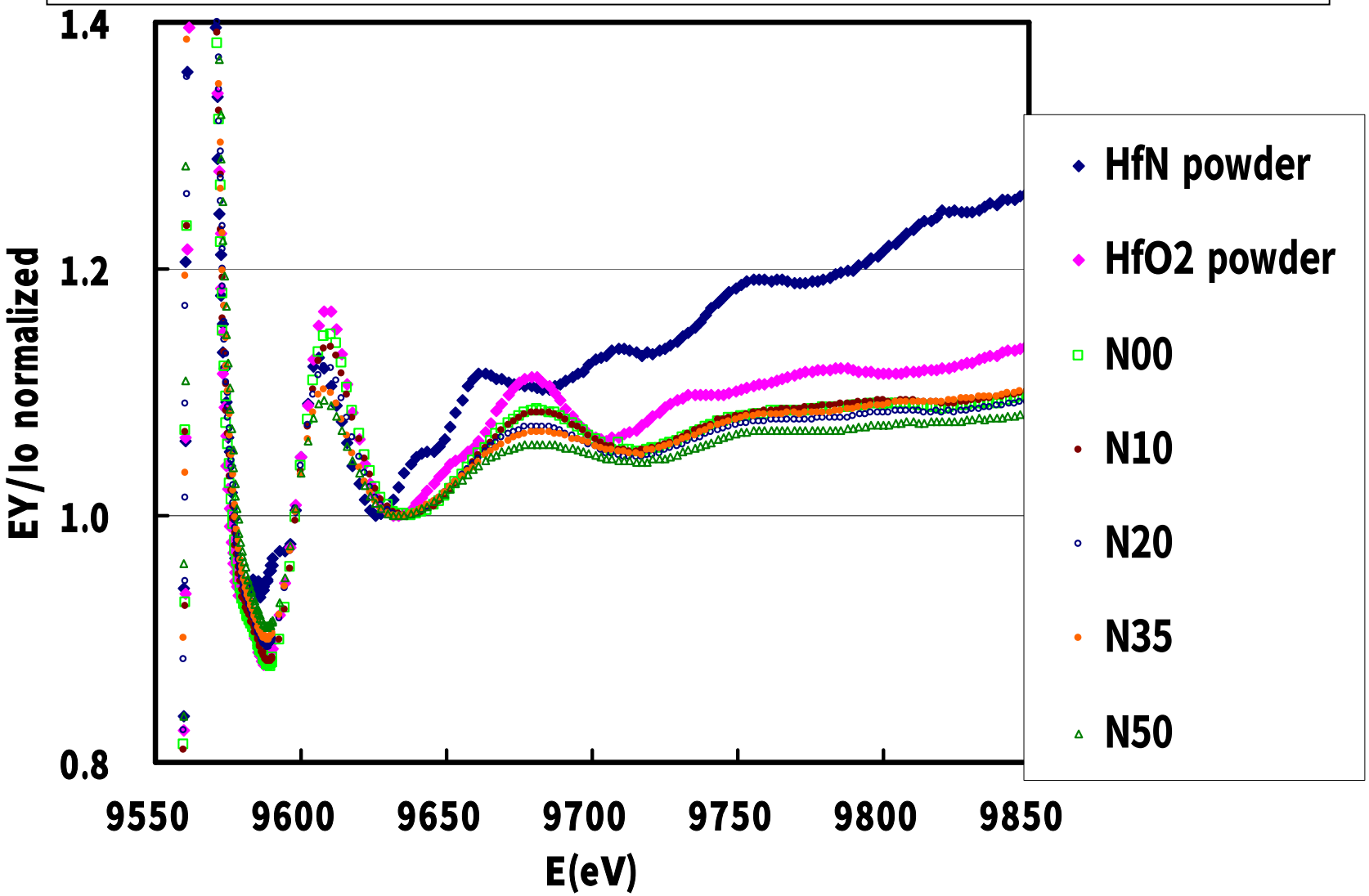
Sample name	Thickness*1	Composition*2		
	(Å)	Hf/(Hf+Si) (at%)	N content (at%)	N/(N+O) (at%)
N00	720	80	0	0
N10	860	80	9	14
N20	920	80	20	33
N35	970	78	35	60
N50	1020	78	51	85
HfO2 powder	(φ～2μm)	(100)	(0)	(0)
HfN powder		(100)	(100)	(100)

*1 Film thickness is determined using SEM.

