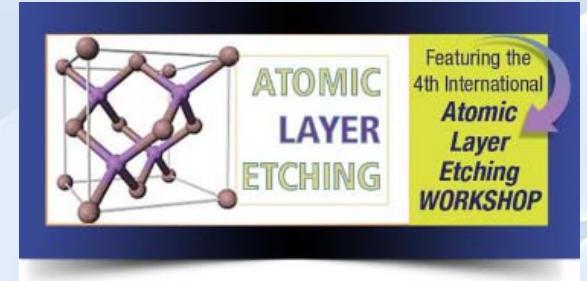


ALE 2017 Tutorial

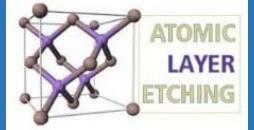


# Atomic Layer Etching with Ion/Neutral Beams

2017. 07. 15.

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Sungkyunkwan University (SKKU), Korea



1

**Introduction of Atomic Layer Etching with Ion/Neutral Beam**

2

ALE of Various Materials  
(Si, III-V Compounds, High-k Dielectrics)

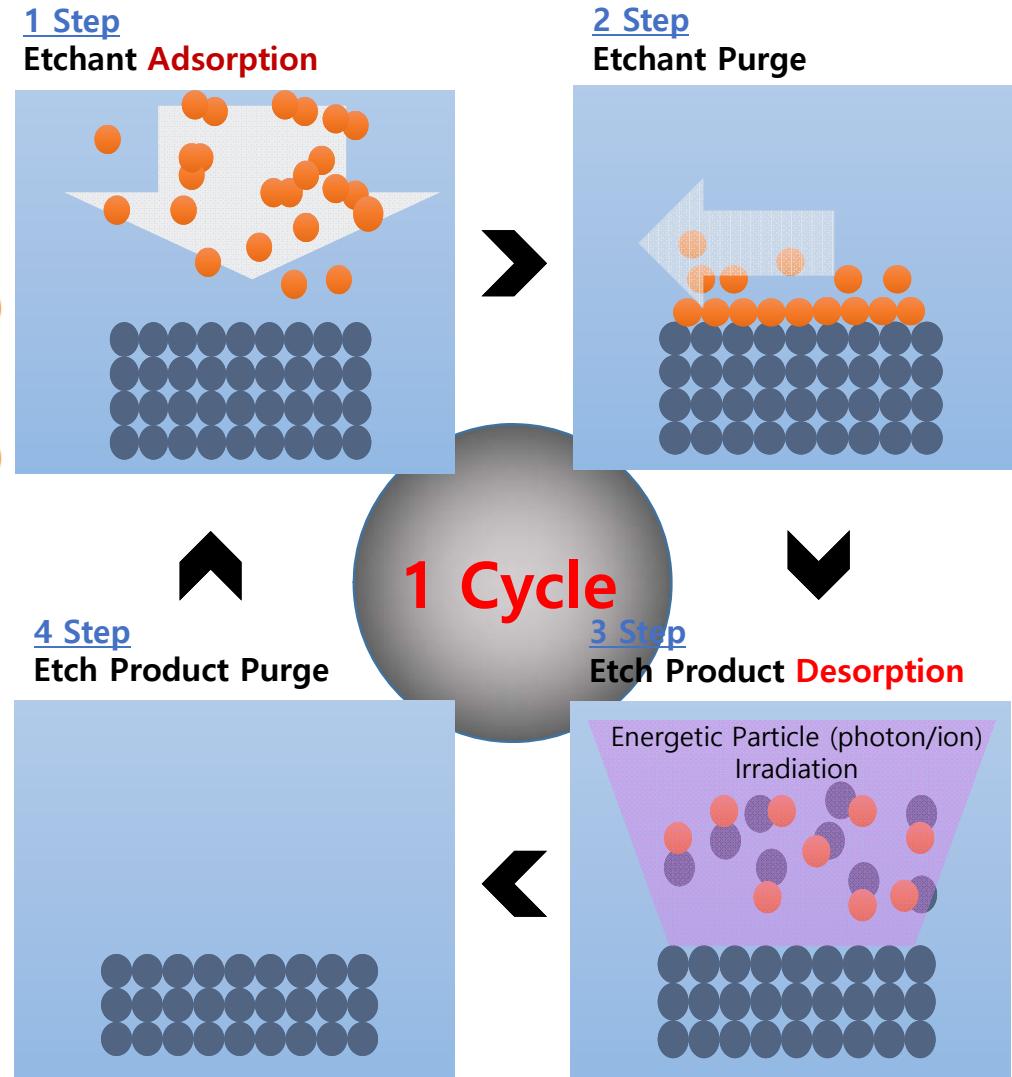
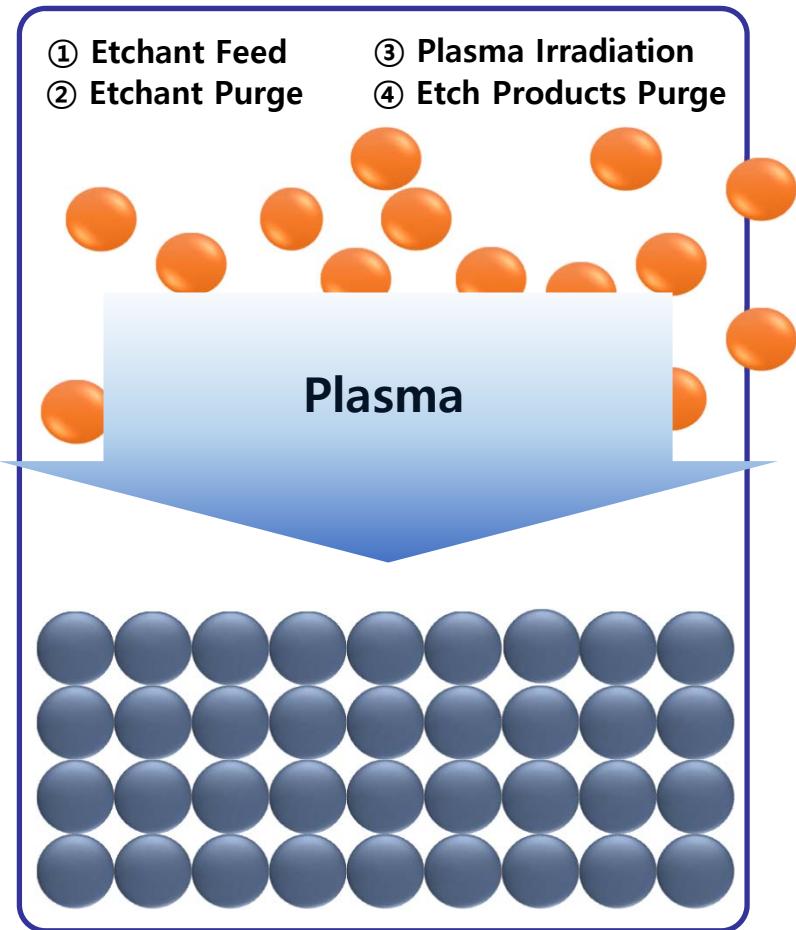
3

Recent Research Trends

4

Summary

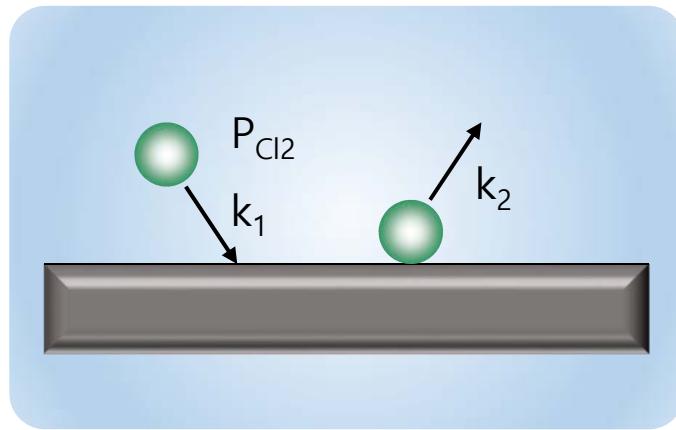
## ◆ Concept of ALET



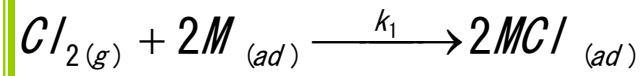
# Mechanism of ALE



## ◆ Chemisorption of Cl<sub>2</sub> on materials



Dissociative Langmuir isotherm chemisorption :

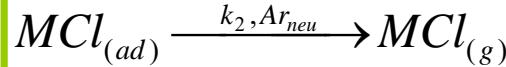


Coverage of the MCl precursor :

$$k_1 = \frac{\theta_{MCl}^2}{(1 - \theta_{MCl})^2 P_{Cl_2}} \quad \Rightarrow \quad \theta_{MCl} = \frac{\sqrt{k_1 P_{Cl_2}}}{1 + \sqrt{k_1 P_{Cl_2}}}$$

## ◆ Desorption of chemisorbed materials by Ar<sup>+</sup> bombardment

Sputtering of MCl by Ar bombardment:

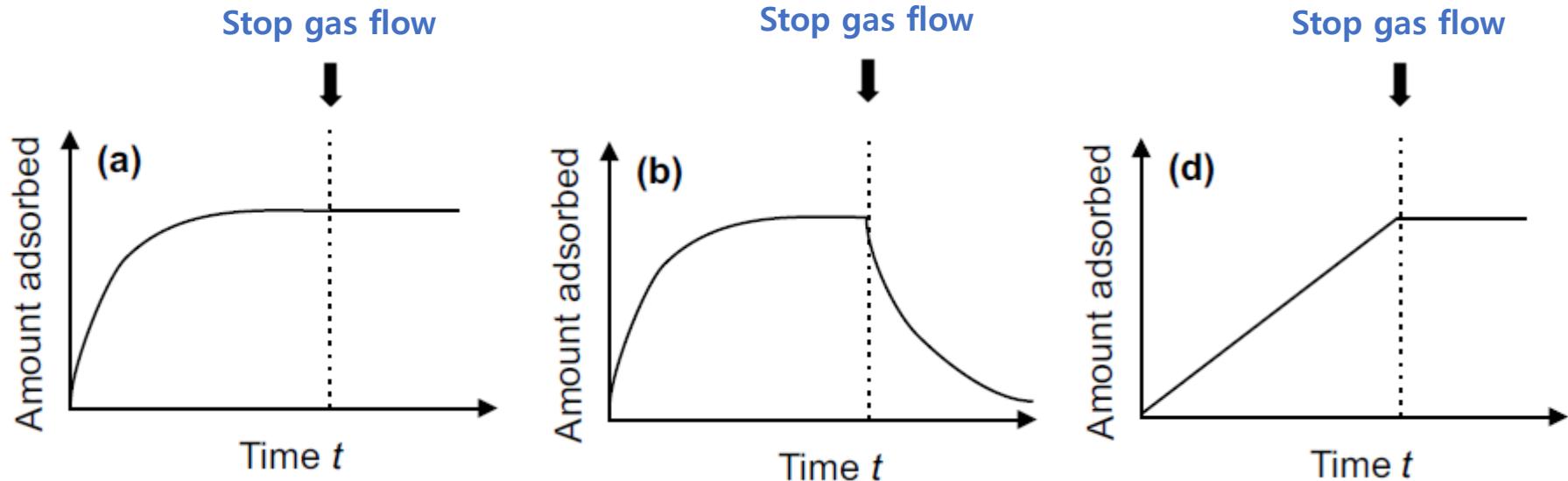
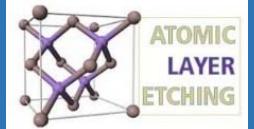


where,  
k<sub>1</sub> : adsorption rate constant (Pa·s)<sup>-1</sup>  
k<sub>2</sub> : desorption rate constant (s)<sup>-1</sup>  
P<sub>Cl<sub>2</sub></sub> : Cl<sub>2</sub> pressure (Pa)

Sputtering rate of Cl-adsorbed Material (MCl) :

$$f_{MCl} \propto k_2 \theta_{MCl} f_{Ar_{neu}}$$

# Adsorption Condition for ALE



- ◆ **Irreversible saturation:**  
- Required for ALE

Surface saturates with a monolayer of precursor, strong chemisorption (=chemical bonds formed)

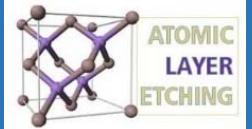
- ◆ **Reversible saturation:**

Physisorption only (weak bonds like van der Waals): once precursor flux is stopped, surface species will desorb.

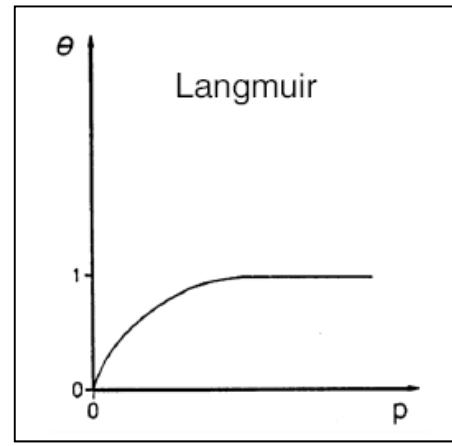
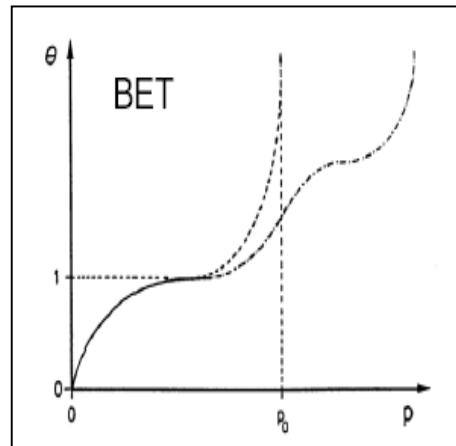
- ◆ **Irreversible non-saturation:**

Physisorption multilayers and continuous deposition

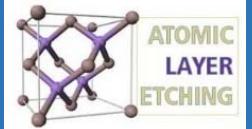
# Adsorption and Reaction at Surfaces



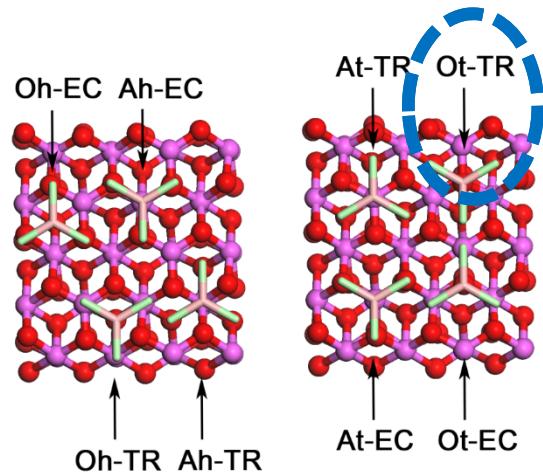
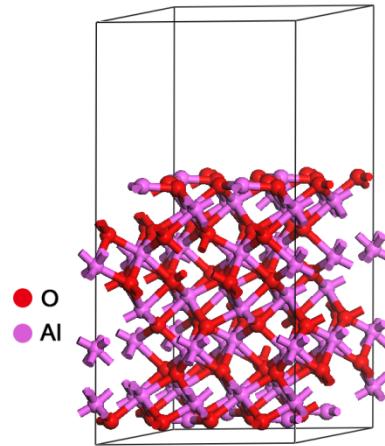
Physisorption	Chemisorption
<b>weak, long range bonding</b> Van der Waals interactions	<b>strong, short range bonding</b> Chemical bonding involving orbital overlap and Charge transfer
<b>Not surface specific</b>	<b>Surface specific</b>
$\Delta H_{ads} = 5\text{--}50 \text{ kJ/mol}$	$\Delta H_{ads} = 50\text{--}500 \text{ kJ/mol}$
<b>No surface reaction</b>	<b>Surface reactions may take place</b> Dissociation, reconstruction, catalysis
<b>Multilayer adsorption</b> BET Isotherm used to model adsorption equilibrium	<b>Monolayer adsorption</b> Langmuir Isotherm used to model adsorption equilibrium



# First Principle Study of $\text{Al}_2\text{O}_3$ ALE

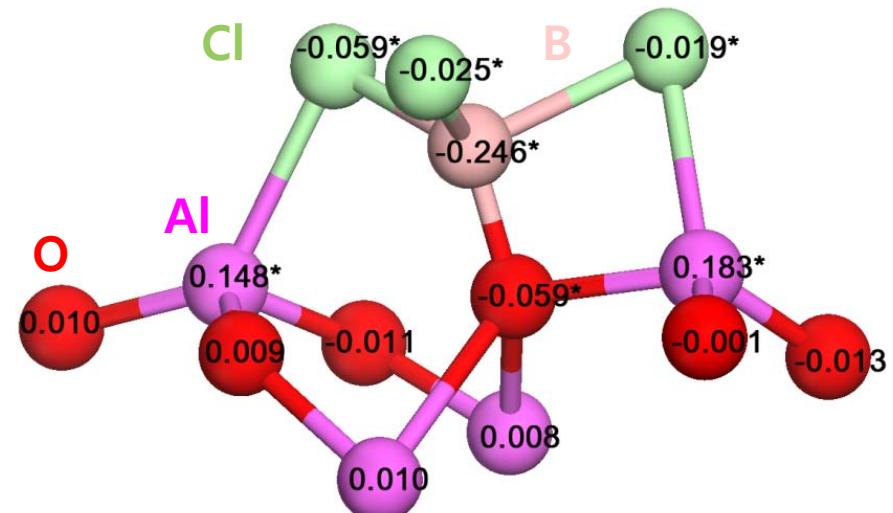


## ◆ Adsorption



Configuration	Ah-EC	Ah-TR	At-EC	AT-TR
Energy (Kcal/mol)	-32.293	-32.142	-15.347	-17.574
Configuration	Oh-EC	Oh-TR	Ot-EC	Ot-TR
Energy (Kcal/mol)	-32.633	-31.707	-45.617	<b>-58.986</b>

