Etching of high-*k* dielectric HfO_2 films in BCl-containing plasmas without rf biasing

D. Hamada, K. Nakamura, K. Eriguchi, K. Ono

Department of Aeronautics and Astronautics,
Graduate School of Engineering, Kyoto University,
Yoshida-Honmachi, Sakyo-ku, Kyoto 606-8501, Japan

Outline

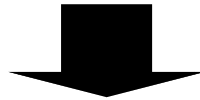
1. Objective
   - Requirements for etching of high-*k* materials
   - Etching of HfO_2 in BCl_3-containing plasma
2. Experimental
3. Results and discussions
   - BCl_3, BCl_3/O_2 plasma
   - BCl_3/Cl_2, $BCl_3/Cl_2/O_2$ plasma
   - BCl_3/Ar plasma
4. Conclusions

Objective

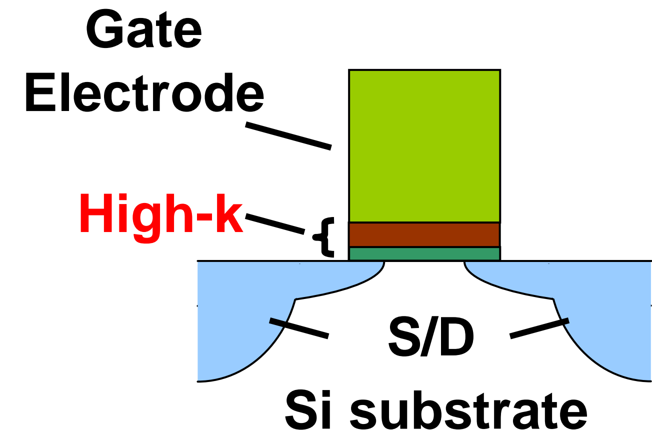
■ Requirements for advanced LSI :

• Down scaling of EOT※

• Controlling of gate leakage current



High-k gate dielectric materials



■ Process-related issue :

Etching high-*k* with high etch rate, selectivity,
AND lower damage (= ion energy)
for chamber cleaning / highly controlled process
& higher device performance

■ This work :

To study HfO_2 etching by BCl_3 without RF-biasing
- characteristics and its mechanism

※ Equivalent Oxide Thickness

Etching of High-k Materials

High-*k*: strong metal-oxygen bonds / non-volatile products

Physical properties of potential product species

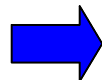
Element	Halogen compound	Melting Point (°C)	Boiling Point (°C)
Al (Z=13)	AlF_3 $AlCl_3$ $AlBr_3$	2250 192.6 97.5	1276 – 255
Si (Z=14)	SiF_4 $SiCl_4$ $SiBr_4$	– 90.2 – 68.85 5.2	–86 57.65 154
Zr (Z=40)	ZrF_4 $ZrCl_4$ $ZrBr_4$	– – –	912 *sp 331 *sp 360 *sp
Hf (Z=72)I	HfF_4 $HfCl_4$ $HfBr_4$	– – –	970 *sp 317 *sp 323 *sp