*2 Element composition is determined by Rutherford backscattering spectrometry.

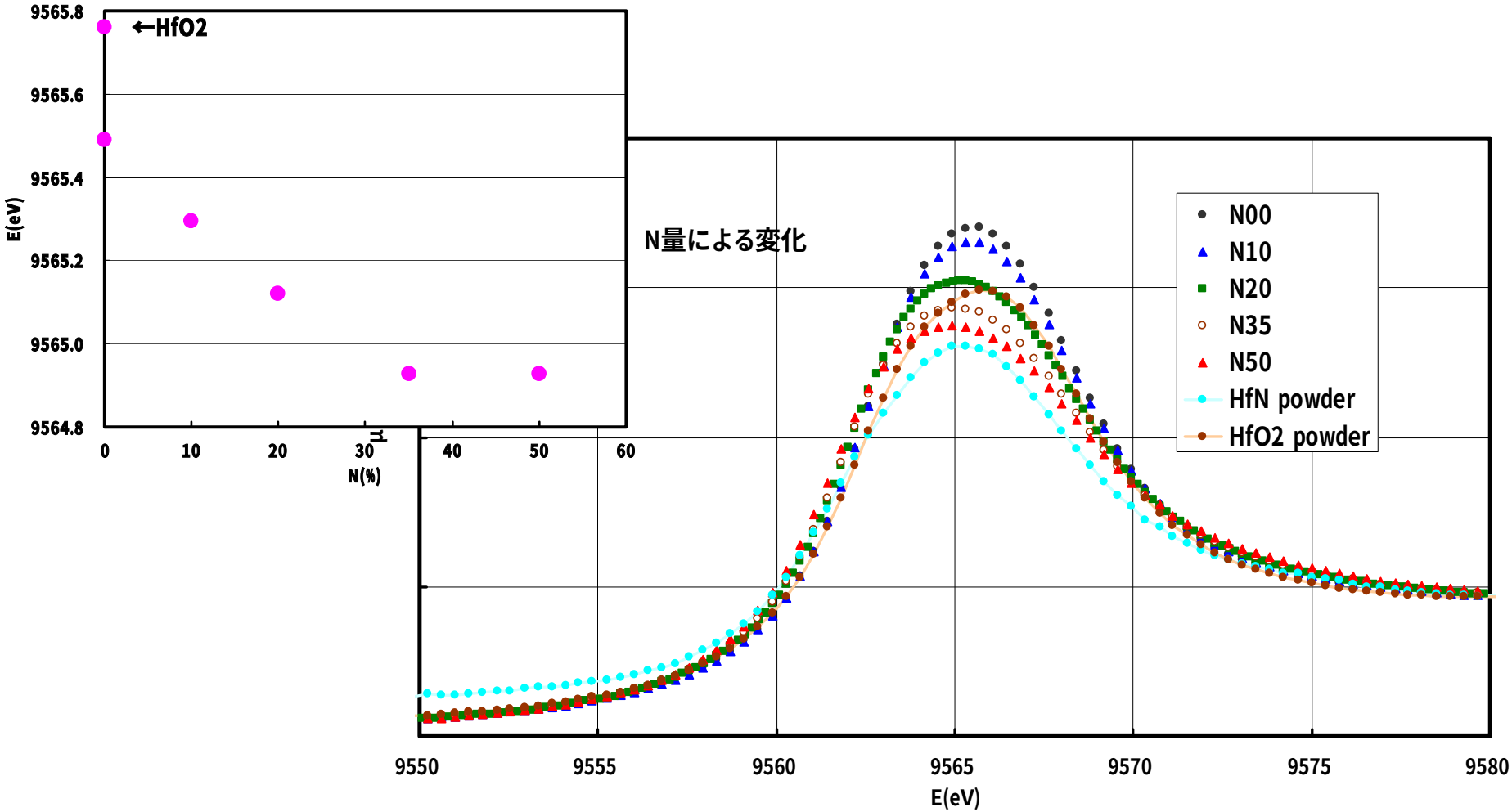
Hf L-XAFS spectrum：at low energy region

XAFS spectra for the five Hf silicates have the same shape. They all resemble that for HfO_2. The spectrum for the sample containing nitrogen 50 at% also does not resemble that for HfN.