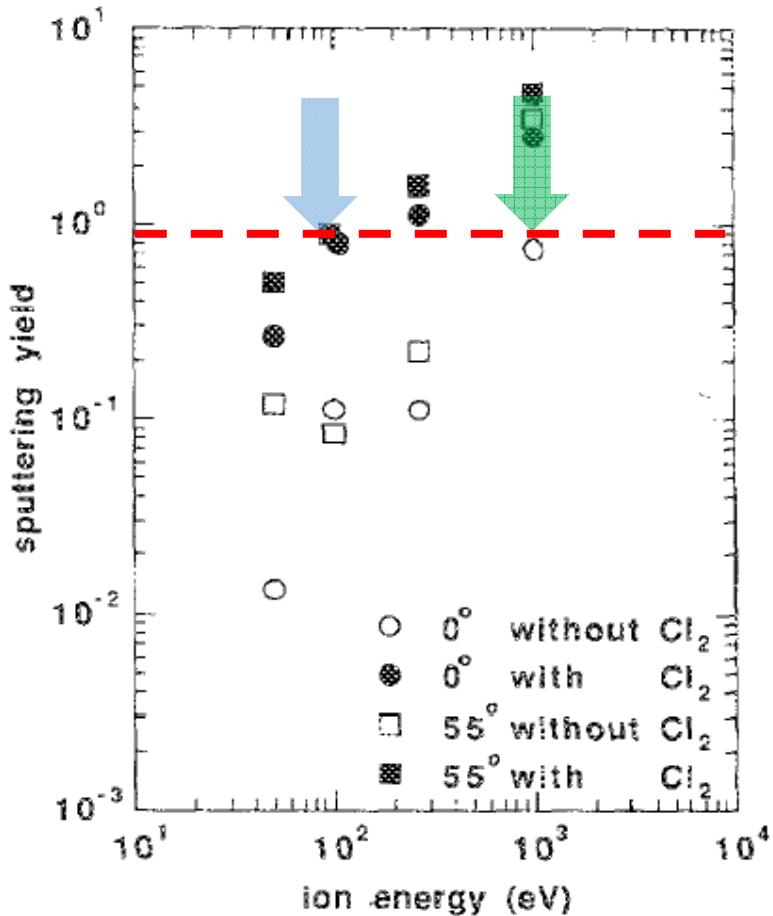
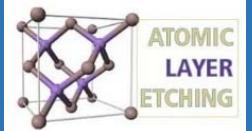
Ot-TR configuration led to the most stable  $\text{BCl}_3$  adsorption with an adsorption energy of 58.99 Kcal/mol



\*: significant electron population change upon the  $\text{BCl}_3$  adsorption

"Understanding time-resolved processes in atomic-layer etching of ultra-thin  $\text{Al}_2\text{O}_3$  film using  $\text{BCl}_3$  and Ar neutral beam"  
Young I. Jhon, Kyung S. Min, G. Y. Yeom, and Young Min Jhon  
Appl. Phys. Lett. 105, 093104 (2014)

# Sputter Rate of Silicon in a Cl<sub>2</sub> Environment



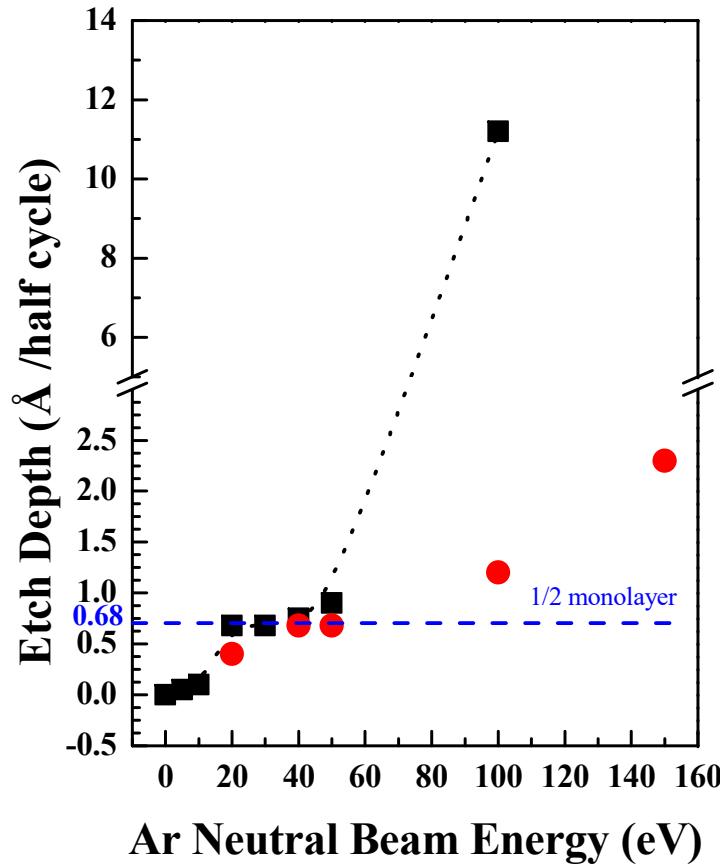
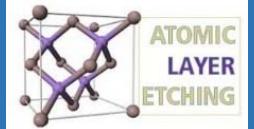
◆ Average product yield

Yield	Average value $\pm$ (95% confidence intervals)
Si	$0.013 \pm 0.002$ (8%)
Cl	$0.040 \pm 0.003$
Ar	$0.803 \pm 0.078$
Ar thermalization	$0.192 \pm 0.062$
Ar trapped permanently	$<0.01$
SiCl	$0.145 \pm 0.035$ (84%)
SiCl <sub>2</sub>	$0.014 \pm 0.003$ (8%)

"Near threshold sputtering of Si and SiO<sub>2</sub> in a Cl<sub>2</sub> environment"  
D. J. Oostra, R. P. van Ingen, A. Haring, and A. E. de VriesG. N. A. van Veen  
Appl. Phys. Lett. 50, 1506 (1987)

"Molecular dynamics simulation of atomic layer etching of silicon"  
Satish D. Athavale and Demetre J. Economou  
J. Vac. Sci. Technol. A 13 (2) (1995)

# Si ALE as a function of Ar Beam Energy



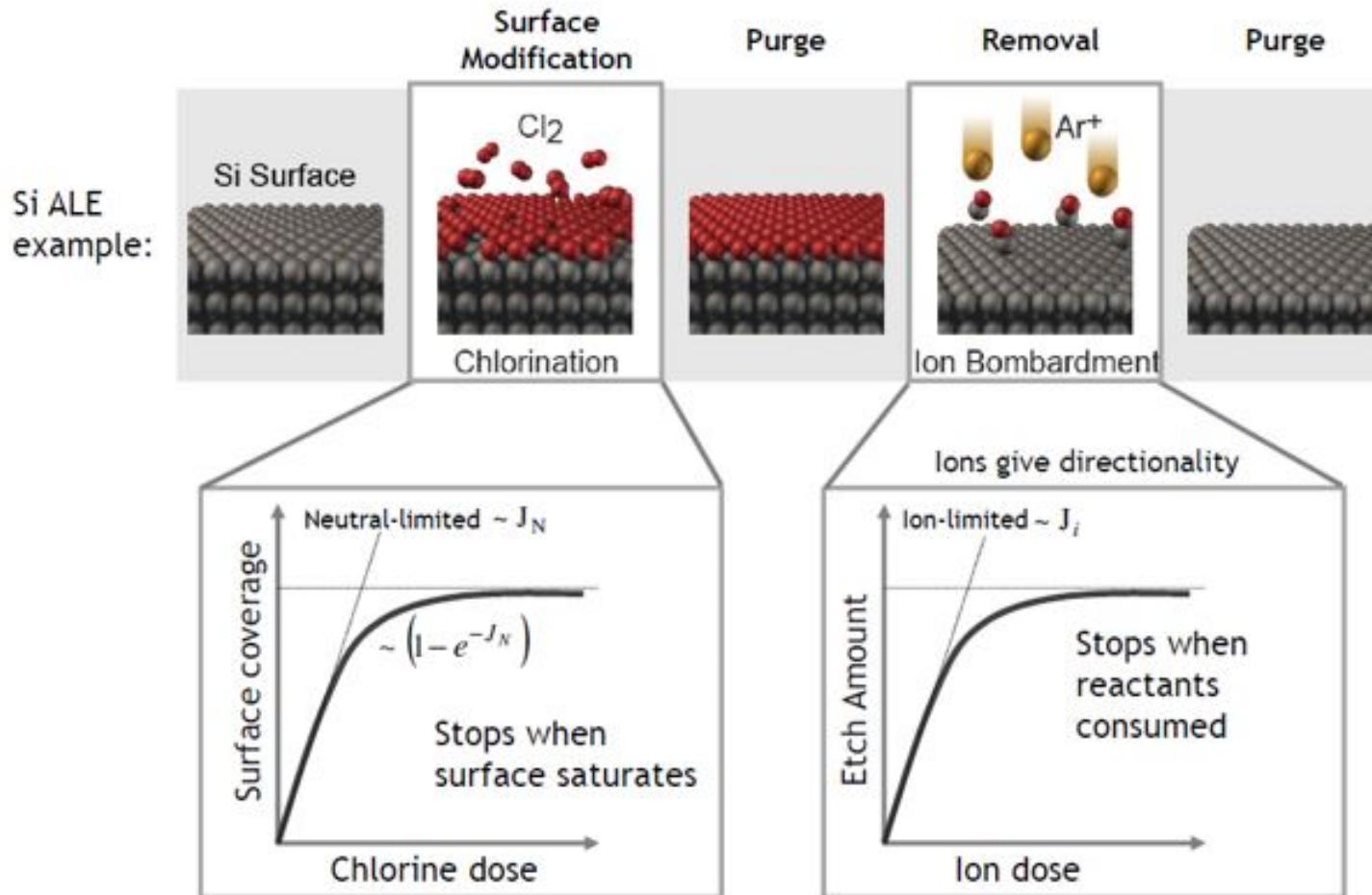
Base pressure	$2.0 \times 10^{-6}$ Torr
Operating pressure	$4.0 \times 10^{-4}$ Torr
Cl <sub>2</sub> partial pressure	10 mPa
$t_{\text{Cl}_2}$	20 sec
$t_{\text{Ar}^+}$	5 sec
Ar flow rate	40 sccm
RF power	50 W
Ion acceleration voltage	40 ~ 150 V

Below about 50 eV of energy, the chemical etching is found to be more dominant than the physical sputtering. Etch rate increase by Ar energy (Threshold E < 50 eV)

# Si ALE as a function of Etch Parameters



## ◆ Use time domain to simplify

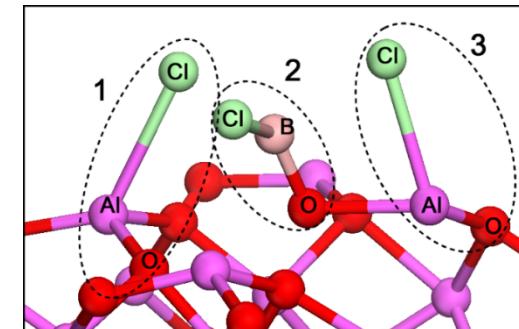
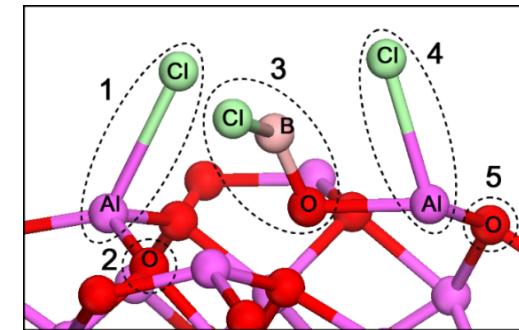
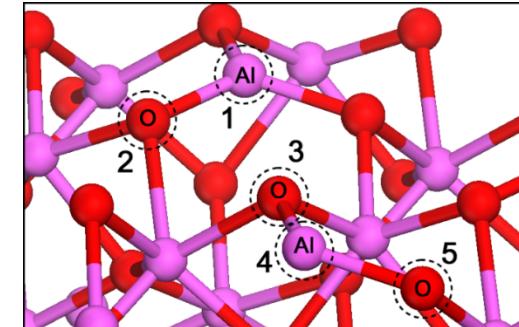
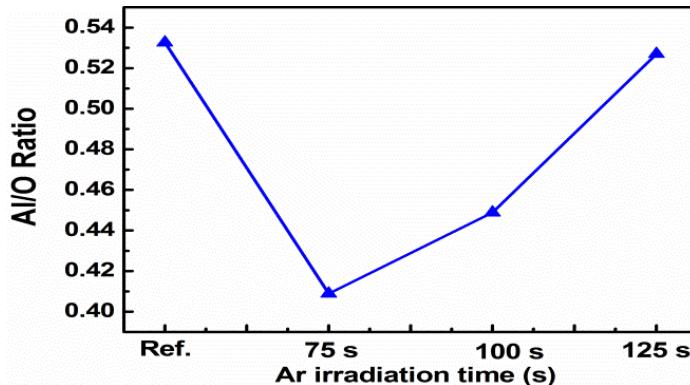
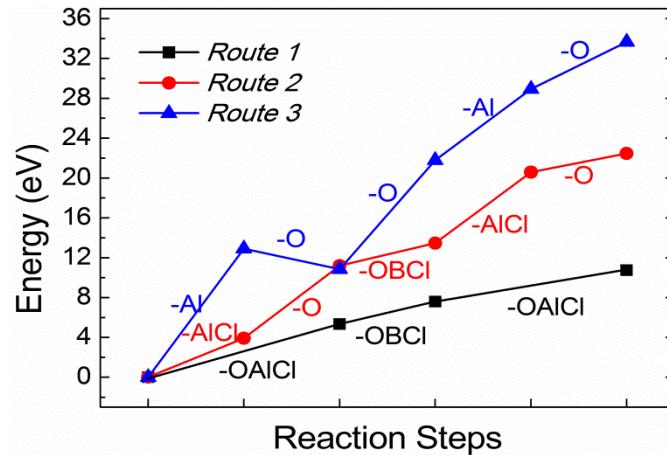
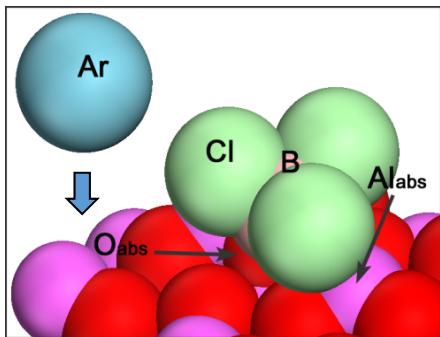
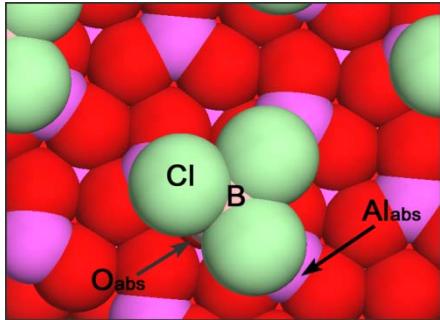


"Overview of atomic layer etching in the semiconductor industry"  
Keren J. Kanarik, Thorsten Lill, Eric A. Hudson, Saravanapriyan Sriraman, Samantha Tan, Jeffrey Marks, Vahid Vahedi, and Richard A. Gottscho  
J. Vac. Sci. Technol. A 33 (020802) (2015)

# First Principle Study of $\text{Al}_2\text{O}_3$ ALE

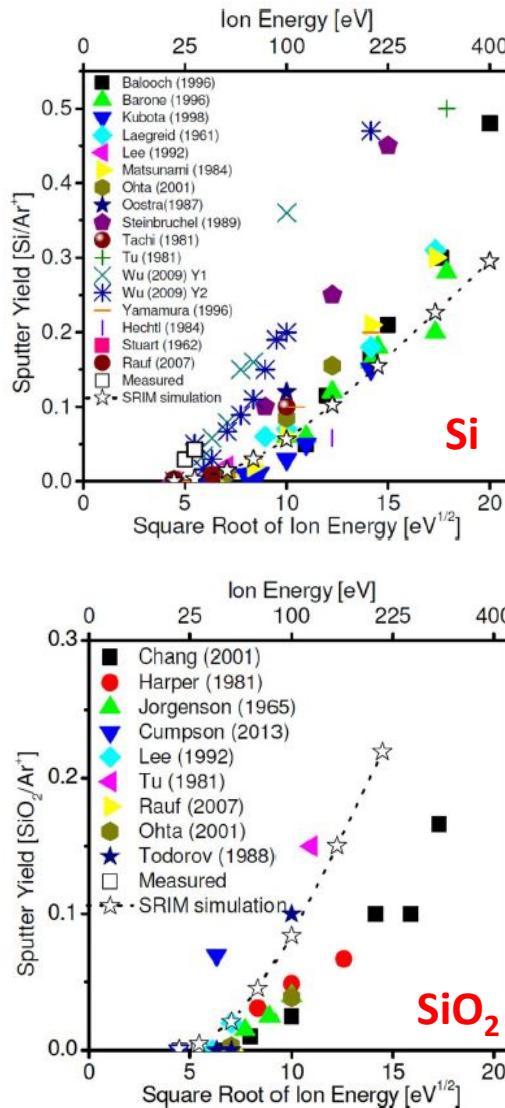
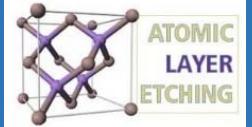


## ◆ Desorption



"Understanding time-resolved processes in atomic-layer etching of ultra-thin Al<sub>2</sub>O<sub>3</sub> film using BCl<sub>3</sub> and Ar neutral beam"  
Young I. Jhon, Kyung S. Min, G. Y. Yeom, and Young Min Jhon  
Appl. Phys. Lett. 105, 093104 (2014)

# Threshold Energy for Sputtering



- ◆ Ion energy control is essential to enable atomic scale precision
- Energy threshold chosen specifically to enable reactant activation and removal of one material selective to all others

TABLE 1 Threshold Energies

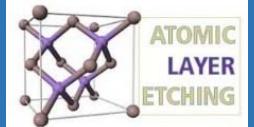
	Ne	Ar	Kr	Xe	Hg		Ne	Ar	Kr	Xe	Hg
Be.....	<b>12</b>	15	15	15		Mo....	24	24	<b>28</b>	<b>27</b>	32
Al.....	<b>13</b>	13	15	18	18	Rh....	25	24	<b>25</b>	<b>25</b>	
Ti.....	<b>22</b>	<b>20</b>	17	18	25	Pd....	20	20	<b>20</b>	15	20
V.....	21	<b>23</b>	<b>25</b>	28	25	Ag....	12	15	<b>15</b>	17	
Cr.....	22	<b>22</b>	18	20	23	Ta....	25	26	30	<b>30</b>	30
Fe.....	22	<b>20</b>	<b>25</b>	23	25	W....	35	33	30	<b>30</b>	30
Co.....	20	<b>25</b>	<b>22</b>	22		Re....	35	35	25	<b>30</b>	35
Ni.....	23	<b>21</b>	<b>25</b>	20		Pt....	27	25	22	<b>22</b>	25
Cu.....	17	17	<b>16</b>	15	20	Au....	20	20	20	<b>18</b>	
Ge.....	23	<b>25</b>	<b>22</b>	18	25	Th....	20	24	25	<b>25</b>	
Zr.....	23	22	18	<b>25</b>	30	U....	20	23	25	<b>22</b>	27
Nb.....	27	25	<b>26</b>	<b>32</b>							

Boldface values are those for which the energy-transfer factor  $4m_1m_2/(m_1 + m_2)^2$  is 0.9 or higher.