*sp: sublimation point

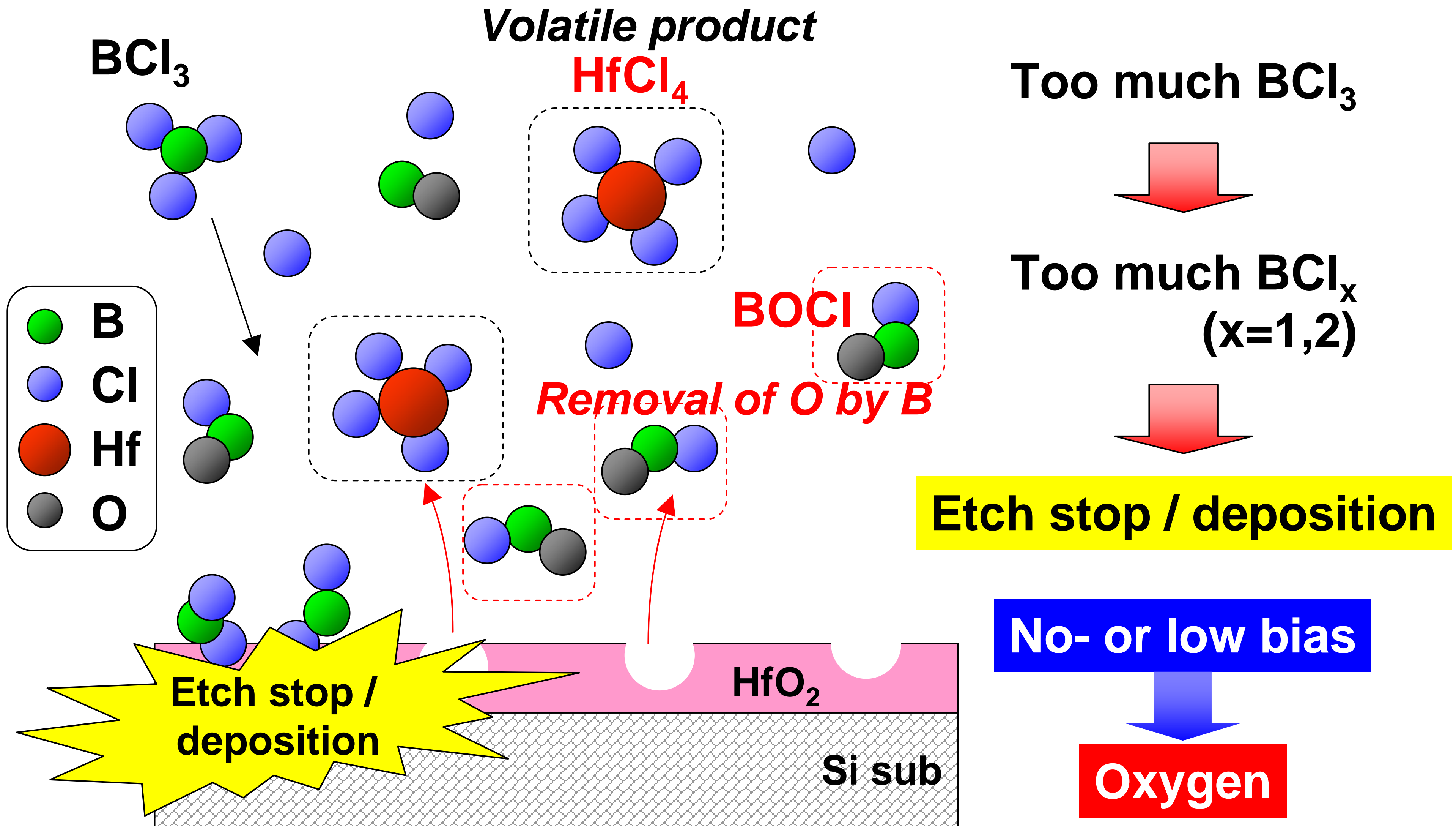
Bond strengths for diatomic species

Bond	Bond Strength (eV)	Bond	Bond Strength (eV)
B-O B-F B-Cl B-Br	8.38 7.85 5.30 4.11	Si-O Si-F Si-Cl Si-Br Si-Si	8.29 5.73 4.21 3.81 3.39
C-O C-F C-Cl C-Br	11.15 5.72 4.11 2.90	Zr-O Zr-F Zr-Cl Zr-Br	8.03 6.38 5.11 –
Al-O Al-F Al-Cl Al-Br	5.30 6.88 5.30 4.45	Hf-O Hf-F Hf-Cl Hf-Br	8.30 6.73 5.16 –

(from CRC Handbook of Physics and Chemistry, 1998)

$HfCl_4$, BO  **BCl_3-based gas chemistry**

Basic mechanism of HfO_2 etch in BCl_3 plasma



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Experimental setup for ECR plasma etching