Hf L_{III}-edge shift with nitrogen incorporation

The local structure around Hf does not greatly change but the oxidation state of Hf continuously decreases with nitrogen incorporation.



HfO_2 crystal structure

Monoclinic at room temperature

a=0.51156nm b=0.51722nm c=0.52948nm β =99.18deg

$P2_1/c$

The first nearest neighbor is seven fold oxygen.

Hf-O = 2.031～2.254A, average 2.149A

→tetragonal at 1720C

Distorted CaF_2-type cubic structure

a=0.514nm c=0.525nm $P4_2/nmc$

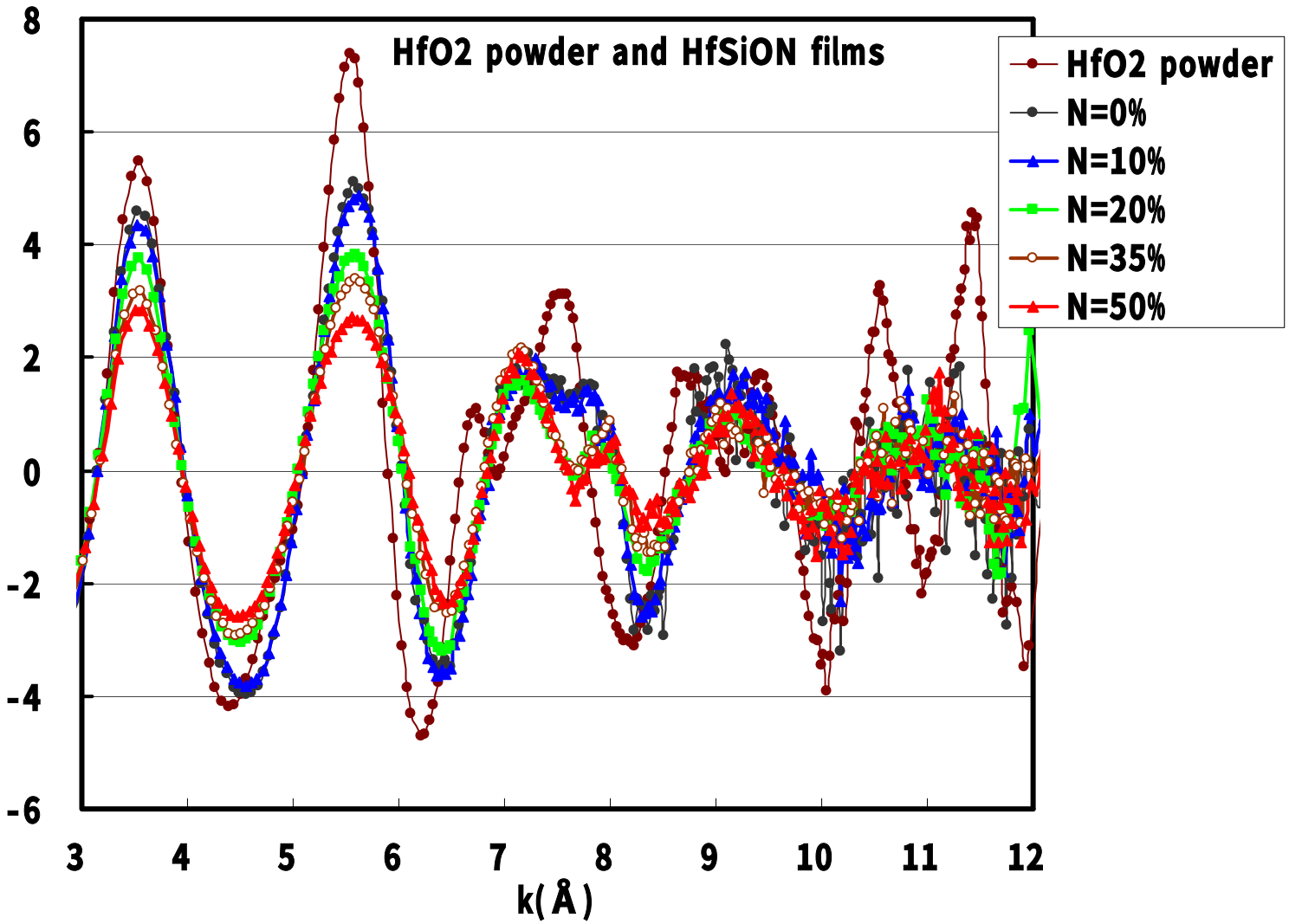
→Cubic at 2600C

CaF_2-type structure, a =0.5110nm F_{3m3}

→liquid at 2800C

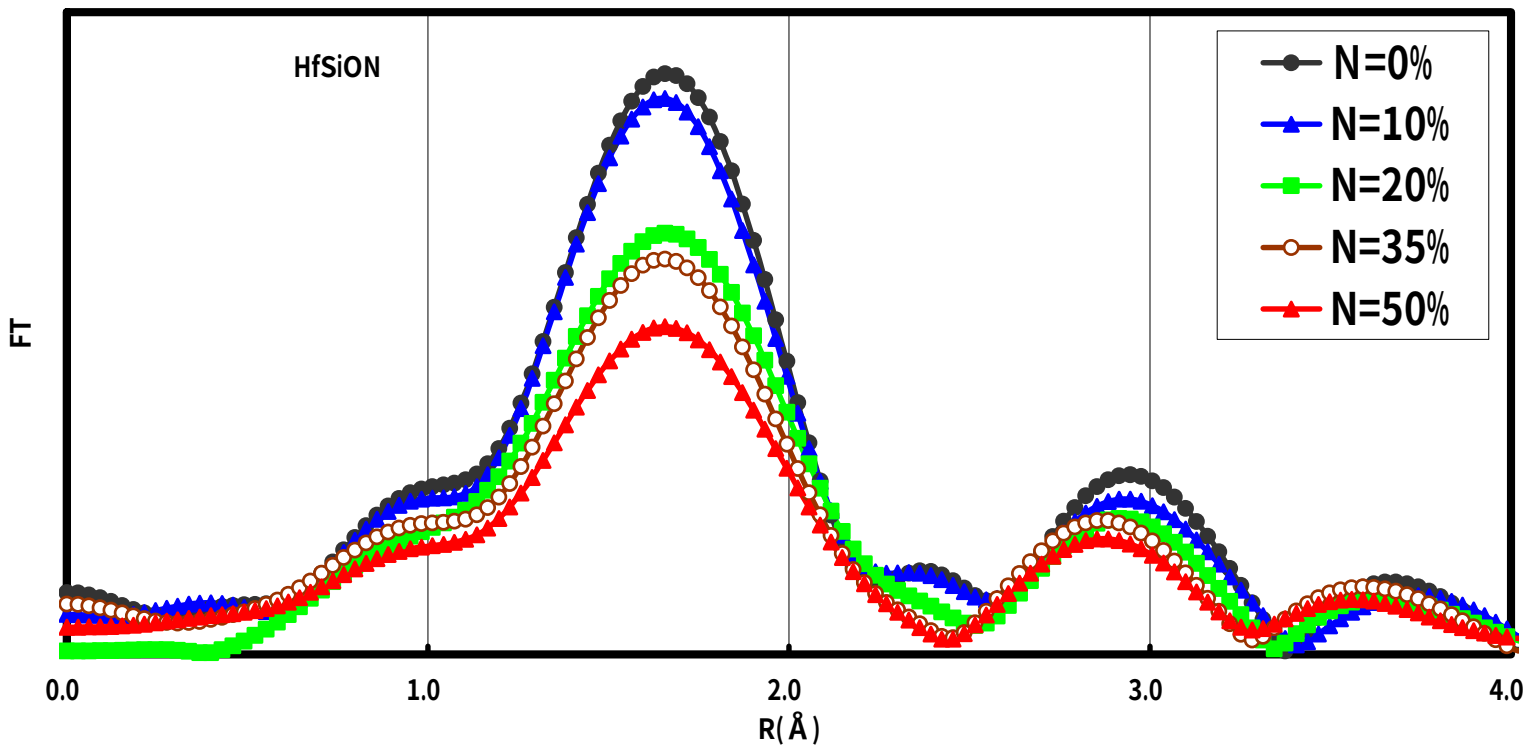
Ref. J. Wang, H. P. Li and R. Stevens, J. Mat. Sci. **27** (1992) 5397-5430.