"Atomic Layer Etching at the Tipping Point: An Overview"  
G. S. Oehrlein, D. Metzler, and C. Li  
ECS Journal of Solid State Science and Technology, 4 (6) N5041-N5053 (2015)

"Sputtering Yields at Very Low Bombarding Ion Energies"  
R. V. Stuart and G. K. Wehner  
Journal of Applied Physics, 7 (33) (1962)

# Energy Control of Energetic Particles for Desorption

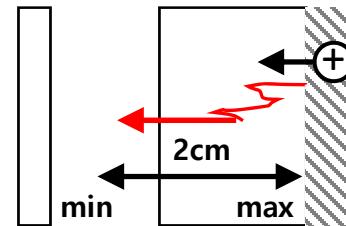


- ◆ Energy distribution of the ions incident to the electrode by the above oscillation

500 eV Ar<sup>+</sup> : velocity =  $5 \times 10^6$  cm/sec



It takes 400 ns for the movement of 2 cm

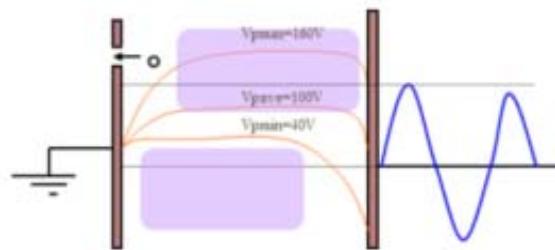


Oscillation period at 13.56MHz

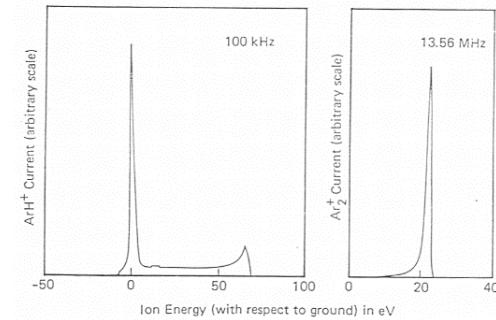
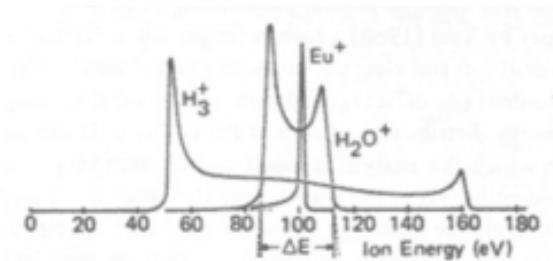
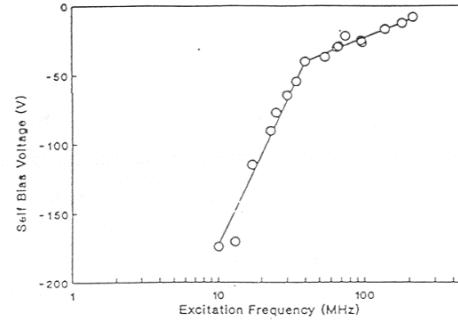
$$t = \frac{1}{13.56 \times 10^6} \approx 74 \text{ ns}$$

∴ During the pass of sheath, the incident ions oscillate for a few times

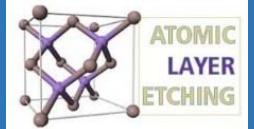
## 1) Ion mass



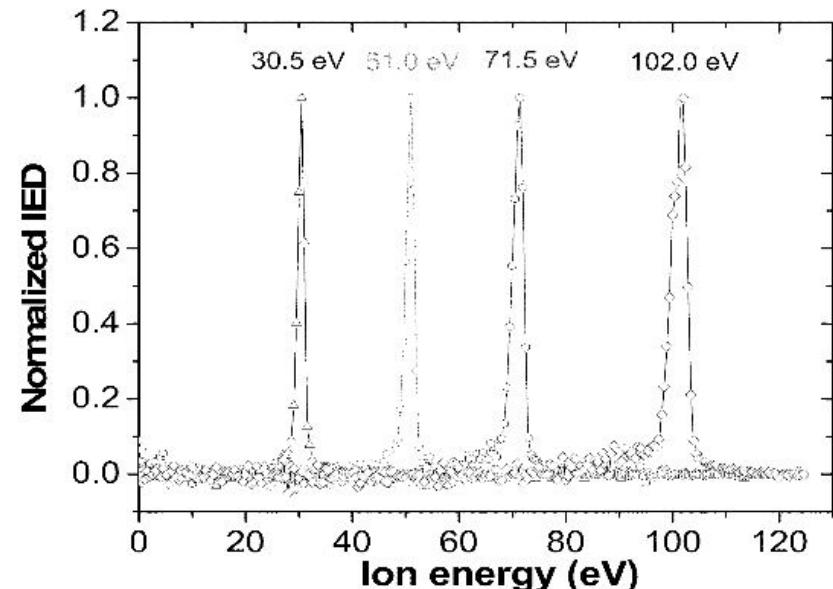
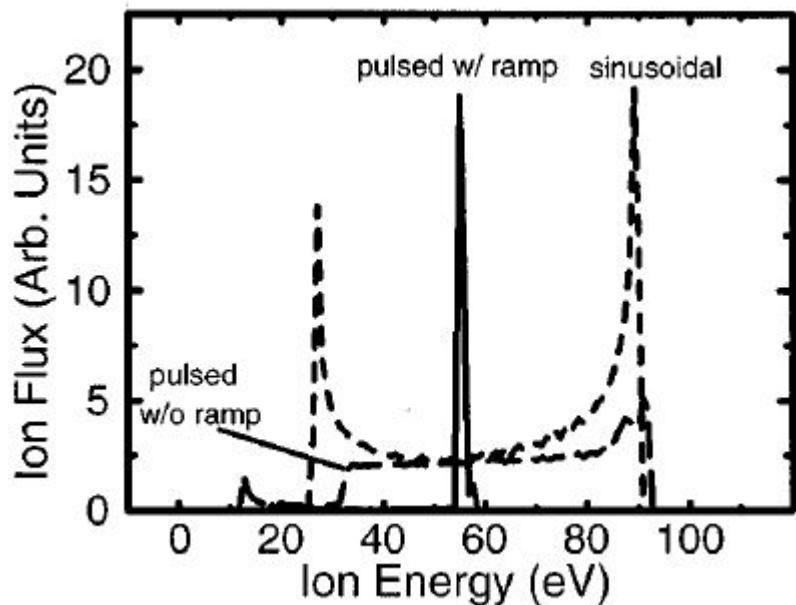
## 2) Frequency



# Energy Control of Energetic Particles for Desorption



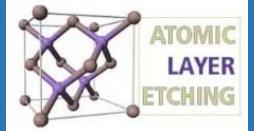
- ◆ Novel plasma pulsing methods (waveforms) can be used to tailor ion energy distribution function



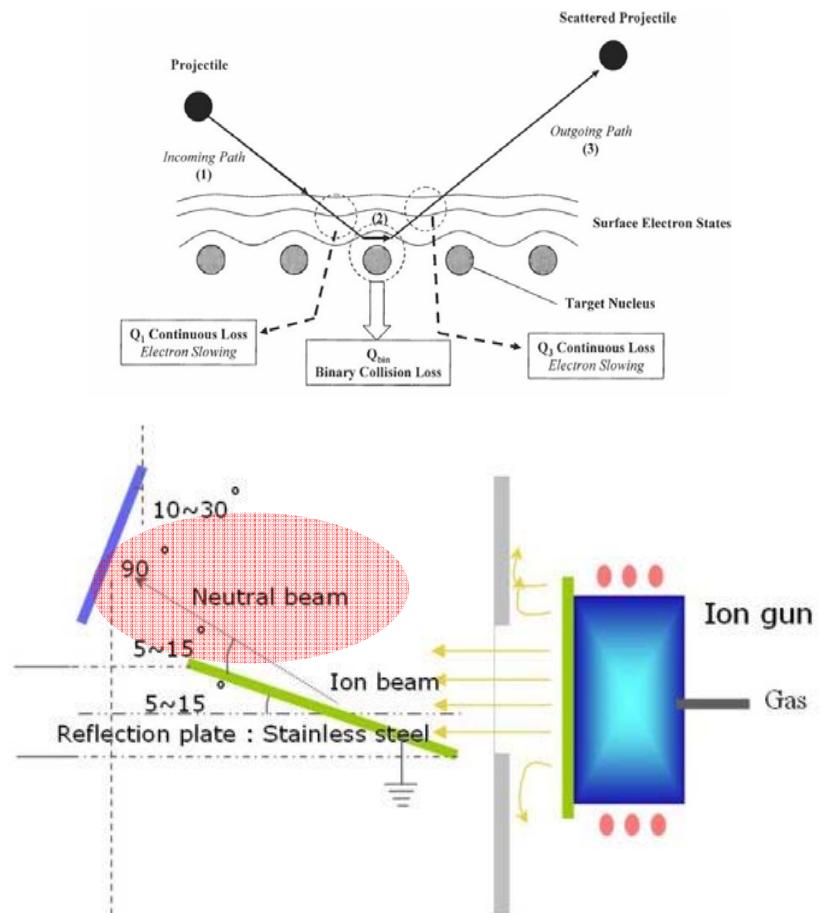
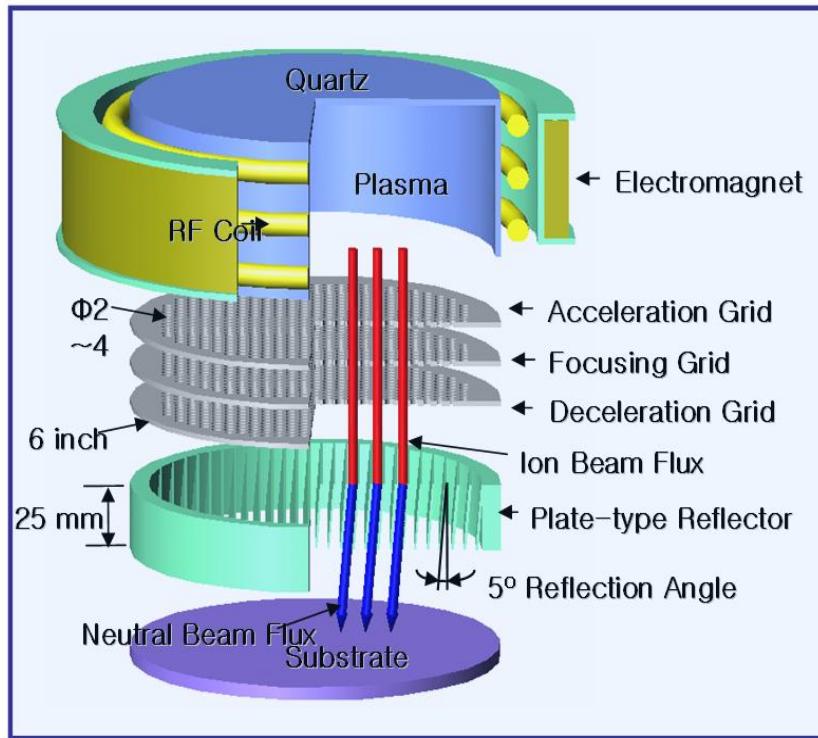
"Control of ion energy distribution at substrates during plasma processing"  
S.-B. Wang and A. E. Wendt  
Journal of Applied Physics 88, 643 (2000)

"Atomic layer etching with pulsed plasmas"  
Vincent M. DONNELLY, Demetre J, and ECONOMOU  
US 20110139748A1, 2011

# Formation of Energetic Neutral Beam

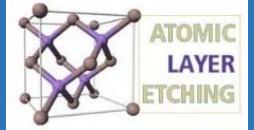


## ◆ Ion-surface neutralization



When the ion beam was reflected by a reflector at the angles lower than 15°, most of the ions reflected were neutralized and the lower reflector angle showed the higher degree of neutralization.

# Contents



**1**

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**2**

**ALE of Various Materials  
(Si, III-V Compounds, High-k Dielectrics)**

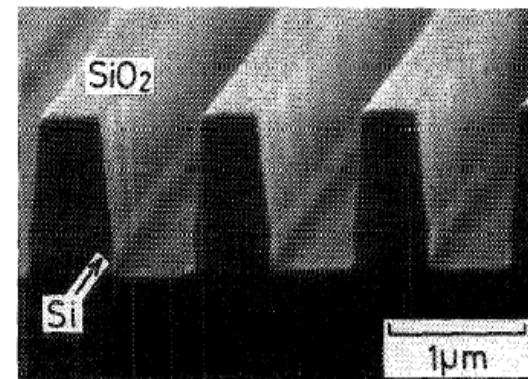
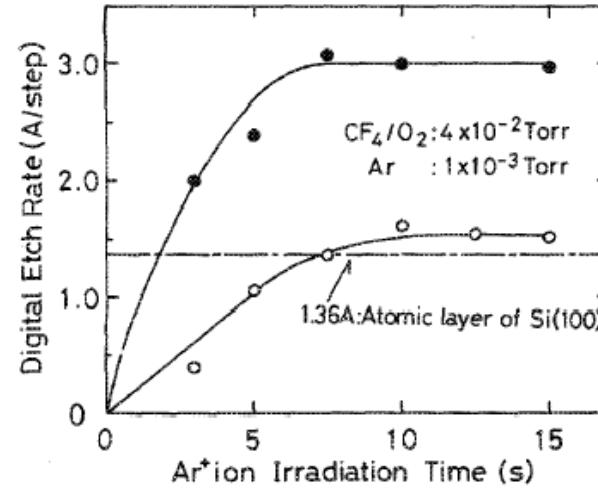
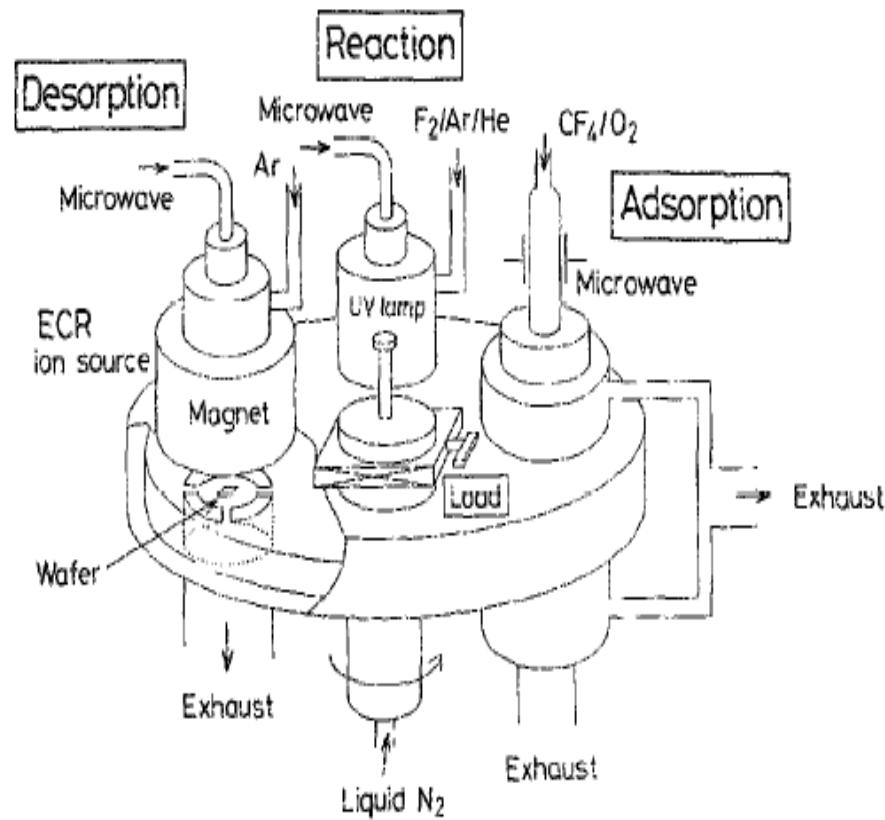
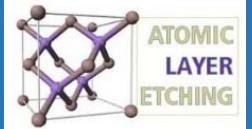
**3**

Recent Research Trends

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Summary

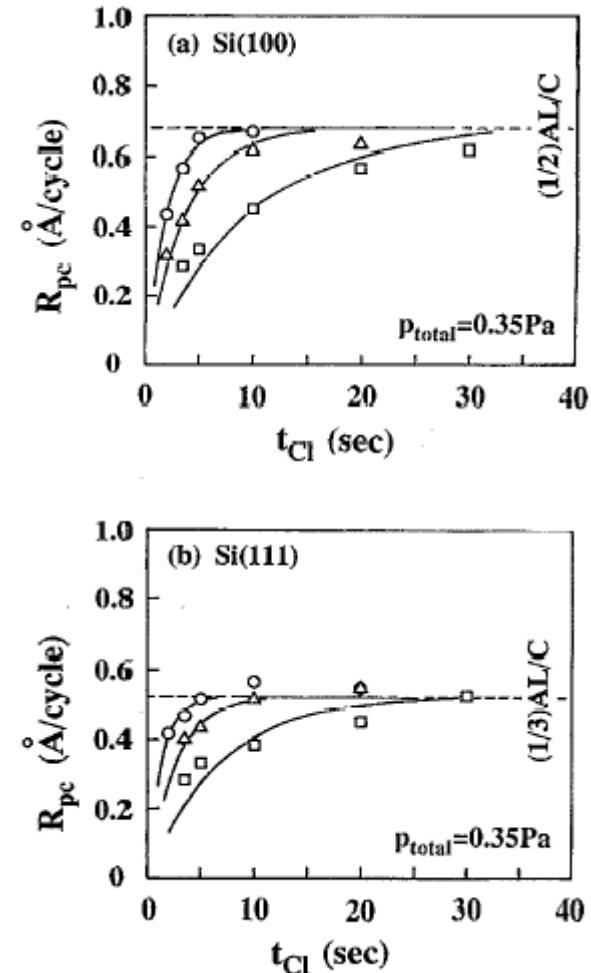
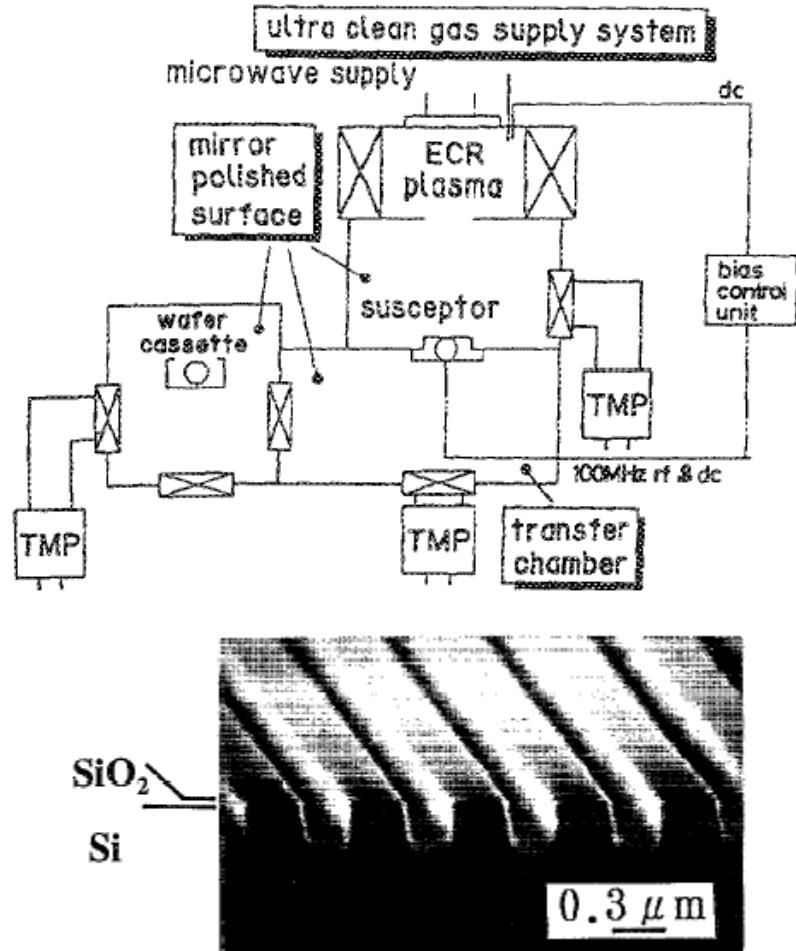
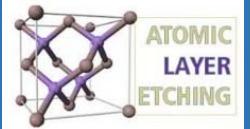
# ALE using ECR Ion Source