Experimental parameters

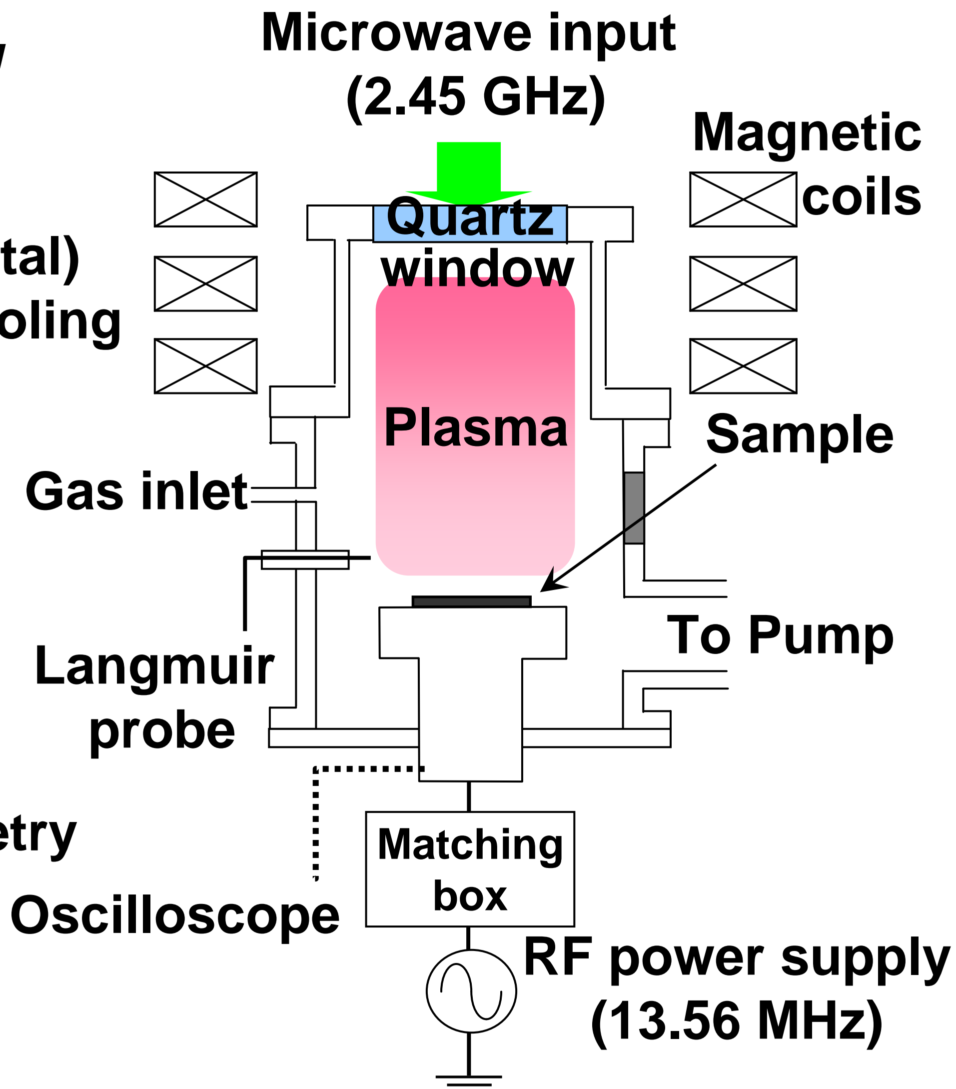
- Microwave : 2.45 GHz, 600 W
- Gas : Cl_2, BCl_3, Ar, O_2
- Pressure : 5 ~ 20 mTorr
- Gas flow rate : 40 sccm (in total)
- Stage temperature : water cooling
- RF bias : 13.56 MHz, 0 W

Samples

- CVD-HfO_2 (50nm) / Si
- Si, SiO_2

Measurement

- Stylus profilometry, Ellipsometry
- XPS, OES, Langmuir probe



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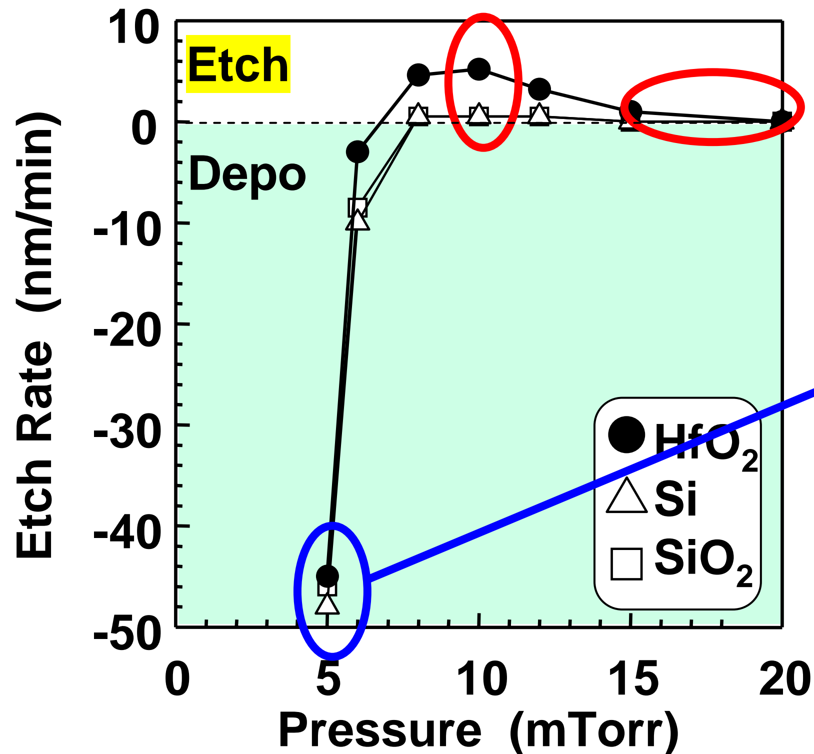
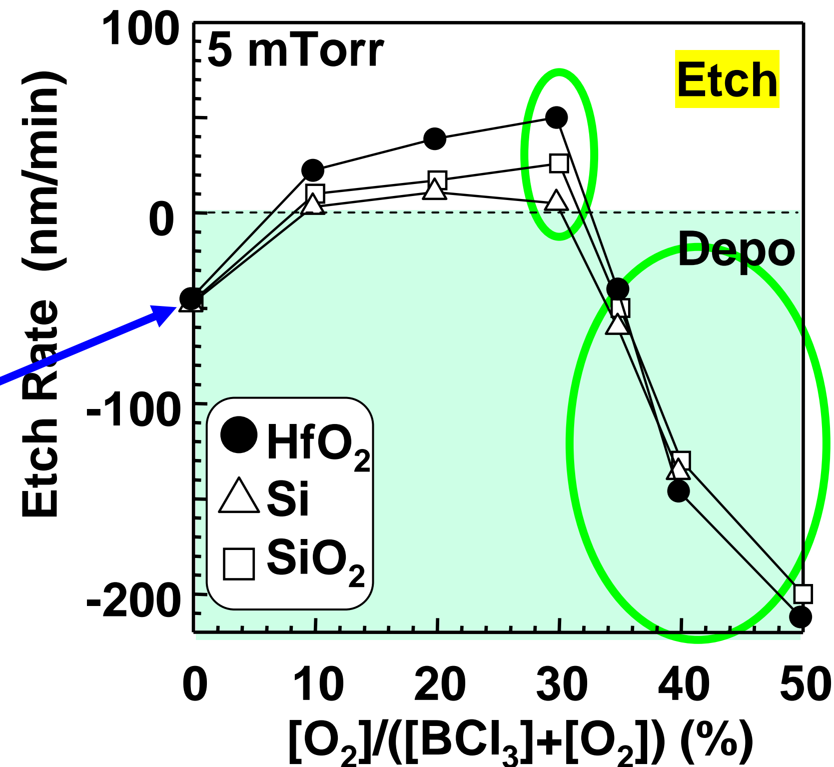
HfO_2 etch in BCl_3 ,BCl_3/O_2 plasmas