Hf-L EXAFS oscillations for HfSiON films



Comparison of Fourier transforms of EXAFS for HfSiON films of various N contents

The amplitude of the nearest coordination decreases with nitrogen incorporation.



EXAFS analysis result for HfSiON

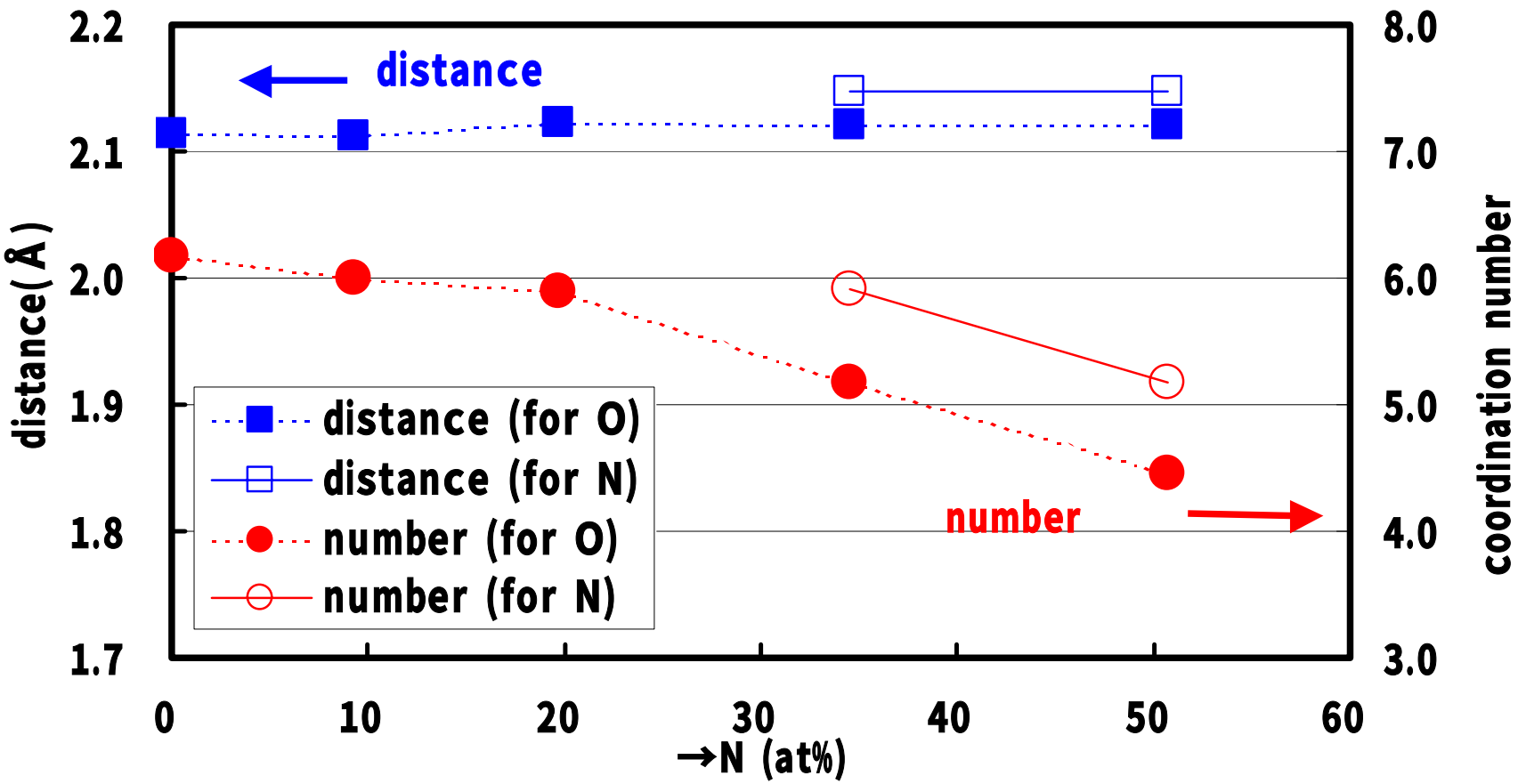
The coordination number decreases as nitrogen increases.