CF<sub>4</sub>/O<sub>2</sub>

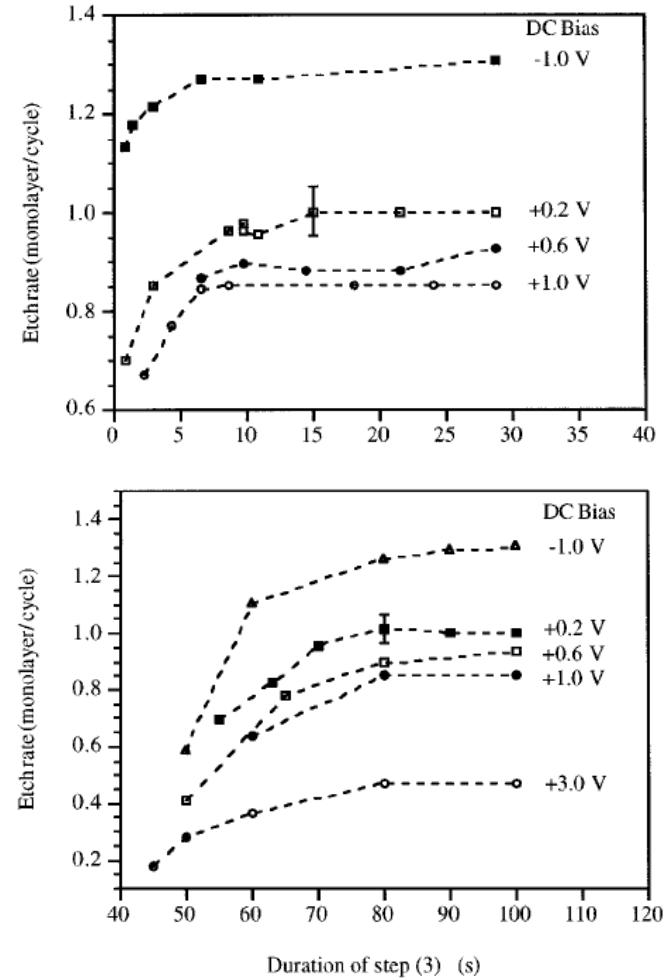
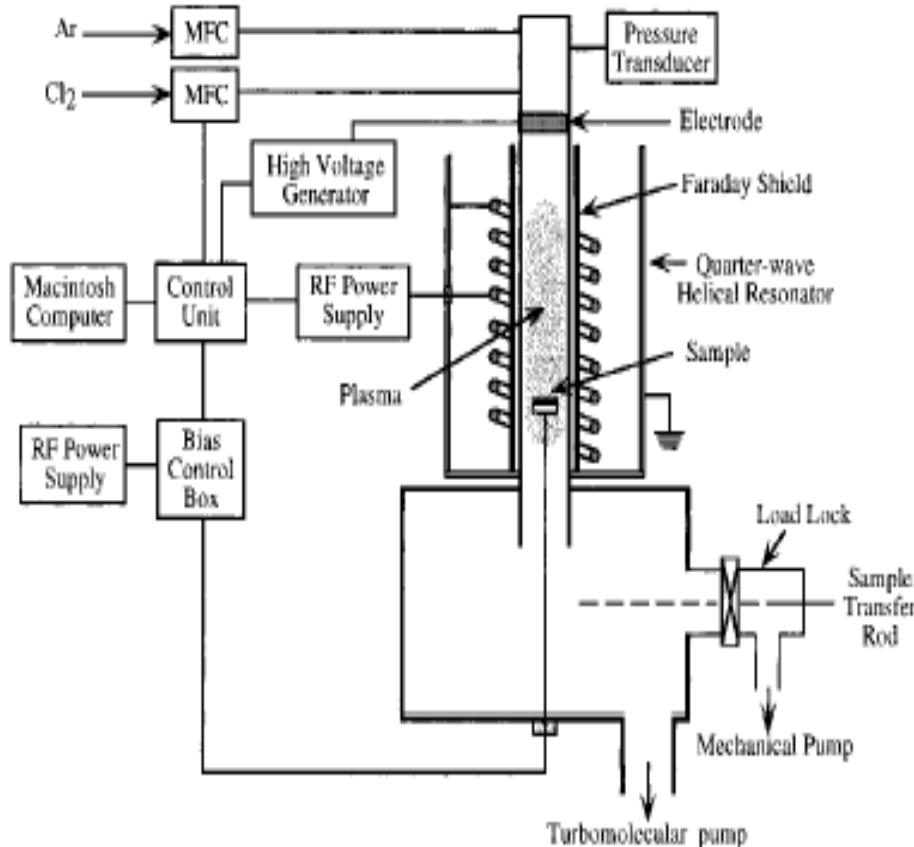
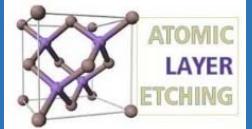
"Digital chemical vapor deposition and etching technologies for semiconductor processing"  
Y. Horiike, T. Tanaka, M. Nakano, S. Iseda, H. Sakaue, A. Nagata, H. Shindo, S. Miyazaki, and M. Hirose  
J. Vac. Sci. Technol. A 8 (3) (1990)

# ALE of Si using Low Energy Ion (ECR)



"Selflimited layerbylayer etching of Si by alternated chlorine adsorption and  $\text{Ar}^+$  ion irradiation"  
Takashi Matsuura, Junichi Murota, Yasuji Sawada, and Tadahiro Ohmi  
Appl. Phys. Lett. 63 (20) (1993)

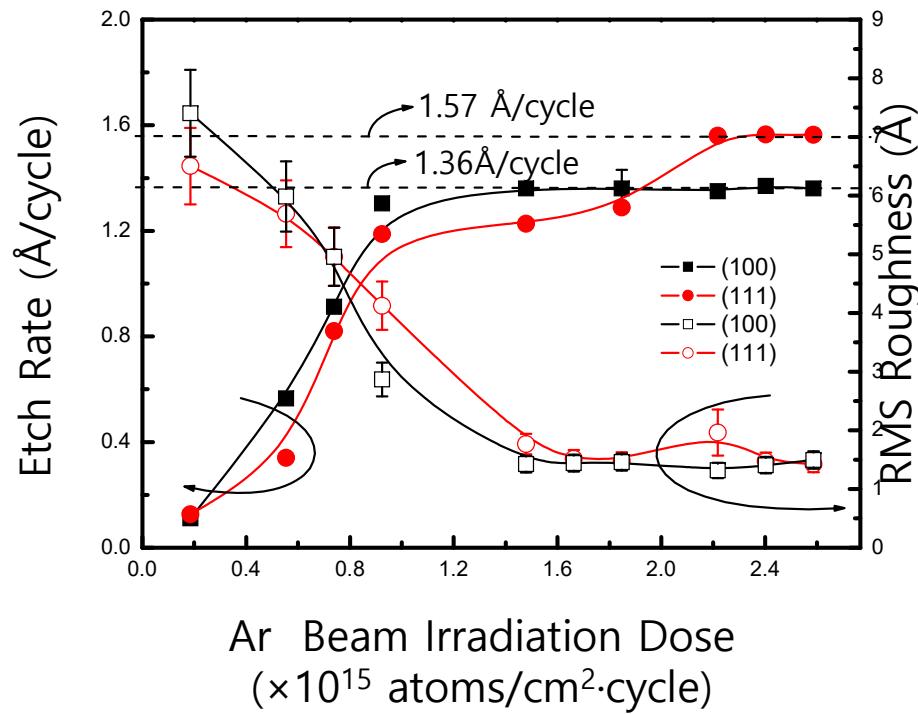
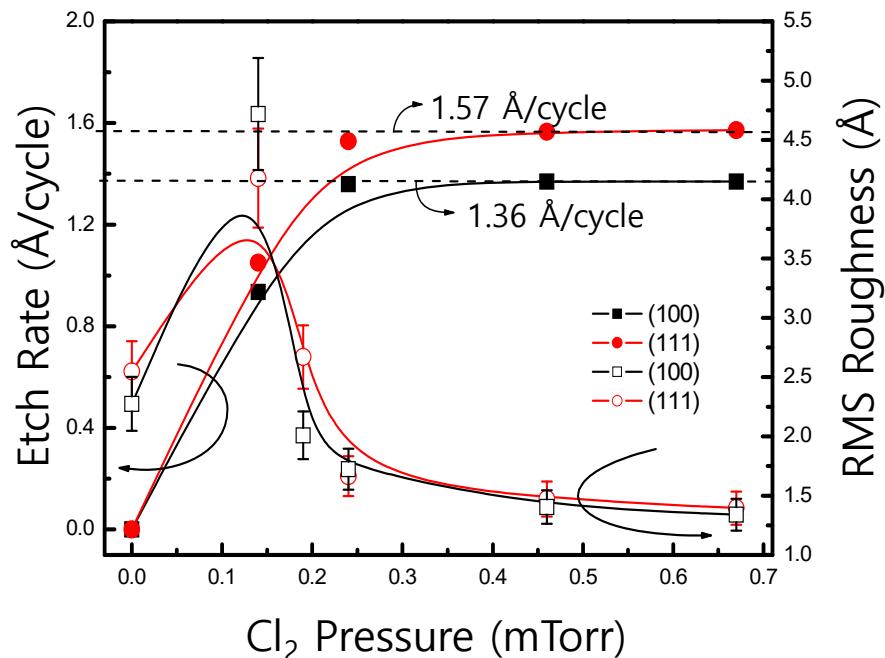
# ALE using Helical Plasma Source



"Realization of atomic layer etching of silicon"  
Satish D. Athavale and Demetre J. Economou  
J. Vac. Sci. Technol. B 14(6) (1996)

◆ Conditions :

Base pressure	$2.0 \times 10^{-6}$ Torr	Chamber pressure	$2.5 \times 10^{-4}$ Torr	Inductive power	800 Watts
Acceleration voltage	50 Volts	Ar flow rate	10 sccm	Ar beam irradiation dose	$0 \sim 2.587 \times 10^{15}$ atoms/cm <sup>2</sup> ·cycle
Cl <sub>2</sub> pressure	0~0.67 mTorr	Cl <sub>2</sub> supply time ( $t_{Cl_2}$ )	20 sec	Cycle	75 cycle



"Surface Roughness Variation during Si Atomic Layer Etching by Chlorine Adsorption Followed by an Ar Neutral Beam Irradiation"  
 S. D. Park, C. K. Oh, D. H. Lee, and G. Y. Yeom  
 Electrochemical and Solid-State Letters, 8 11 C177-C179 (2005)

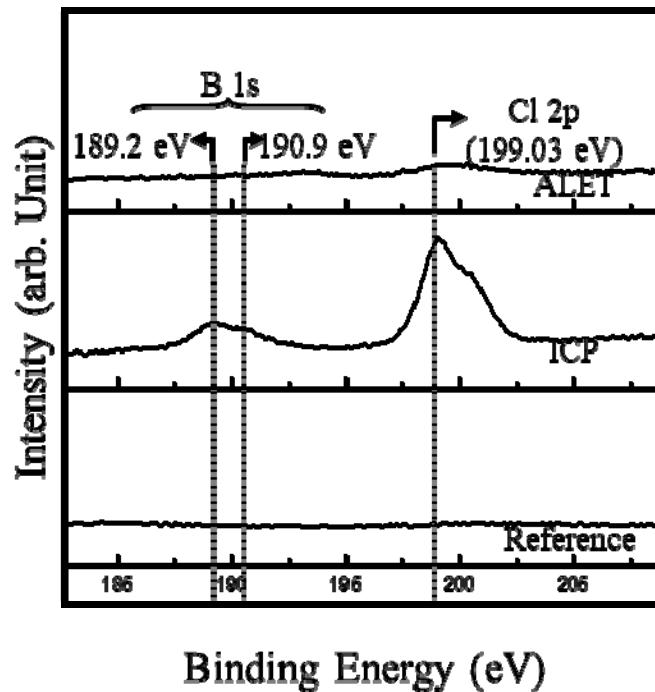
# Etch Residue



## ◆ Conditions :

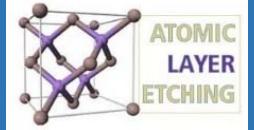
- ICP Etching :  $\text{BCl}_3$  (50 sccm)/Ar (50 sccm), 300 W, -60 V, 12 mTorr, 149 sec
- Atomic Layer Etching : Ne beam irradiation dose ( $1.485 \times 10^{17}$  atoms/cm<sup>2</sup>·cycle),  $\text{BCl}_3$  pressure (0.33 mTorr), Etch cycle (217 cycle)

Etched surface by XPS



"Precise Depth Control and Low-Damage Atomic-Layer Etching of  $\text{HfO}_2$  using  $\text{BCl}_3$  and Ar Neutral Beam"  
S. D. Park, W. S. Lim, B. J. Park, H. C. Lee, J. W. Bae, and G. Y. Yeom  
Electrochemical and Solid-State Letters, 11 4 H71-H73 (2008)

# Contents



1

Introduction of Atomic Layer Etching (ALE) with Ion/Neutral Beam

2

**ALE of Various Materials  
(Si, III-V Compounds, High-k Dielectrics)**

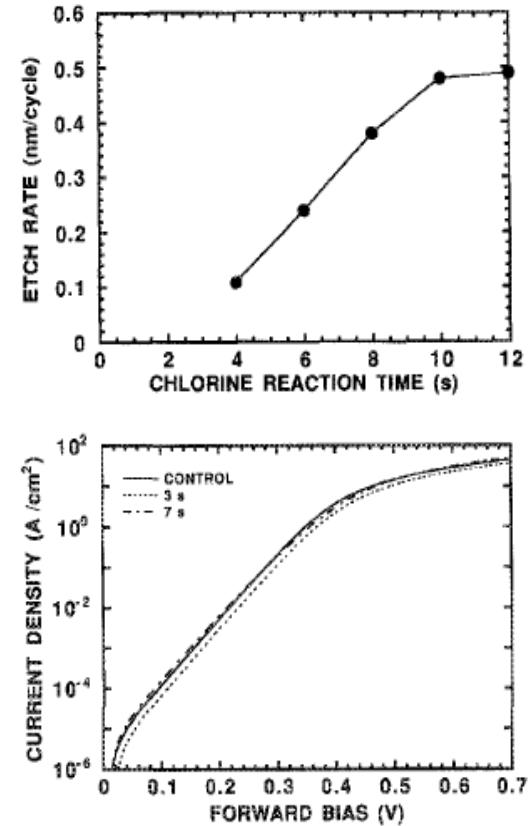
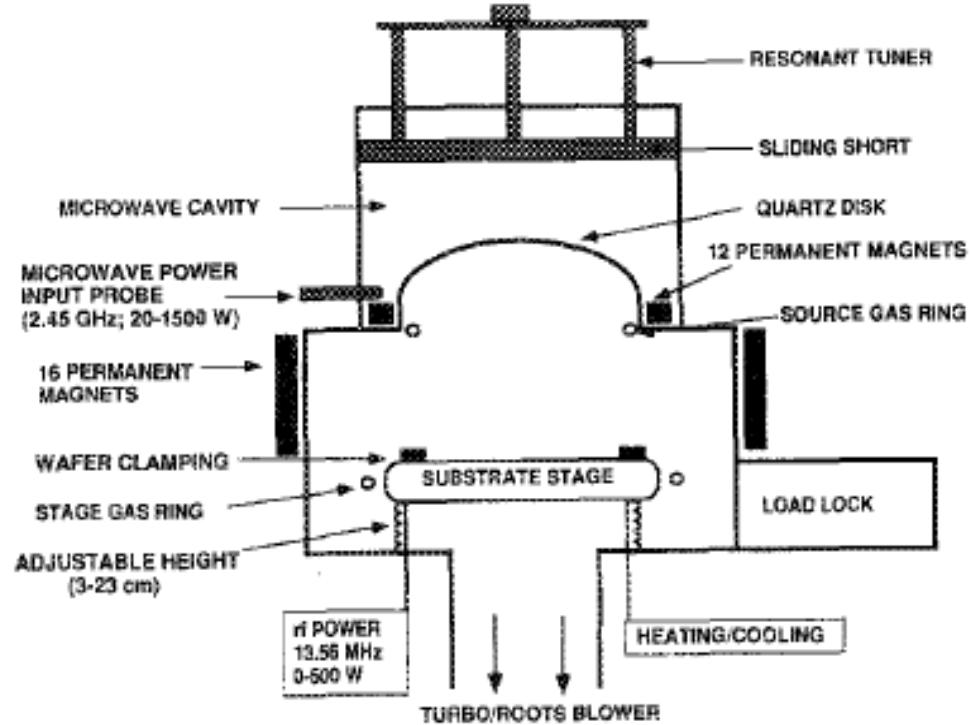
3

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# GaAs ALE using ECR Source

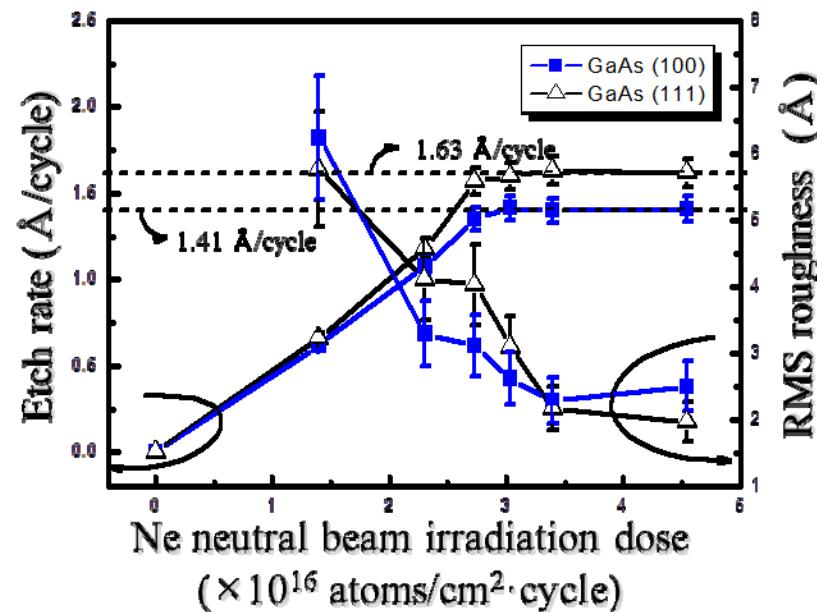
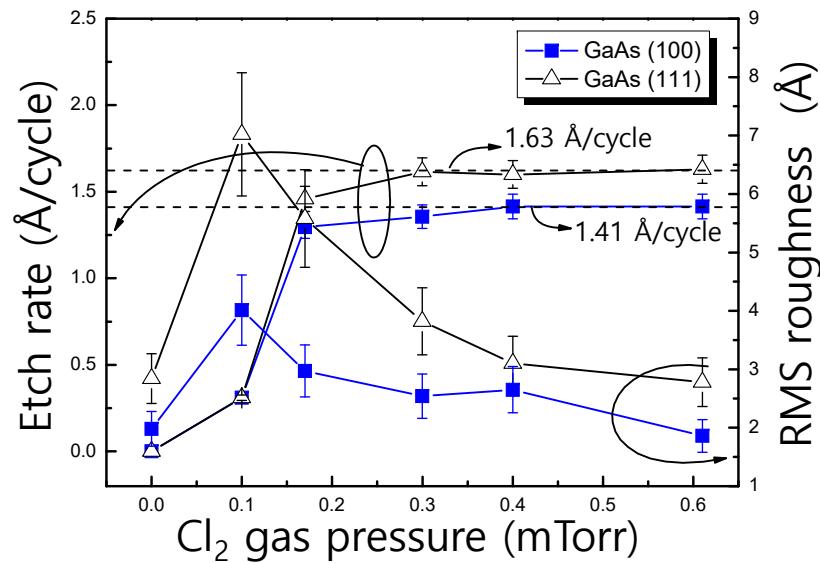


Layer by layer etching with the etch rate in the range of 0.5 nm/cycle has been achieved on GaAs.