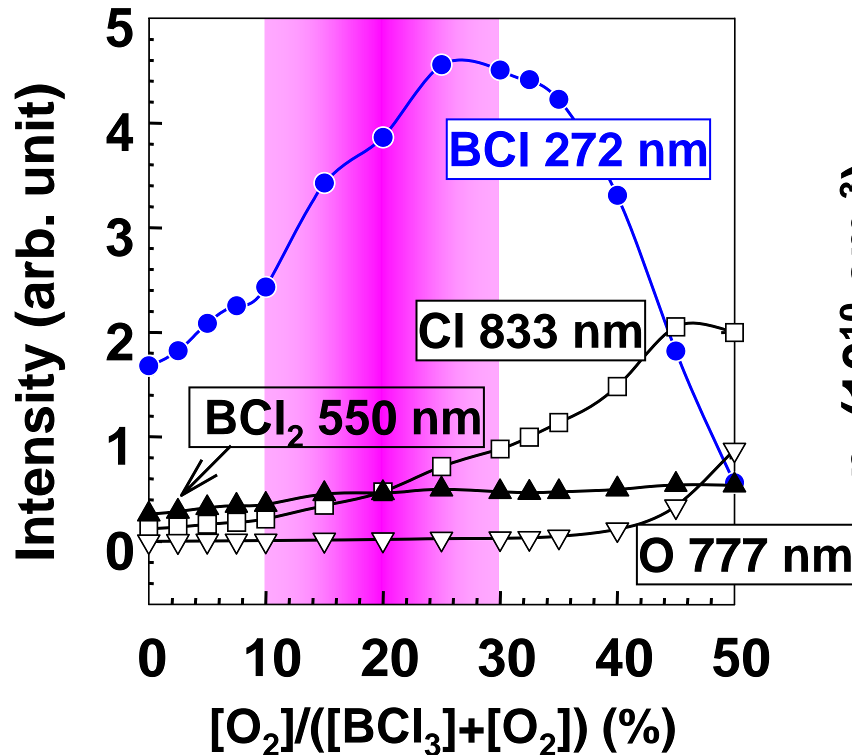




	Max. etch rate of HfO_2	Max. select. HfO_2/Si	Deposition
BCl_3	~6 nm/min @ P =10mTorr	~10 @ P =10mTorr	P < 8 mTorr
BCl_3/O_2	~55 nm/min @ O_2 30%	~10 @ O_2 30%	O_2 > 30%