Composition (Hf-Si-O-N) (at%)				sample	RESULT		
					number	Distance (Å)	DW
Hf	Si	O	N				
23.5	6.8	68.1	0.0	N00	6.2	2.11	0.096
24.5	6.3	58.2	9.3	N10	6.0	2.11	0.096
30.9	7.6	39.9	19.7	N20	5.9	2.12	0.111
31.5	8.7	23.2	34.5	N35	5.2	2.12	0.110
29.4	8.4	9.3	50.7	N50	4.5	2.12	0.110

The element composition is determined by Rutherford backscattering spectrometry.

EXAFS analysis result for HfSiON

The coordination number decreases as nitrogen increases.



References for Hf oxynitrides ?

We could not find a reference for amorphous Hf oxynitrides.

References for Hf oxynitride crystals are limited.

But Hf compounds are known to be isostructural with Zr compounds.

There are valuable references for Zr oxynitride crystals (as below), some of which have superlattice structure.

Some references for the Zr oxynitride crystal structures

*1 M.Lerch, F.Krumeich, and R.Hock, Solid State Ionics 95, 87-93 (1997)

*2 S.J.Clarke, C.W.Michie, and M.J.Rosseinsky, J of Solid State Chem. 146, 399-405 (1999).

*3 G. Van Tendeloo, and G. Thomas, Acta Metall. 31, 1611-1618 (1983)

Anion vacancies are introduced into ZrO_2 crystals with nitrogen incorporation*1

The four Zr oxynitride phases are known. They all include anion vacancies in the unit cell. Two of them have superstructure.

phase	composition	Crystal	Unit
	ZrO_2	monoclinic	Zr_4O_8
β ′	$Zr_7O_{11}N_2$	trigonal superlattice	$Zr_7O_{14} + Zr_7O_8N_4V_2$
β ″	$Zr_7O_{9.2}N_{3.2}$	trigonal superlattice	$Zr_7O_{14} + 4(Zr_7O_8N_4V_2)$
β	$Zr_7O_8N_4$	trigonal	$Zr_7O_8N_4V_2$ (Bevan cluster *3)
γ	Zr_2ON_2 *2	cubic	$Zr_{32}O_{16}N_{32}V_{16}$

*1 M.Lerch, F.Krumeich, and R.Hock, Solid State Ionics 95, 87-93 (1997)