"Controllable layerbylayer etching of III-V compound semiconductors with an electron cyclotron resonance source"  
K. K. Ko and S. W. Pang  
J. Vac. Sci. Technol. B 11(6) (1993)

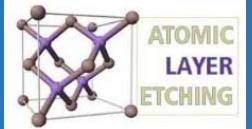
## ◆ Conditions :

Base pressure	$3.0 \times 10^{-7}$ Torr	1 <sup>st</sup> grid voltage	10 Volts	Cl <sub>2</sub> pressure	0~0.62 mTorr
Chamber pressure	$2.0 \times 10^{-4}$ Torr	2 <sup>nd</sup> grid voltage	-250 Volts	Ne beam Irradiation dose	$0 \sim 4.55 \times 10^{16}$ atoms/cm <sup>2</sup> ·cycle
Inductive power	300 Watts	Ne flow rate	70 sccm	Cl <sub>2</sub> supply time ( $t_{Cl_2}$ )	10 sec



"Atomic layer etching of (100)/(111) GaAs with chlorine and low angle forward reflected Ne neutral beam"  
 Woong Sun Lim, Sang Duk Park, Byoung Jae Park, Geun Young Yeom  
 Surface & Coatings Technology 202, 5701–5704 (2008)

# Stoichiometry Modification of GaAs Surface

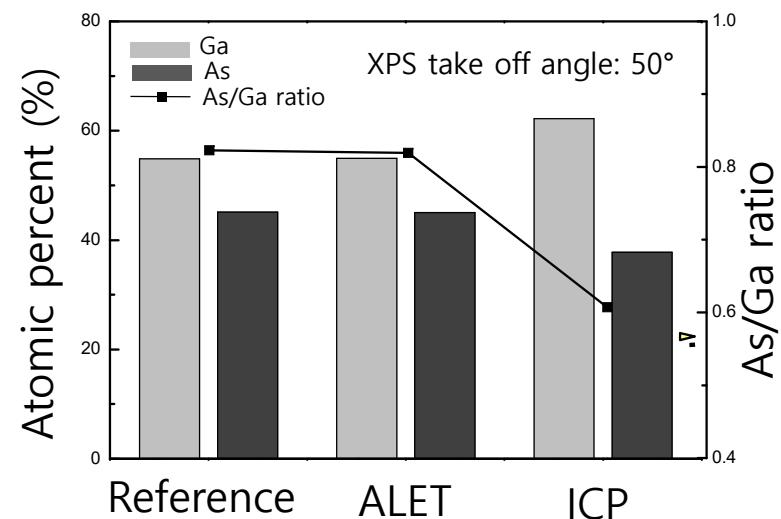
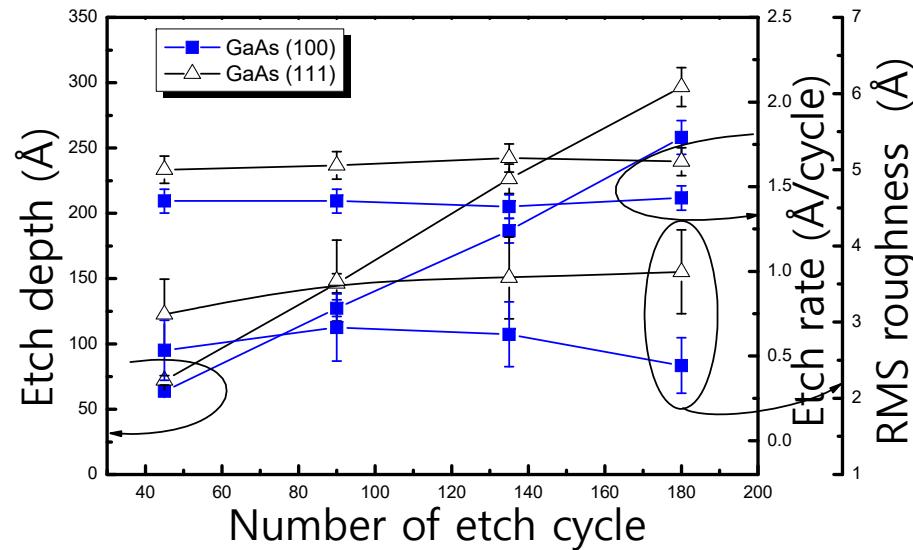


ALET

Base pressure	$3.0 \times 10^{-7}$ Torr	1 <sup>st</sup> grid voltage	10 Volts	Cl <sub>2</sub> pressure	0.4 mTorr
Chamber pressure	$2.0 \times 10^{-4}$ Torr	2 <sup>nd</sup> grid voltage	-250 Volts	Ne neutral beam Irradiation dose	$3.03 \times 10^{16}$ atoms/cm <sup>2</sup> ·cycle
Inductive power	300 Watts	Ne flow rate	70 sccm	Cl <sub>2</sub> supply time (t <sub>Cl<sub>2</sub></sub> )	10 sec

ICP

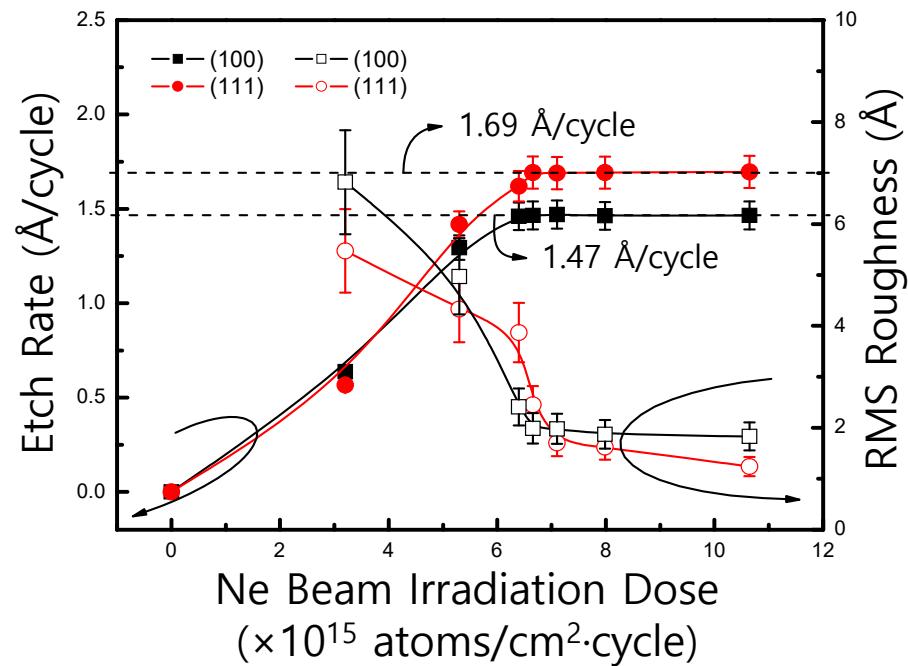
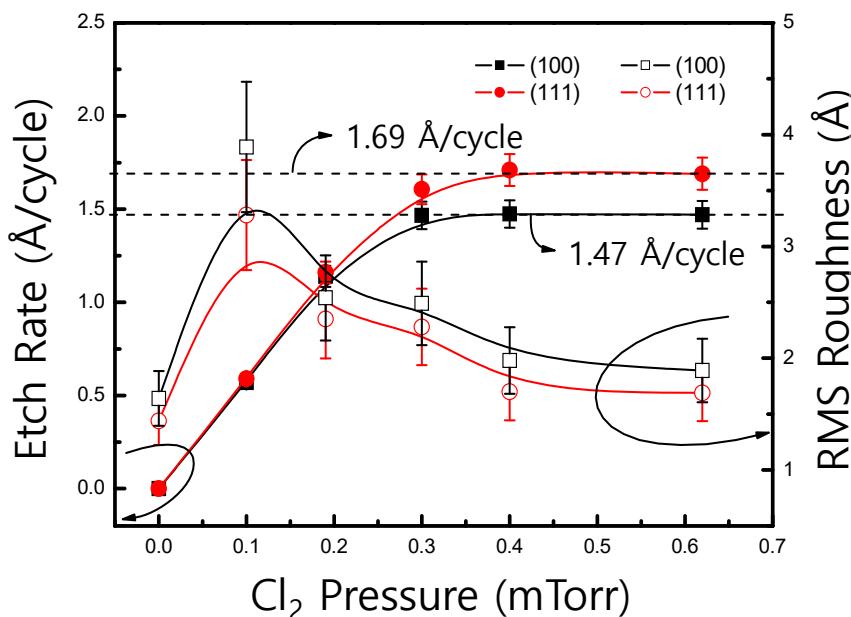
Inductive power	700 Watts	Etch time	12sec
D.C bias voltage	-100 Volts	Gas pressure	12 mTorr [Cl <sub>2</sub> (70sccm)/Ar(30sccm)]



"Atomic layer etching of (100)/(111) GaAs with chlorine and low angle forward reflected Ne neutral beam"  
Woong Sun Lim, Sang Duk Park, Byoung Jae Park, Geun Young Yeom  
Surface & Coatings Technology 202, 5701–5704 (2008)

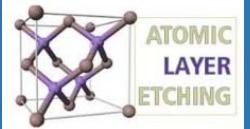
## ◆ Conditions :

Base pressure	$3.0 \times 10^{-7}$ Torr	Chamber pressure	$8.9 \times 10^{-5}$ Torr	Inductive power	300 Watts
1 <sup>st</sup> grid voltage	5 Volts	2 <sup>nd</sup> grid voltage	-250 Volts	Ne flow rate	70 sccm
Ne neutral beam irradiation dose	$0 \sim 10.6 \times 10^{15}$ atoms/cm <sup>2</sup> ·cycle	Cl <sub>2</sub> pressure	$0 \sim 0.62$ mTorr	Cl <sub>2</sub> supply time (t <sub>Cl<sub>2</sub></sub> )	10 sec



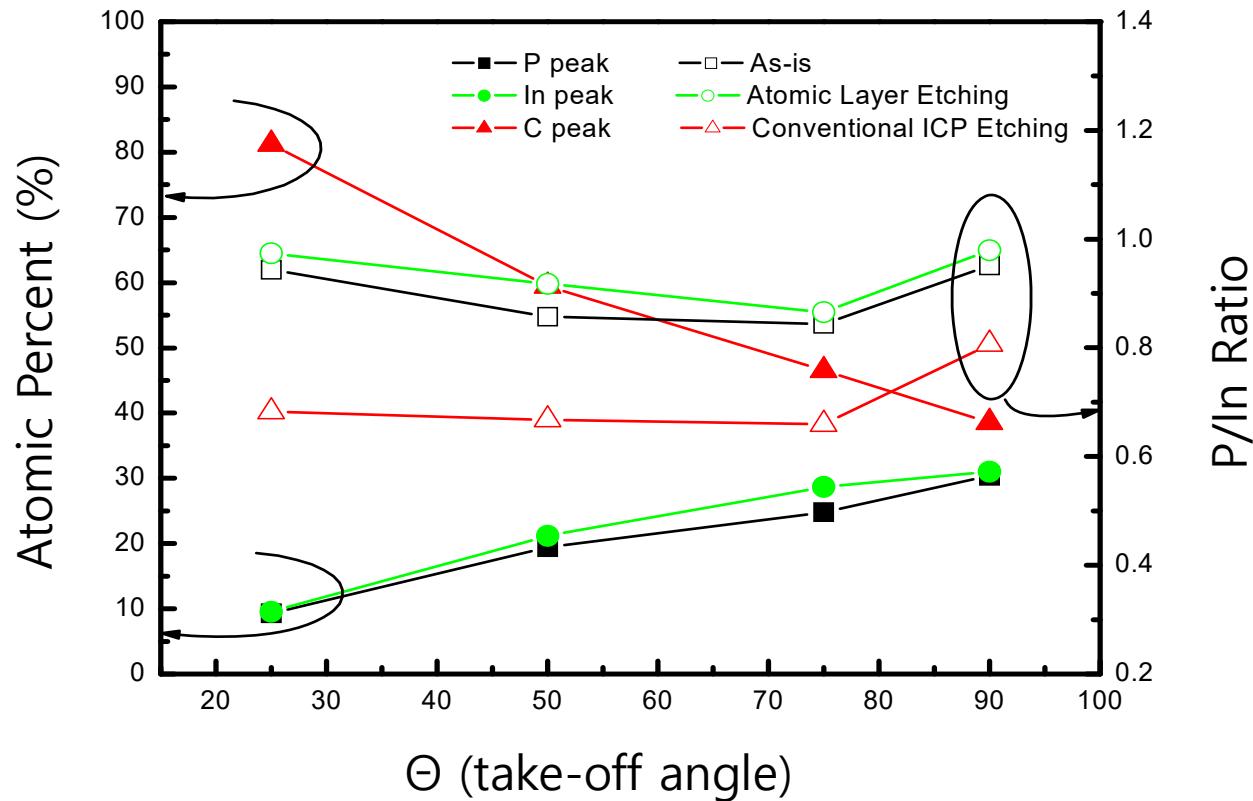
"Atomic layer etching of InP using a low angle forward reflected Ne neutral beam"  
 S. D. Park, C. K. Oh, J. W. Bae, G. Y. Yeom, T. W. Kim  
 Appl. Phys. Lett. 89, 043109 (2006)

# Stoichiometry Modification of InP Surface



## ◆ Conditions :

- ICP Etching : Cl<sub>2</sub> (70 sccm)/Ar (30 sccm), 700 W, -100 V, 12 sec
- Atomic Layer Etching : Ne beam irradiation dose ( $7.2 \times 10^{15}$  atoms/cm<sup>2</sup>·cycle), Cl<sub>2</sub> pressure (0.4 mTorr), Etch cycle (100 cycle)



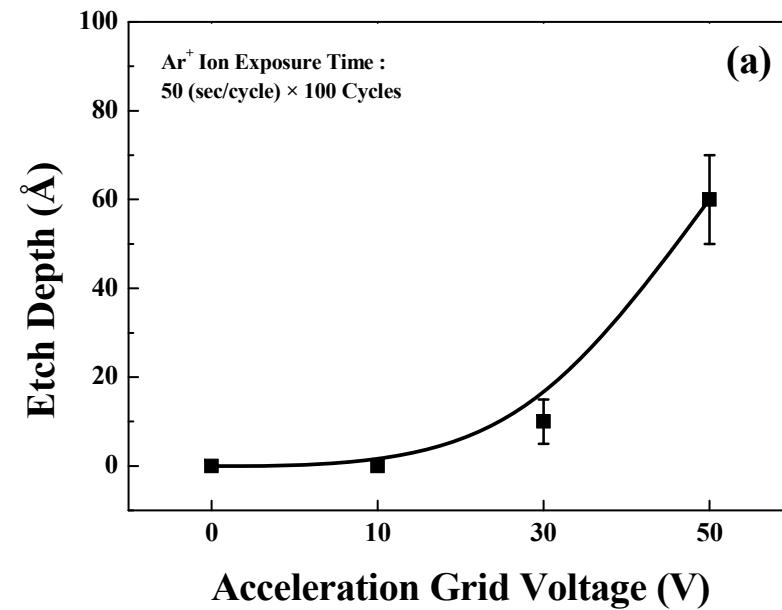
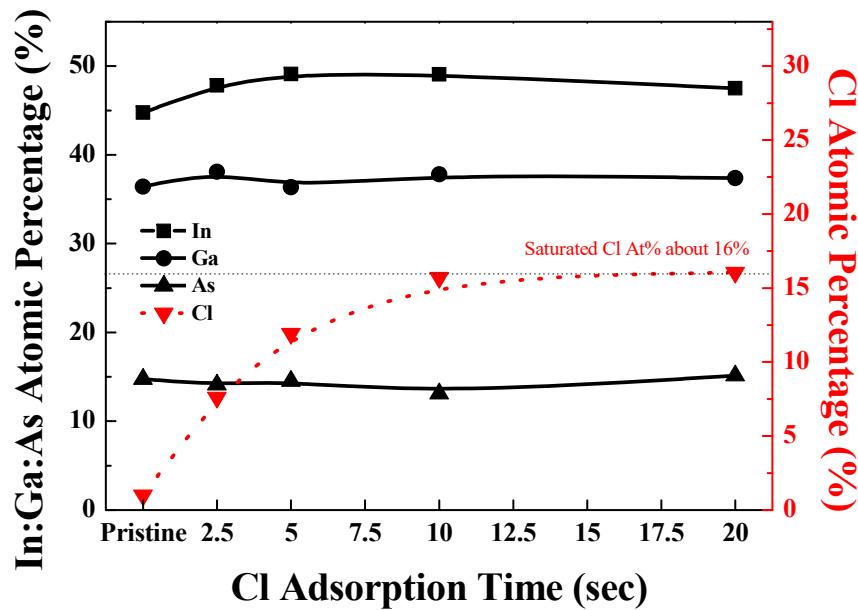
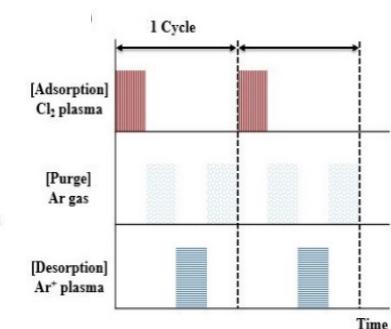
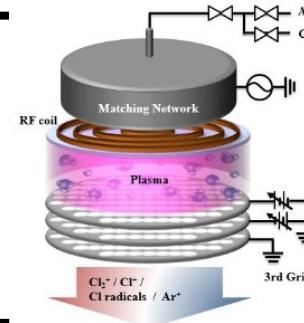
"Atomic layer etching of InP using a low angle forward reflected Ne neutral beam"  
S. D. Park, C. K. Oh, J. W. Bae, G. Y. Yeom, T. W. Kim  
Appl. Phys. Lett. 89, 043109 (2006)