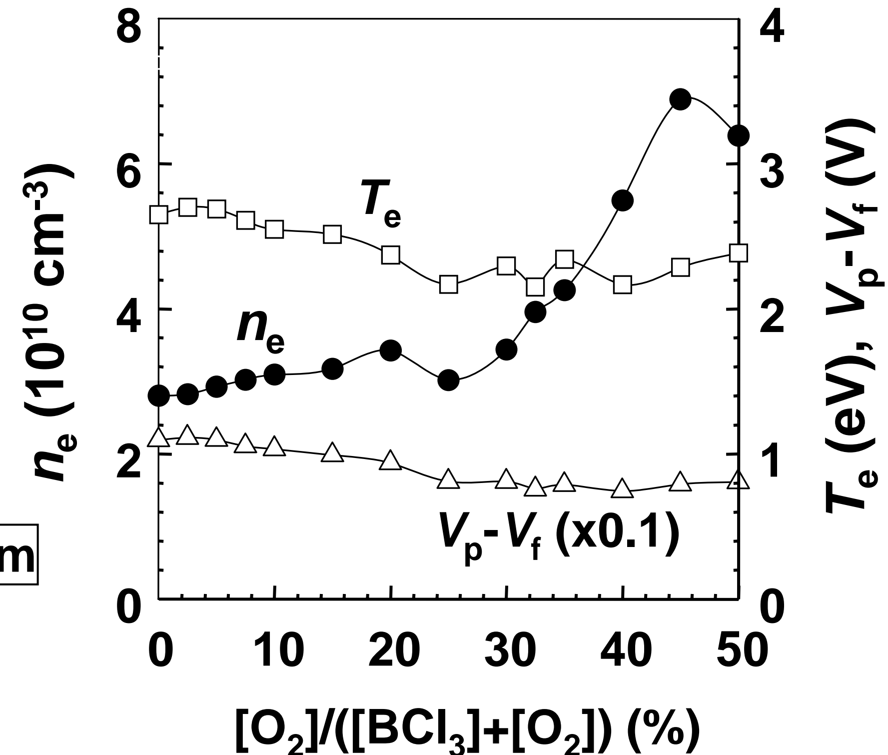
Plasma diagnostics - BCl_3/O_2 plasma

Optical Emission



Langmuir probe

MW: 600 W
P_0= 5 mTorr



BCl, Cl, O intensities ~ Etch rate

BCl --- a key role in etching of HfO_2

XPS analysis for surface exposed layers

Etched HfO_2 surfaces

XPS Intensity

Hf 4$f_{7/2}$ Hf 4$f_{5/2}$

16 12 8 4 0

25 20 15 10

Binding Energy (eV)

Cl 2p

B 1s

8 6 4 2 0

205 200 195 190 185 180

Binding Energy (eV)

O 1s (HfO_2)

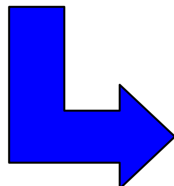
25 20 15 10 5 0

540 535 530 525 520 515

Binding Energy (eV)

w/o plasma exposure
BCl_3 (10 mTorr)
30% O_2 / 70% BCl_3 (5 mTorr)

Etched surface



Only HfO_2
No Cl- or BO-compounds

XPS analysis for surface exposed layers

Deposited HfO_2 surfaces

XPS Intensity

Hf 4*f*

16
12
8
4
0

25 20 15 10

Binding Energy (eV)

Cl 2*p*

B 1*s* (B-Cl)

B 1*s* (B-O)

8
6
4
2
0

205 200 195 190 185 180

Binding Energy (eV)

O 1*s* (B_2O_3)

25
20
15
10
5
0

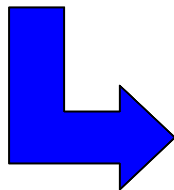
540 535 530 525 520 515

Binding Energy (eV)

BCl_3 (5 mTorr)

50% O_2 / 50% BCl_3 (5 mTorr)

Deposited surface



No apparent HfO_2 peak
Cl- or BO-compounds

Summary of XPS results

	Hf	O	B	Cl
Before plasma exposure	30.0 %	70.0 %	0 %	0 %
(i) BCl_3 5 mTorr (depo)	0.1 %	19.0 %	55.8 %	25.1 %
(ii) BCl_3 10 mTorr (etch)	26.0 %	61.6 %	7.4 %	5.0 %
(iii) 30% O_2 / 70% BCl_3 (etch)	27.5 %	63.1 %	5.6 %	3.8 %
(iv) 50% O_2 / 50% BCl_3 (depo)	0.1 %	39.0 %	52.3 %	8.6 %

1. No Hf spectrum is observed on deposited surfaces.
2. At low pressures in a pure BCl_3 plasma, the deposited B_xCl_y are found.
3. At excessive O_2 addition in BCl_3/O_2 plasmas, the deposited B_xO_y are found.