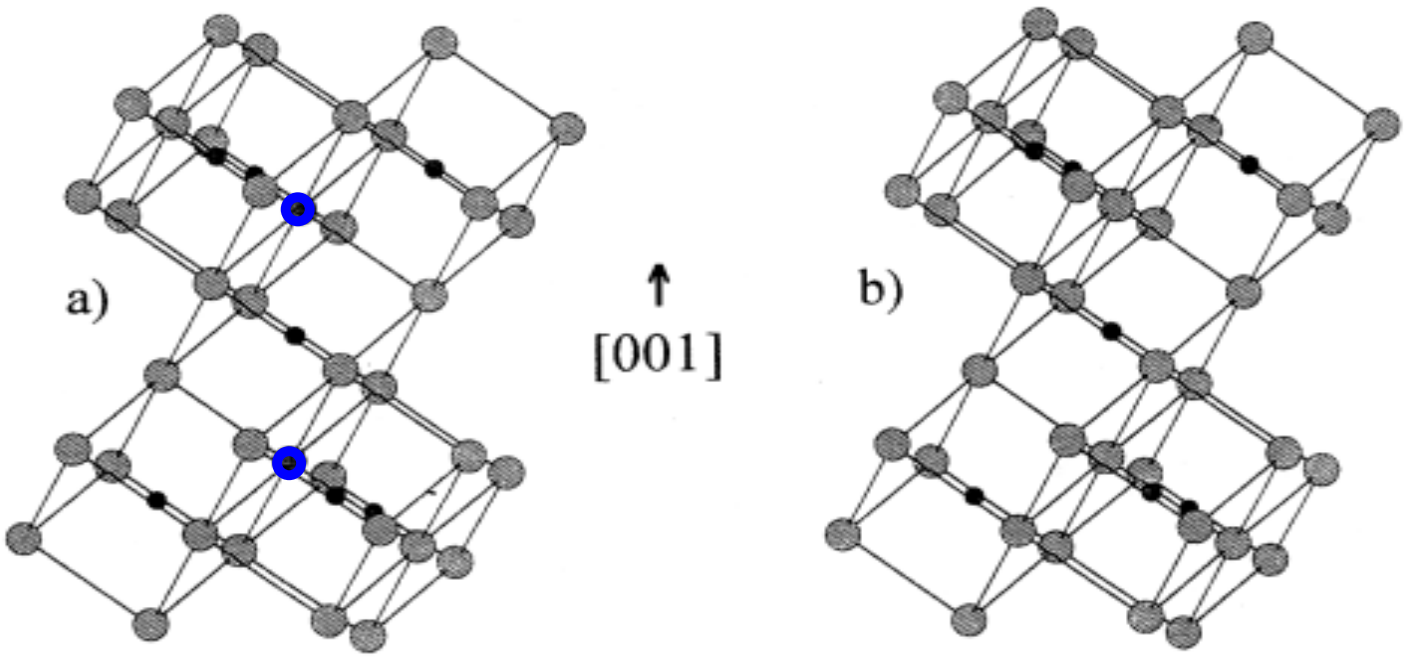
*2 S.J.Clarke, C.W.Michie, and M.J.Rosseinsky, J of Solid State Chem. 146, 399-405 (1999).

*3 D.J.M.Bevan, and R.L.Martin, Zeit. Anorg. Allgem. Chem 625, 57-69 (1999)

A Bevan cluster[*1] ($Zr_7O_8N_4$) and a Zr_7O_{14} unit[*2]

A sixfold coordination was found for the Zr in the central cube of $Zr_7O_8N_4$, whereas the metal atoms in the six other cubes are coordinated by seven anions.

In the Zr_7O_{14} unit, all Zr atoms show an eightfold coordination.



$Zr_7O_8N_4$ (Bevan cluster)

Zr_7O_{14}

Cations are shown as small black circles, anions as large gray circles and vacancies as large blue circles.

*1 D.J.M.Bevan, and R.L.Martin, Zeit. Anorg. Allgem. Chem 625, 57-69 (1999)

*2 M.Lerch, F.Krumeich, and R.Hock, Solid State Ionics 95, 87-93 (1997)

Comparison our samples with the superlattice structures reported in references

The number of **anion vacancies increases with the increase of nitrgen** incorporation.