# InGaAs ALE



## ◆ Conditions :

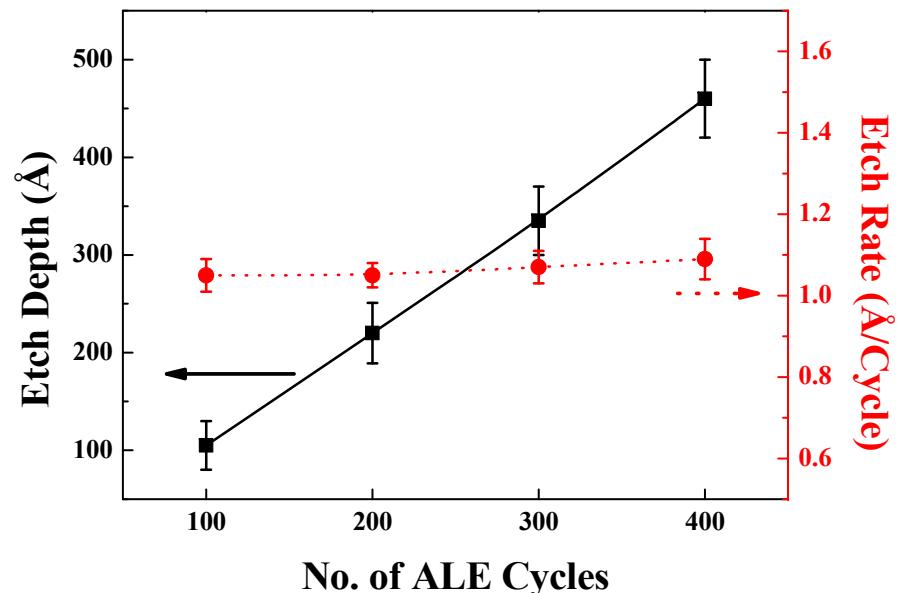
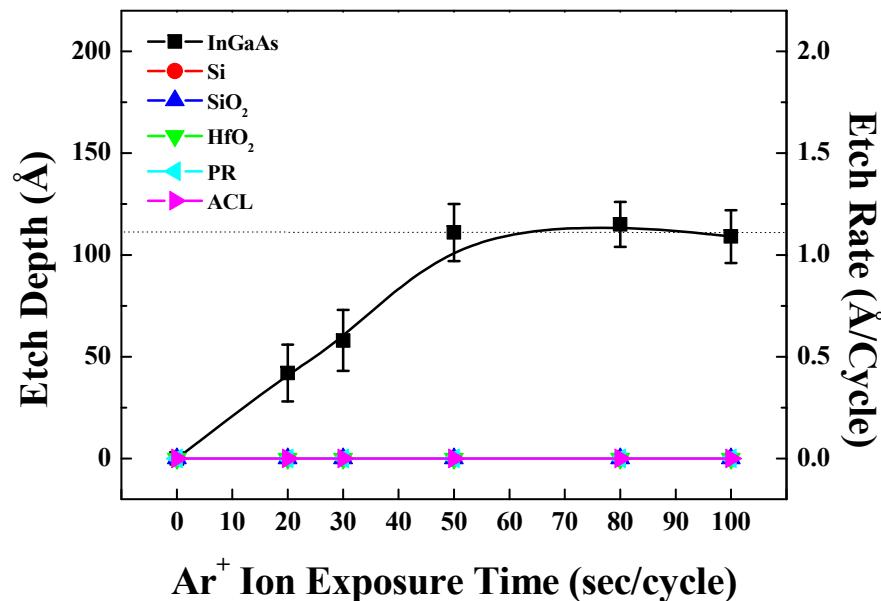
Base pressure	$2.0 \times 10^{-6}$ Torr	Chamber pressure	$2.0 \times 10^{-4}$ Torr
Inductive power	200 Watts		
1 <sup>st</sup> grid voltage	10 Volts	2 <sup>nd</sup> grid voltage	-100 Volts
Cl <sub>2</sub> pressure	1.0 mTorr	Ar pressure	3.0 mTorr
Cl supply time	10 sec	Ar Irradiation time	50 sccm



"Atomic layer etching of InGaAs by controlled ion beam"  
 Jin Woo Park, Doo San Kim, Mu Kyeom Mun, Won Oh Lee, Ki Seok Kim and Geun Young Yeom  
 Accepted by Journal of Physics D: Applied Physics

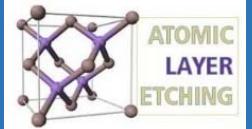
## ◆ Conditions :

Base pressure	$2.0 \times 10^{-6}$ Torr	Chamber pressure	$2.0 \times 10^{-4}$ Torr	Inductive power	200 Watts
1 <sup>st</sup> grid voltage	10 Volts	2 <sup>nd</sup> grid voltage	-100 Volts	Ar pressure	3.0 mTorr
Ar Irradiation time	50 sccm	Cl <sub>2</sub> pressure	1.0 mTorr	Cl supply time	10 sec



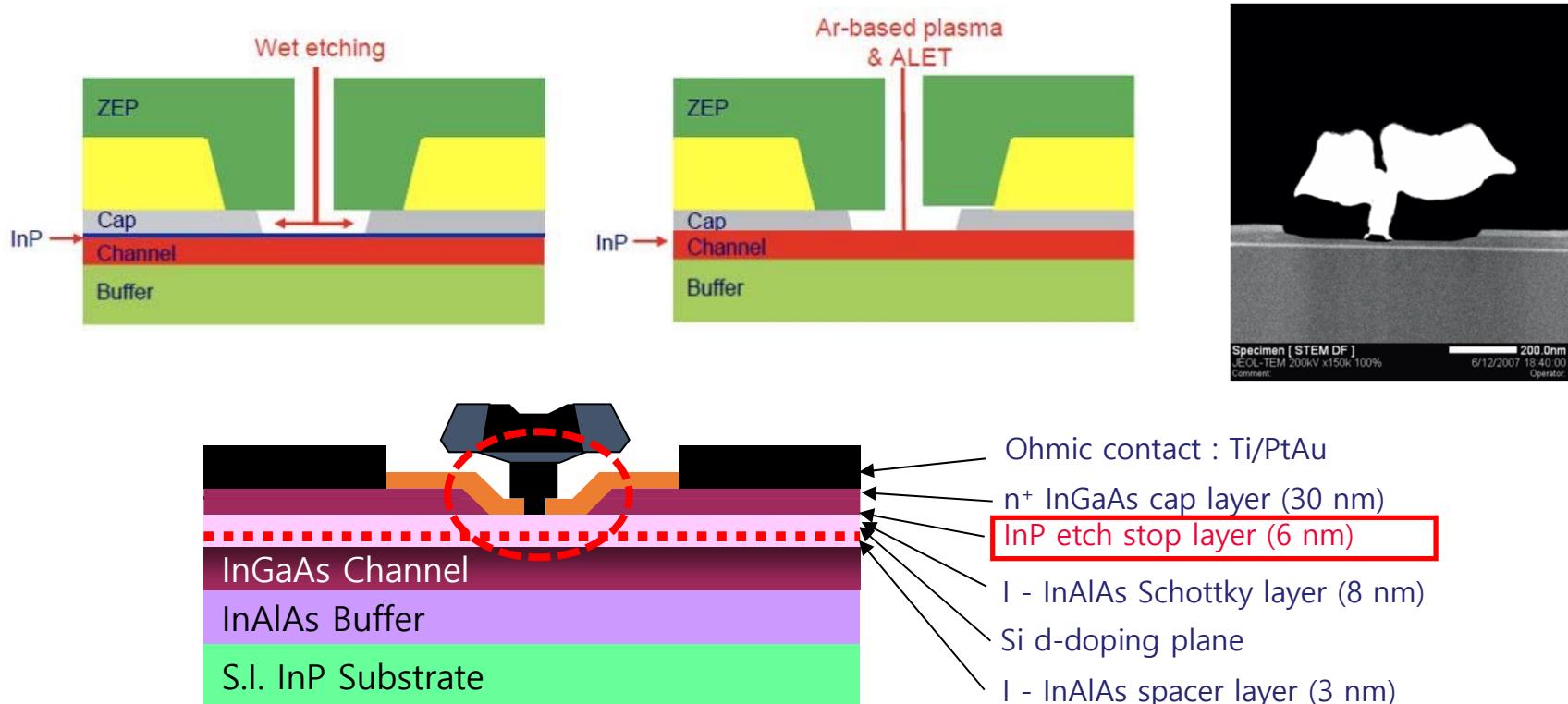
"Atomic layer etching of InGaAs by controlled ion beam"  
 Jin Woo Park, Doo San Kim, Mu Kyeom Mun, Won Oh Lee, Ki Seok Kim and Geun Young Yeom  
 Accepted by Journal of Physics D: Applied Physics

# Application – InP HEMTs (Gate Recess Process)



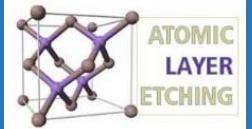
## ◆ Conventional gate recess process : Combination of wet & dry recess etching

- Wet recess : InGaAs cap layer; Citric Acid +  $\text{H}_2\text{O}_2$  = 7:1
- Dry recess : InP etch stop layer; Ar RIE [Ar (50 sccm), 7 W, -65 V, 20 mTorr]



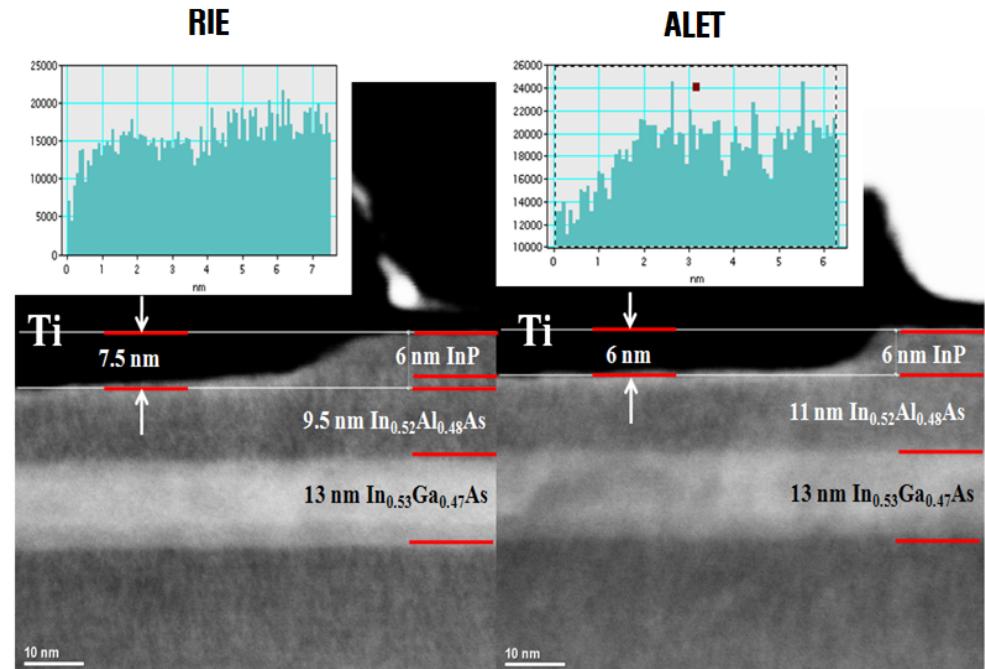
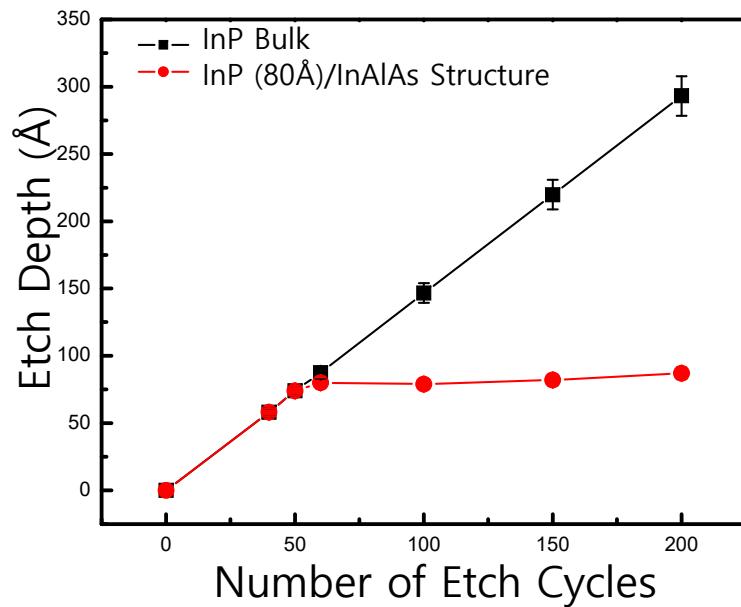
"30 nm gate InAlAs/InGaAs HEMTs lattice-matched to InP substrates"  
Tetsuya Suemitsu, Tetsuyoshi Ishii, Haruki Yokoyama, Yohatru Umeda, Takatomo Enoki, Yasunobu Ishii, Toshiaki Tamamura  
Electron Devices Meeting, (1998). IEDM'98

# InP HEMTs (Gate Recess Process)



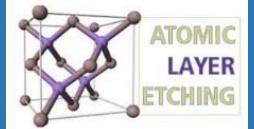
## ◆ Conditions :

Base pressure	$3.0 \times 10^{-7}$ Torr	Chamber pressure	$2.0 \times 10^{-4}$ Torr	Inductive power	300 Watts
1 <sup>st</sup> grid voltage	5 Volts	2 <sup>nd</sup> grid voltage	-250 Volts	Ne flow rate	70 sccm
Ne neutral beam Irradiation dose	$7.2 \times 10^{15}$ atoms/cm <sup>2</sup> ·cycle	Cl <sub>2</sub> pressure	0.4 mTorr	Cl <sub>2</sub> supply time (t <sub>Cl2</sub> )	10 sec



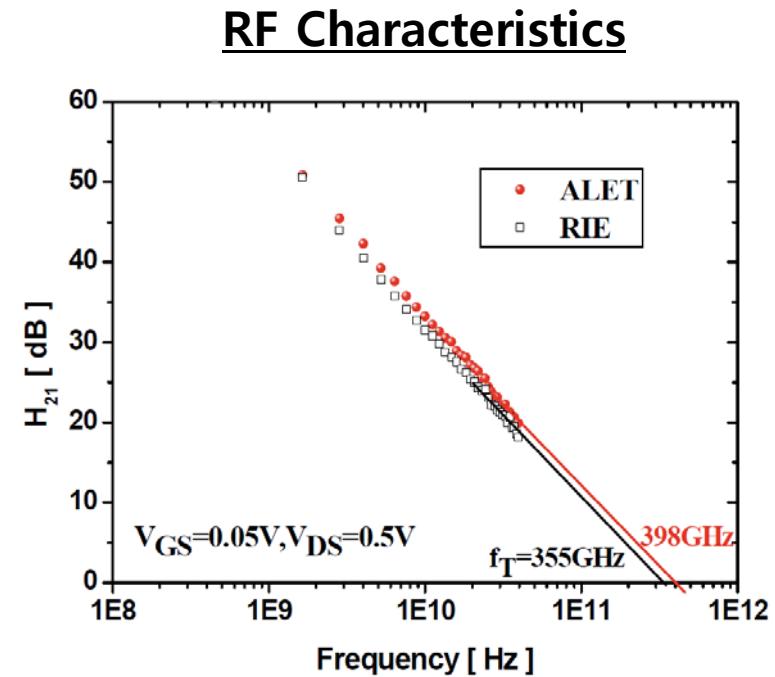
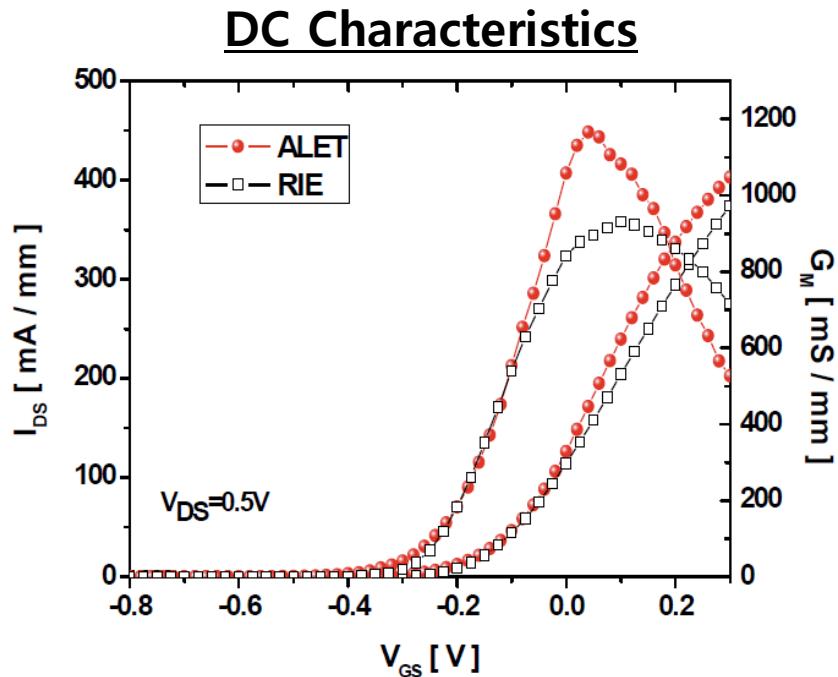
"A Two-Step-Recess Process Based on Atomic-Layer Etching for High-Performance In<sub>0.52</sub>Al<sub>0.48</sub>As/In<sub>0.53</sub>Ga<sub>0.47</sub>As p-HEMTs"  
Tae-Woo Kim, Geun-Young Yeom, Jae-Hyung Jang, Jong-In Song  
IEEE TRANSACTIONS ON ELECTRON DEVICES, 55, 7, (2008)

# 60 nm Depletion Mode InP HEMT



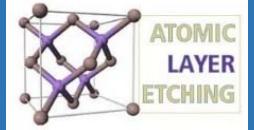
## ◆ Conditions :

- Plasma Etching : Ar (50 sccm), 7 W, -65 V, 20 mTorr, 15 min
- Atomic Layer Etching : Ne beam irradiation dose ( $7.2 \times 10^{15}$  atoms/cm<sup>2</sup>·cycle), Cl<sub>2</sub> pressure (0.4 mTorr), Etch cycle (41 cycle)