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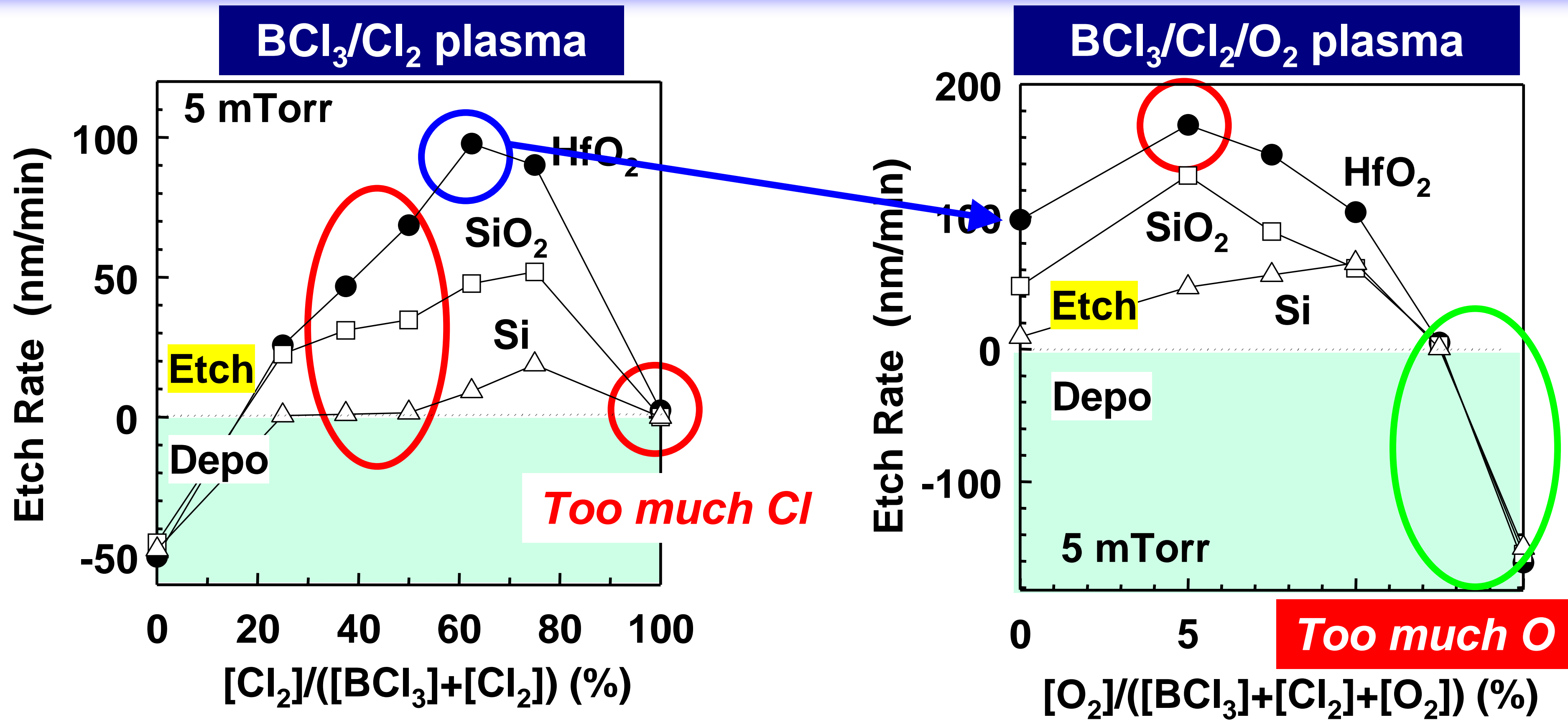
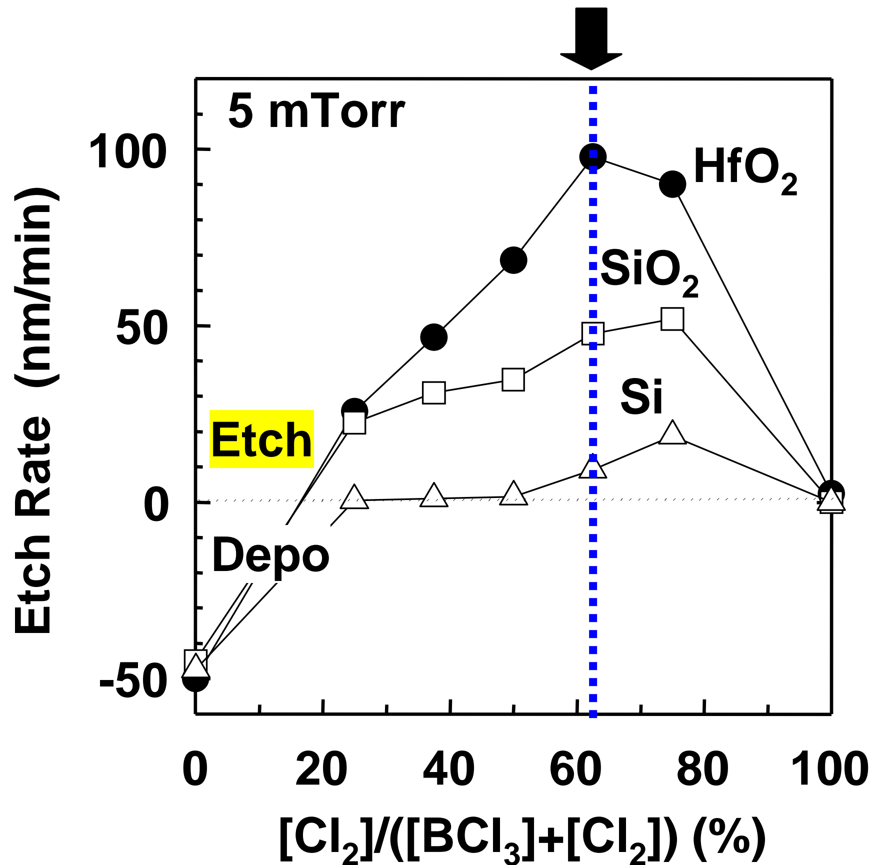
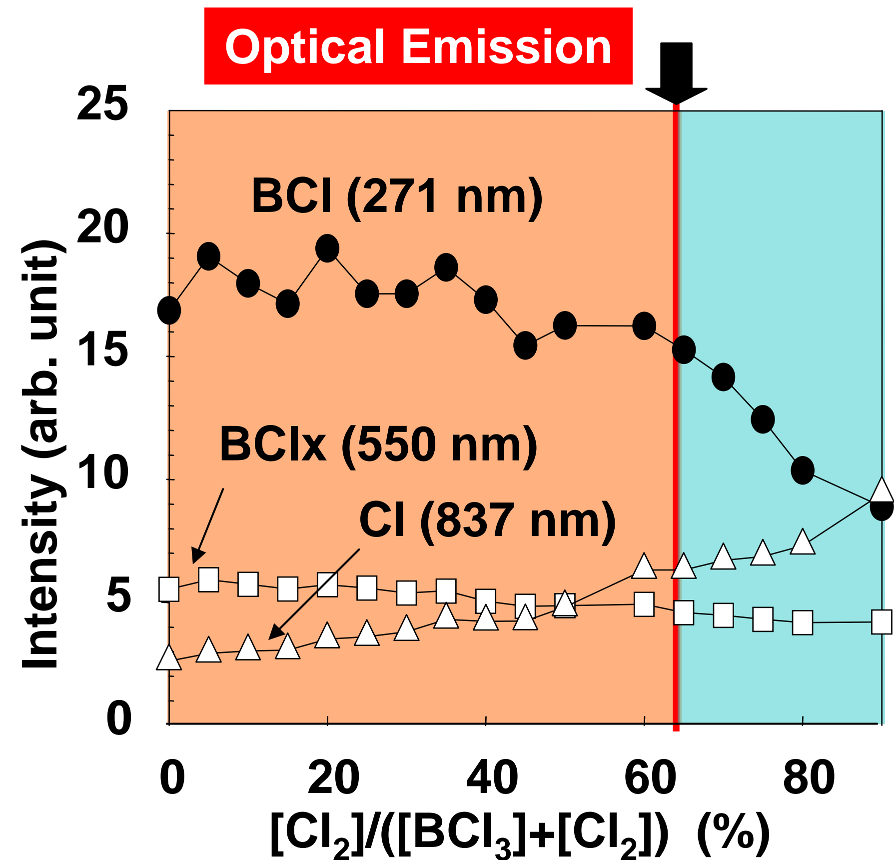
HfO_2 etch in BCl_3/Cl_2, $BCl_3/Cl_2/O_2$ plasmas