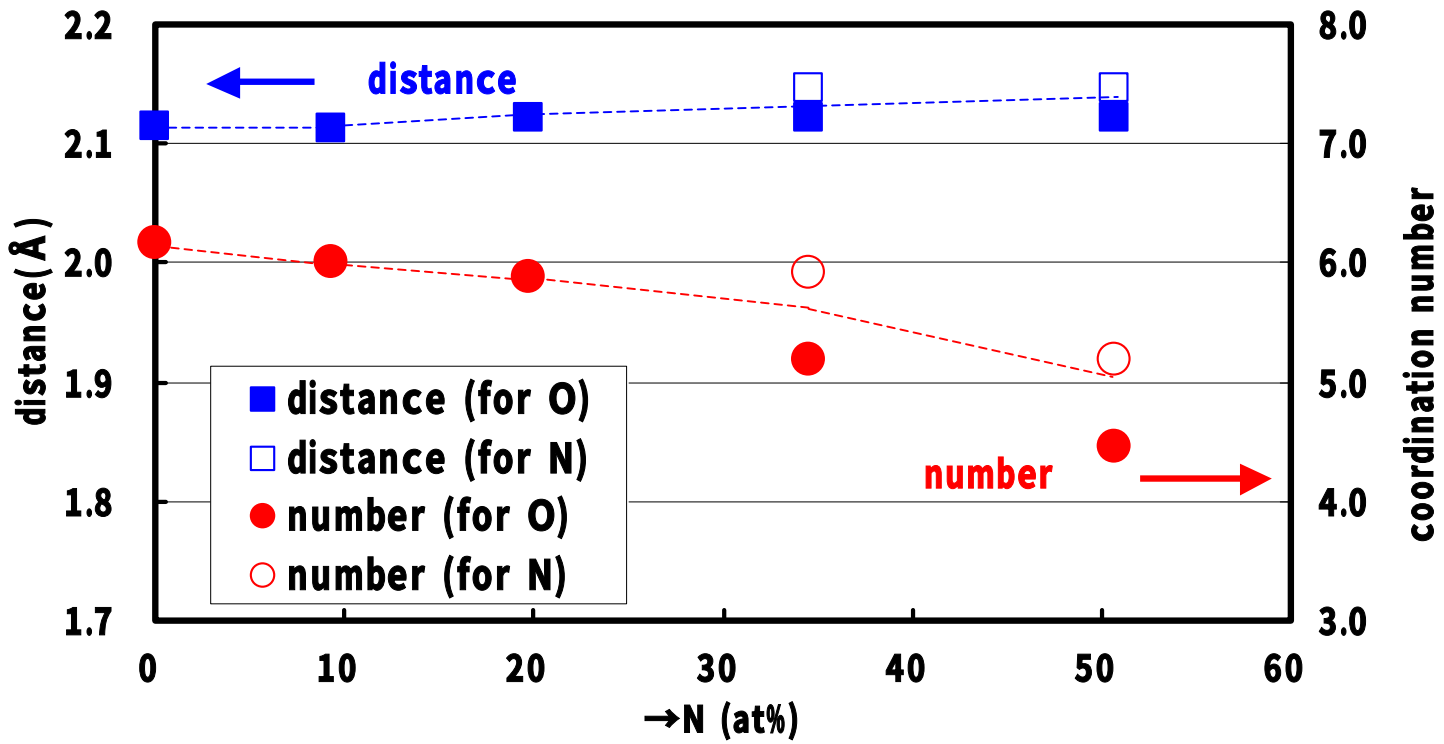
Any oxynitride which contains **N =or> 20at% does not include Hf_7O_{14}** unit.

Sample name	Composition of our samples			From reference			
	Hf (+Si)	O	N	composition	Unit cell	vacancies per a Hf atom	phase
N00	7	15.7	0	HfO_2	Hf_4O_8 Monoclinic	0	
N10	7	13.2	2.1	$Hf_7O_{11}N_2$	Hf_7O_{14} + $Hf_7O_8N_4V_2$ Hexagonal, superlattice	0.14	**β '**
				$Hf_7O_{9.2}N_{3.2}$	Hf_7O_{14} + 4($Hf_7O_8N_4V_2$) Hexagonal, superlattice	0.23	**β "**
N20	7	7.3	3.6	$Hf_7O_8N_4$	$Hf_7O_8N_4V_2$ Hexagonal	0.29	**β**
N35	7	4.0	6.0	Hf_2ON_2	$Hf_{32}O_{16}N_{32}V_{16}$, Cubic	0.50	**γ**
N50	7	1.7	9.4	Hf_2ON_2 +HfN?		>0.50	

EXAFS analysis result for HfSiON

These results should be understood in the context that

nitrogen incorporation has allowed the anion vacancy incorporation to maintain the oxide structure and to maintain electric neutrality in the amorphous HfSiON.



Summary

We conclude as mentioned below concerning the XAFS results and the analogy of Zr oxynitride crystal structure:

- The local structure around Hf does not greatly change with nitrogen incorporation.
- Nitrogen incorporation allows the anion vacancy incorporation to maintain the oxide structure and to maintain electric neutrality in amorphous Hf silicate films.
- Any oxynitride which contains N =or> 20at% does not include Hf_7O_{14} unit, so HfO_2 crystal hardly glows when it is heated.

These results convey useful information concerning investigation of the high-k gate dielectrics, by the XAFS method using the high-brilliance synchrotron radiation at SPring-8.

XAFS experiment was performed as SPring-8 proposal No. C03B16B2-4012-N