$G_{M,\text{Max}}$  of the p-HEMTs fabricated by the ALET process was larger than that using Ar-based RIE by 21%

"A Two-Step-Recess Process Based on Atomic-Layer Etching for High-Performance  $\text{In}_{0.52}\text{Al}_{0.48}\text{As}/\text{In}_{0.53}\text{Ga}_{0.47}\text{As}$  p-HEMTs"  
Tae-Woo Kim, Geun-Young Yeom, Jae-Hyung Jang, Jong-In Song  
IEEE TRANSACTIONS ON ELECTRON DEVICES, 55, 7, (2008)



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(Si, III-V Compounds, High-k Dielectrics)**

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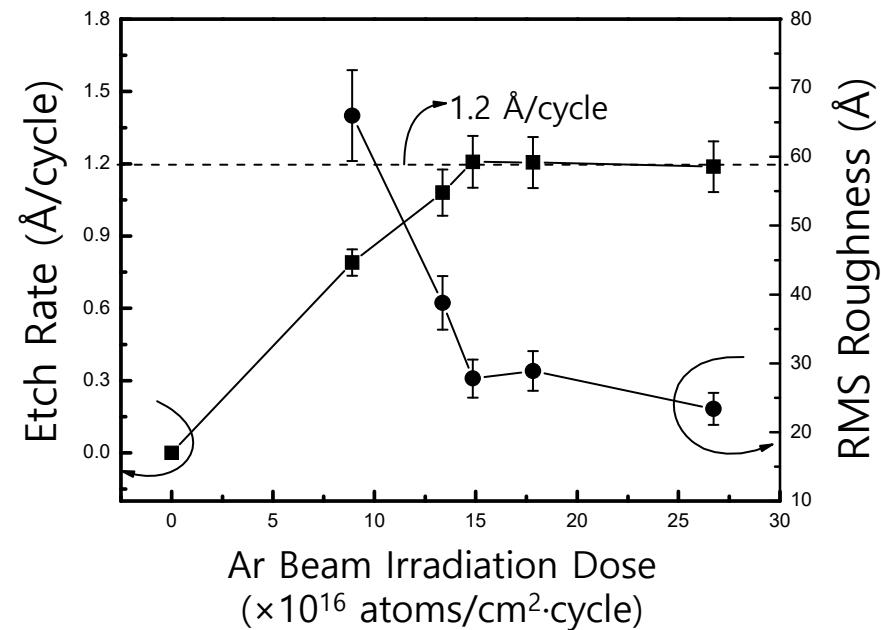
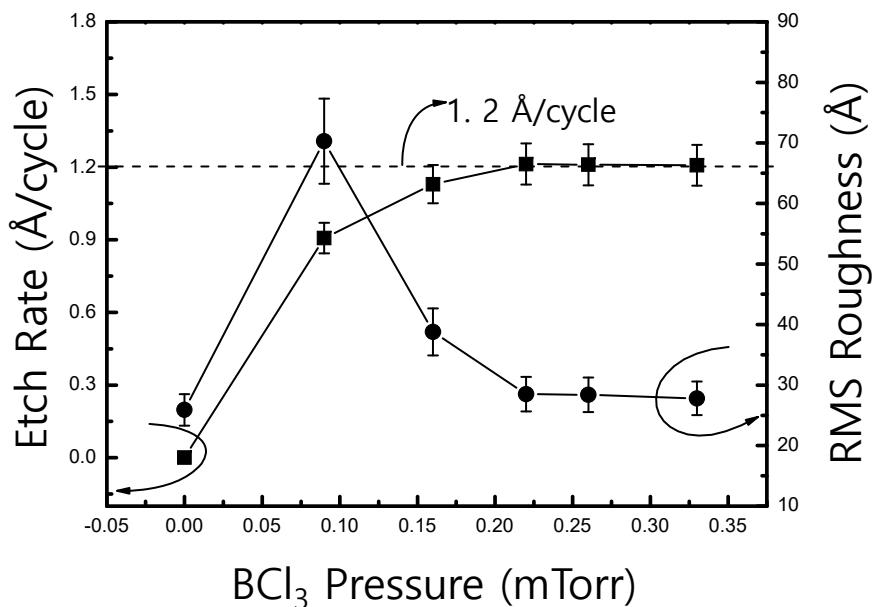
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## ◆ Conditions :

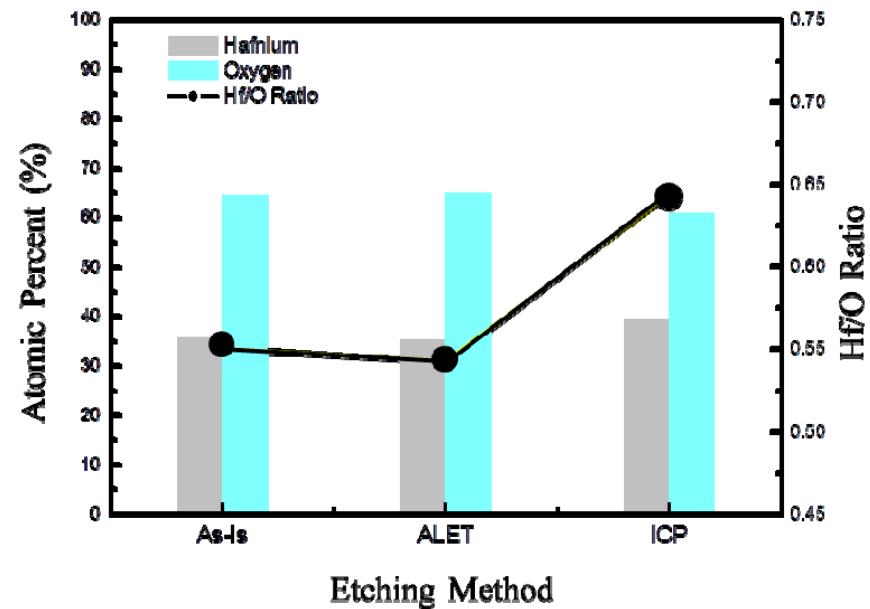
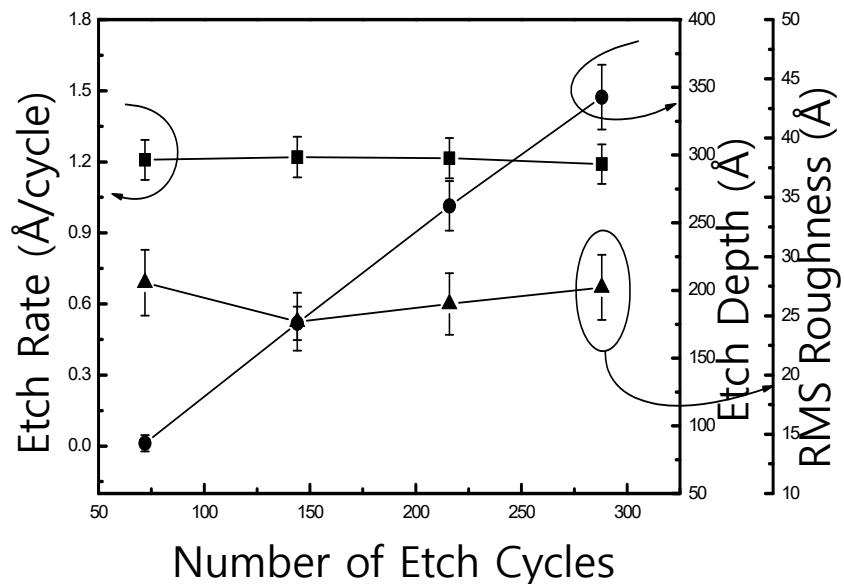
Base pressure	$3.0 \times 10^{-7}$ Torr	Chamber pressure	$2.0 \times 10^{-4}$ Torr	Inductive power	300 Watts
1 <sup>st</sup> grid voltage	60 Volts	2 <sup>nd</sup> grid voltage	-250 Volts	Ar flow rate	30 sccm
Ar beam Irradiation dose	$0 \sim 2.67 \times 10^{17}$ atoms/cm <sup>2</sup> ·cycle	BCl <sub>3</sub> pressure	$0 \sim 0.33$ mTorr	BCl <sub>3</sub> supply time (t <sub>Cl2</sub> )	20 sec



"Precise Depth Control and Low-Damage Atomic-Layer Etching of HfO<sub>2</sub> using BCl<sub>3</sub> and Ar Neutral Beam"  
 S. D. Park, W. S. Lim, B. J. Park, H. C. Lee, J. W. Bae, and G. Y. Yeom  
 Electrochemical and Solid-State Letters, 11 4 H71-H73 (2008)

## ◆ Conditions :

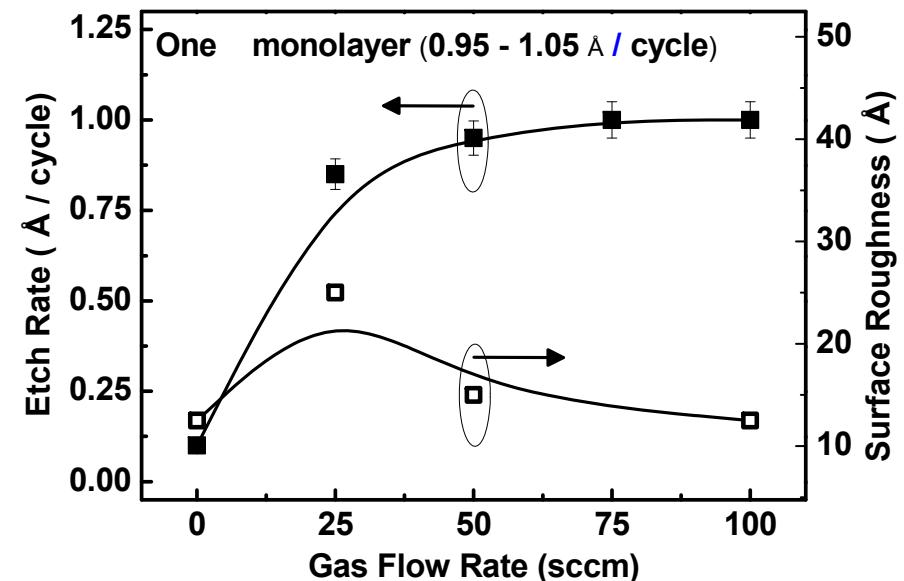
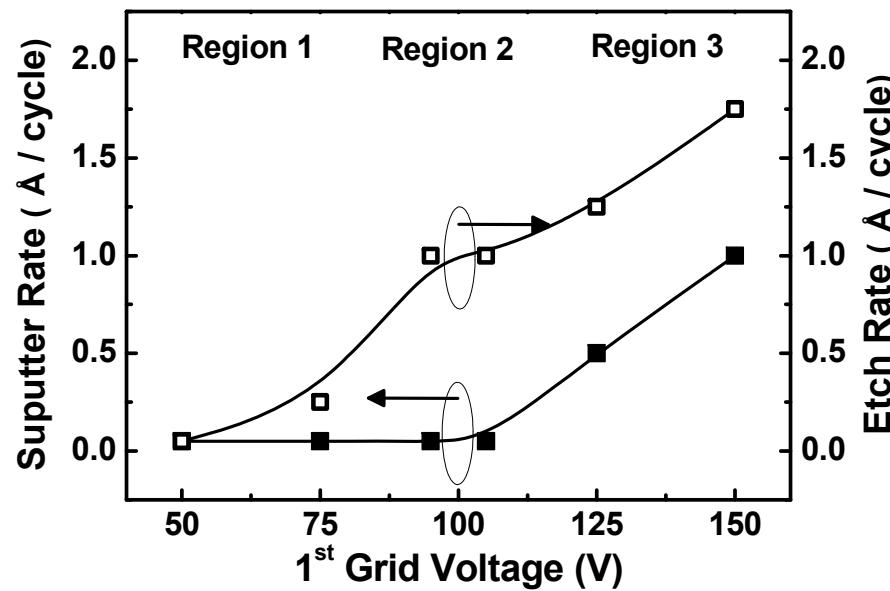
Base pressure	$3.0 \times 10^{-7}$ Torr	Chamber pressure	$2.0 \times 10^{-4}$ Torr	Inductive power	300 Watts
1 <sup>st</sup> grid voltage	60 Volts	2 <sup>nd</sup> grid voltage	-250 Volts	Ar flow rate	30 sccm
Ar neutral beam Irradiation dose	$1.485 \times 10^{17}$ atoms/cm <sup>2</sup> ·cycle	BCl <sub>3</sub> pressure	0.33 mTorr	BCl <sub>3</sub> supply time (t <sub>Cl2</sub> )	20 sec



"Precise Depth Control and Low-Damage Atomic-Layer Etching of HfO<sub>2</sub> using BCl<sub>3</sub> and Ar Neutral Beam"  
 S. D. Park, W. S. Lim, B. J. Park, H. C. Lee, J. W. Bae, and G. Y. Yeom  
 Electrochemical and Solid-State Letters, 11 4 H71-H73 (2008)

## ◆ Conditions :

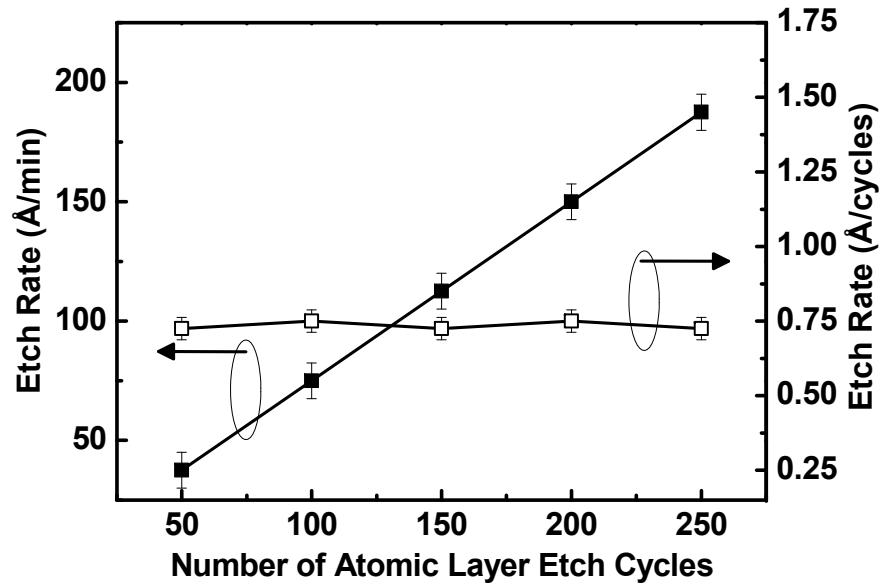
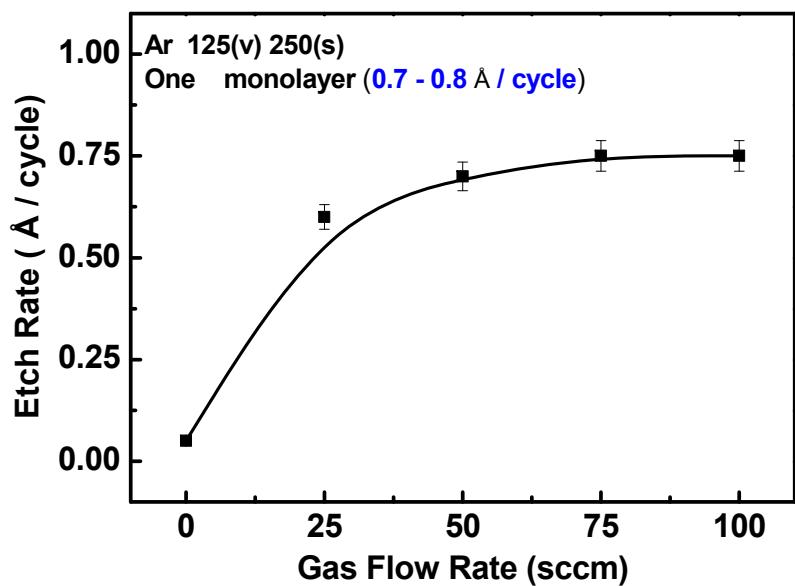
Base pressure	$5.0 \times 10^{-7}$ Torr	Chamber pressure	$2.5 \times 10^{-4}$ Torr	Inductive power	300 Watts
1 <sup>st</sup> grid voltage	100 Volts	2 <sup>nd</sup> grid voltage	-250 Volts	Ar flow rate	50 sccm
$\text{BCl}_3$ gas flow rate	0~100 scmm	$\text{BCl}_3$ supply time ( $t_{\text{Cl}_2}$ )	30 s	Ar neutral beam Irradiation time	125 sec



"Atomic layer etching of  $\text{Al}_2\text{O}_3$  using  $\text{BCl}_3/\text{Ar}$  for the interface passivation layer of III-V MOS devices"  
 K.S. Min a, S.H. Kang a, J.K. Kim a,c, Y.I. Jhon b, M.S. Jhon b, G.Y. Yeom  
 Microelectronic Engineering 110, 457-460 (2013)

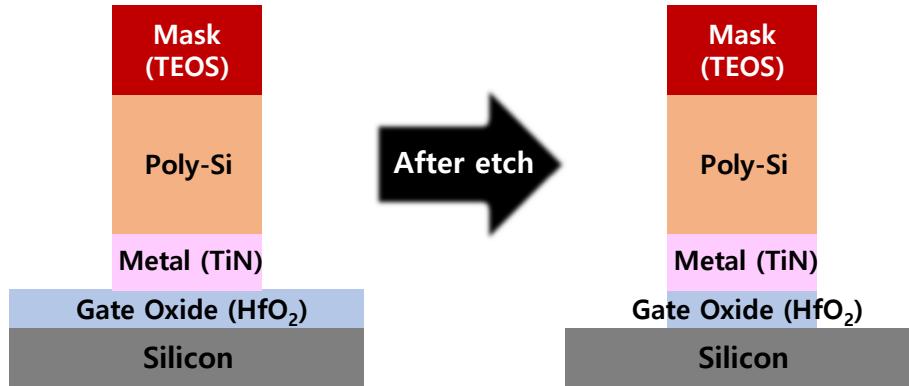
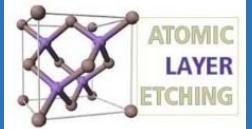
## ◆ Conditions :

Base pressure	$5.0 \times 10^{-7}$ Torr	Chamber pressure	$2.5 \times 10^{-4}$ Torr	Inductive power	300 Watts
1 <sup>st</sup> grid voltage	125 Volts	2 <sup>nd</sup> grid voltage	-250 Volts	Ar flow rate	50 sccm
BCl <sub>3</sub> gas flow rate	0~100 scmm	BCl <sub>3</sub> supply time (t <sub>Cl2</sub> )	30 s	Ar neutral beam Irradiation time	125 sec



"Atomic layer etching of BeO using BCl<sub>3</sub>/Ar for the interface passivation layer of III-V MOS devices"  
 K.S. Min, S.H. Kang, J.K. Kim, J.H. Yumg, Y.I. Jhon, Todd W. Hudnall, C.W. Bielawski, S.K. Banerjee, G. Bersuker, M.S. Jhon, G.Y. Yeom  
 Microelectronic Engineering 114, 121–125 (2014)