	Max. etch rate of HfO_2	Max. select. HfO_2/Si	Deposition
BCl_3/Cl_2	~100 nm/min @Cl_2 62.5%	~50 @ Cl_2 40~50%	Cl_2 < 25%
$BCl_3/Cl_2/O_2$	~150 nm/min @O_2 5%	~10 @O_2 0%	O_2 > 12.5%

HfO_2 etch in BCl_3/Cl_2 plasmas





BCl and Cl intensities ~ Etch rate

It is important to keep balance between BCl and Cl.
(& Optimized O_2 addition suppresses deposition process.)

Summary of OES

BCl (271 nm)
BCl_x (550 nm)
O (777 nm)
Cl (837 nm)

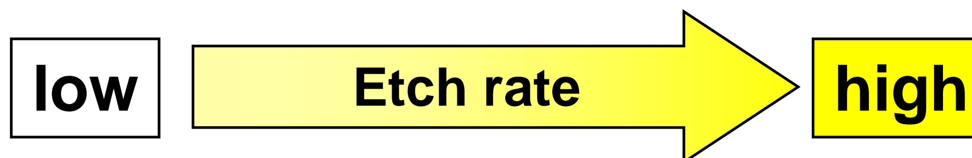
Intensity (arb. unit)

8
6
4
2
0

T_{sub}=90 C
80 C
75 C

BCl_3/O_2 BCl_3/Cl_2 $BCl_3/Cl_2/O_2$

Ratio of BCl/Cl !



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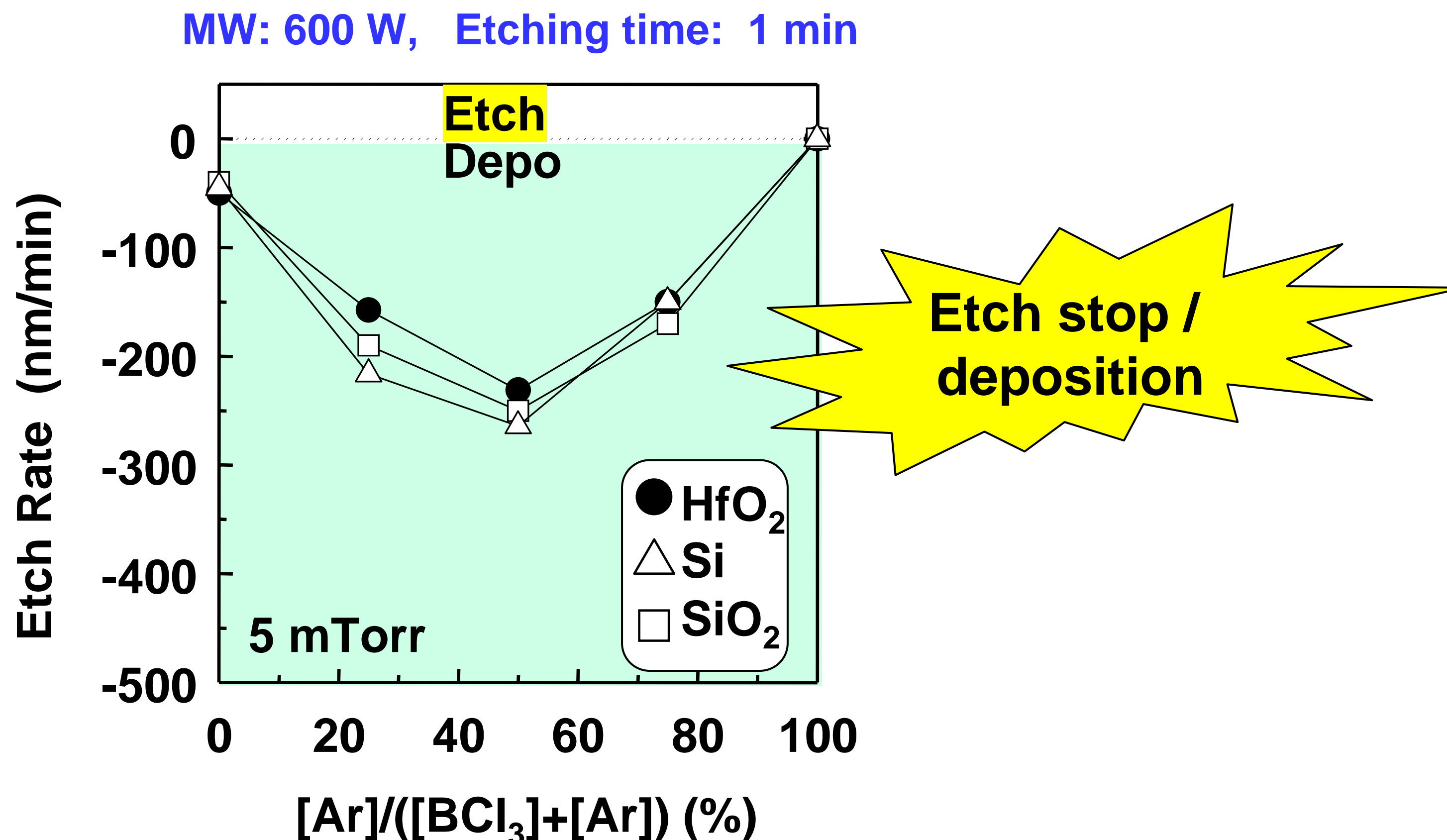
Role of Ar in HfO_2 etch in BCl_3 plasma



Adding Cl_2 and/or O_2 to BCl_3
-> not to dilute BCl_3 to prevent the deposition of BCl,
-> but to enhance chemical reactions / to suppress the deposition.

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Conclusions

	At max. etch rate		At HfO_2/Si max. select. (Si)	
	Etch rate	Select. (Si)	Etch rate	Select.
BCl_3	6 nm/min	~10	6 nm/min	~10
BCl_3/O_2	50 nm/min	~10	50 nm/min	~10
BCl_3/Cl_2	100 nm/min	~5	50 nm/min	~50
$BCl_3/Cl_2/O_2$	150 nm/min	~5	100 nm/min	~5
BCl_3/Ar	(depo)	(depo)	(depo)	(depo)

1. BCl_3 contributes to trigger etching of HfO_2, but excess of BCl_3 results in the deposition.
2. O_2 suppresses the deposition & enhances etching.
3. Cl_2 enhances etching process triggered by BCl_3.

That’s all I want to talk.

Thank you for your attention.