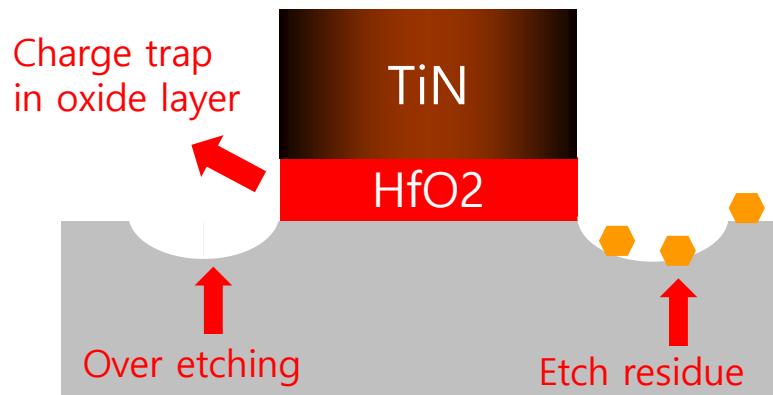
# MOSFET Fabrication with HfO<sub>2</sub> ALE



## ◆ Main etch challenges

- Gate dimensions down to less than 30 nm
- CD control better than 2 nm required
- Low silicon recess (~ 1 nm)

### Convention RIE etcher



### Atomic layer etcher



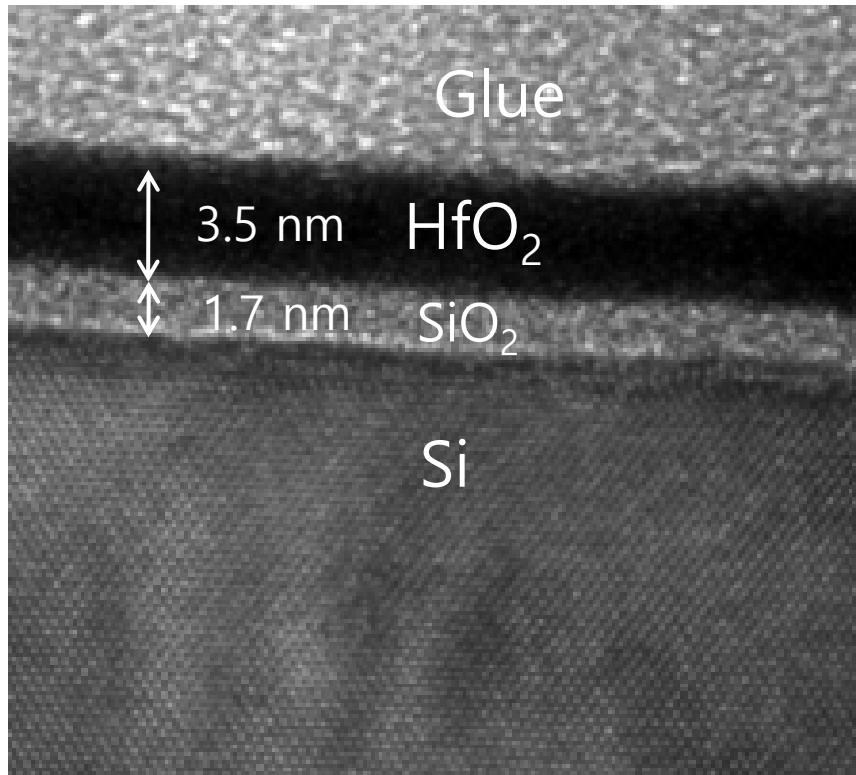
"Atomic layer etching of ultra-thin HfO<sub>2</sub> film for gate oxide in MOSFET devices"  
Jae Beom Park, Woong Sun Lim, Byoung Jae Park, Ih Ho Park, Young Woon Kim and Geun Young Yeom  
J. Phys. D: Appl. Phys. 42, 055202 (2009)

# TEM Image of $\text{HfO}_2$ Etched by ALE

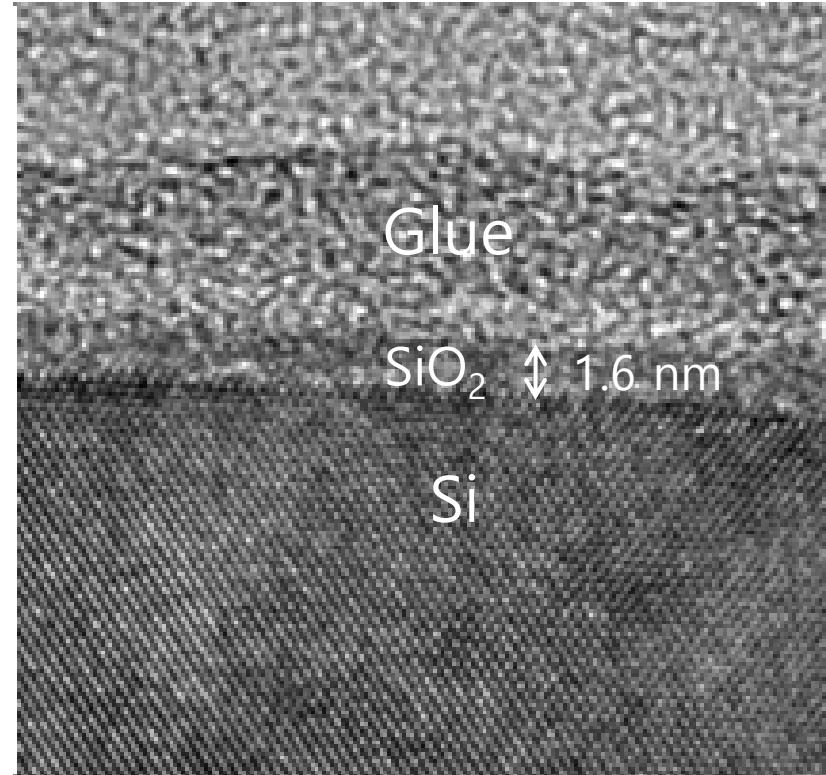


## ◆ Precise etching of $\text{HfO}_2$ on $\text{SiO}_2$ using ALE

: Blank wafer ( $\text{HfO}_2$  on  $\text{SiO}_2$ ) etching



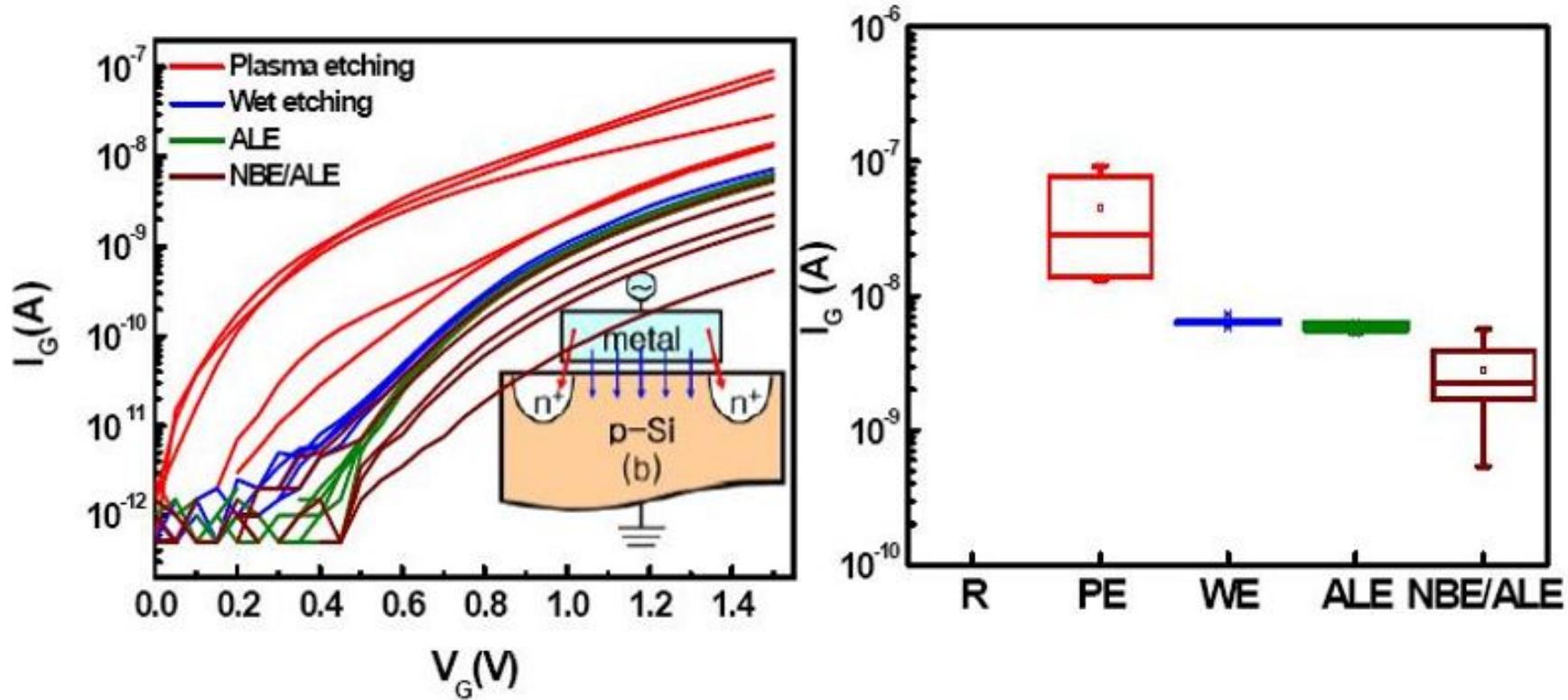
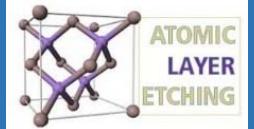
Before ALE process



After 30 cycles of ALE

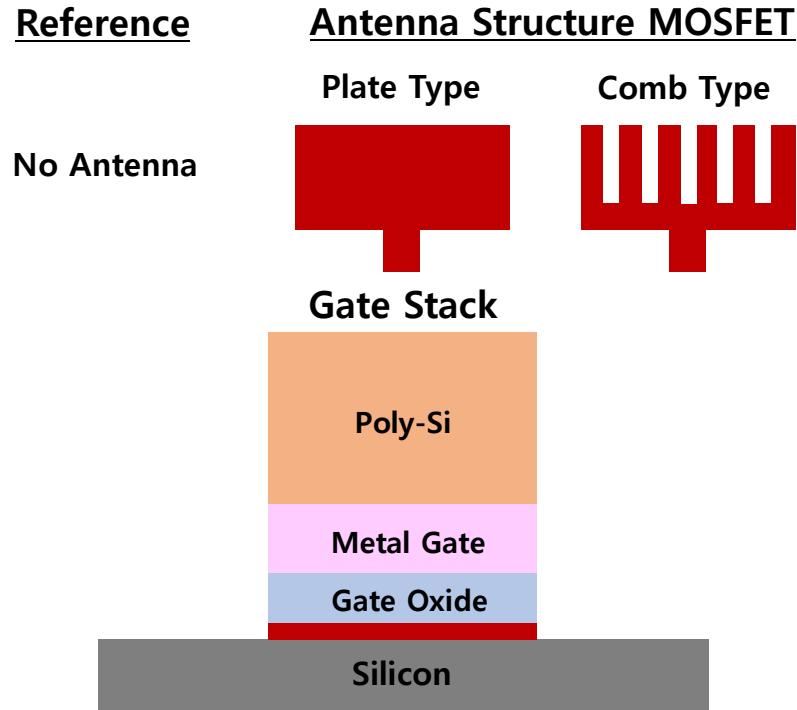
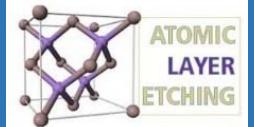
"Atomic layer etching of ultra-thin  $\text{HfO}_2$  film for gate oxide in MOSFET devices"  
Jae Beom Park, Woong Sun Lim, Byoung Jae Park, Ih Ho Park, Young Woon Kim and Geun Young Yeom  
J. Phys. D: Appl. Phys. 42, 055202 (2009)

# MOSFET IG-VG



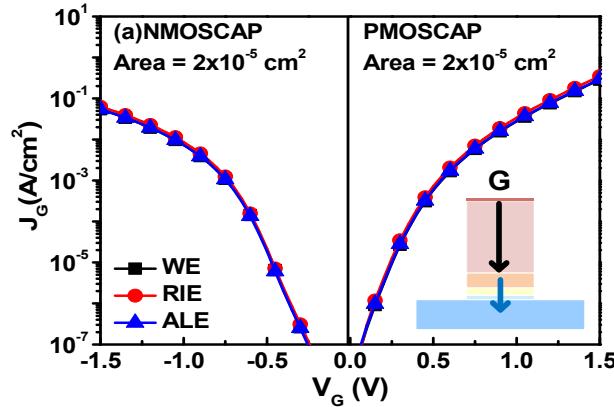
However, there are differences in MOSFET (without S/D active region) due to gate oxide edge damage which could be the leakage path in the heterogeneous interface between the high-k dielectric and the capping nitride layer

# MOSFET IG-VG

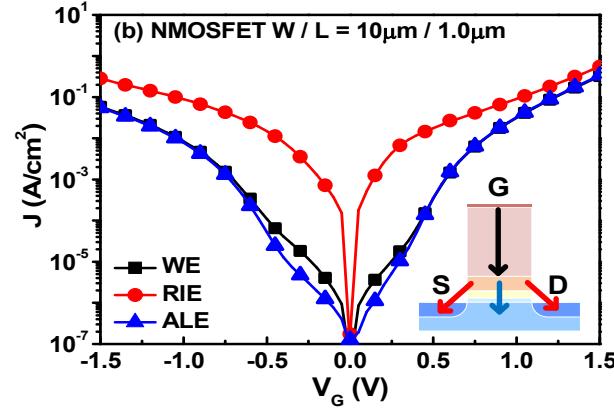


The ALET can minimize the plasma etching damage at the edge of gate oxide.

$I_G$ - $V_G$  characteristics of STI edge transistor



$I_G$ - $V_G$  characteristics of S/D edge transistor

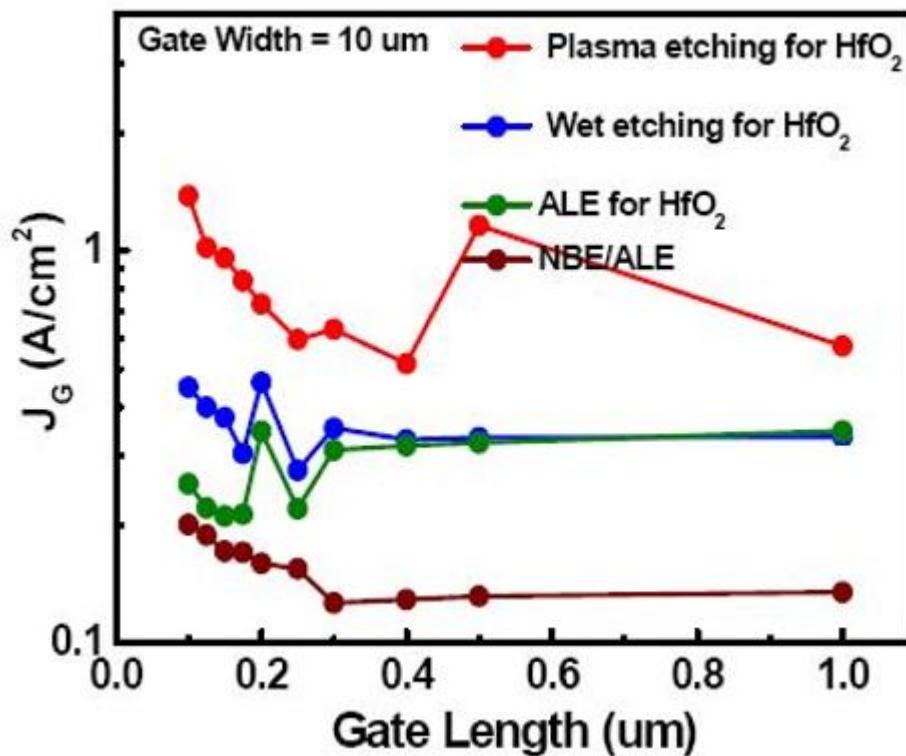


"Atomic layer etching of ultra-thin HfO<sub>2</sub> film for gate oxide in MOSFET devices"  
 Jae Beom Park, Woong Sun Lim, Byoung Jae Park, Ih Ho Park, Young Woon Kim and Geun Young Yeom  
*J. Phys. D: Appl. Phys.* 42, 055202 (2009)

# MOSFET Device as a function of Gate Length



## ◆ MOS Parameter - IG



As gate length decrease from 1 um to 100 nm, the gate leakage current is as low as wet etching compared that of plasma etching

"Atomic layer etching of ultra-thin  $\text{HfO}_2$  film for gate oxide in MOSFET devices"  
Jae Beom Park, Woong Sun Lim, Byoung Jae Park, Ih Ho Park, Young Woon Kim and Geun Young Yeom  
J. Phys. D: Appl. Phys. 42, 055202 (2009)

# Contents



**1**

Introduction of Atomic Layer Etching (ALE) with Ion/Neutral Beam

**2**

ALE of Various Materials  
(III-V Compounds, High-k Dielectirics)

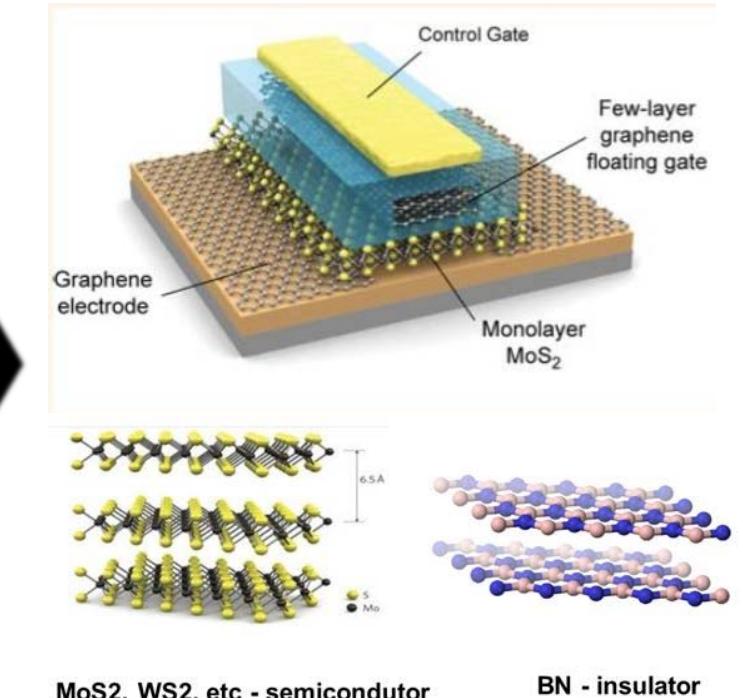
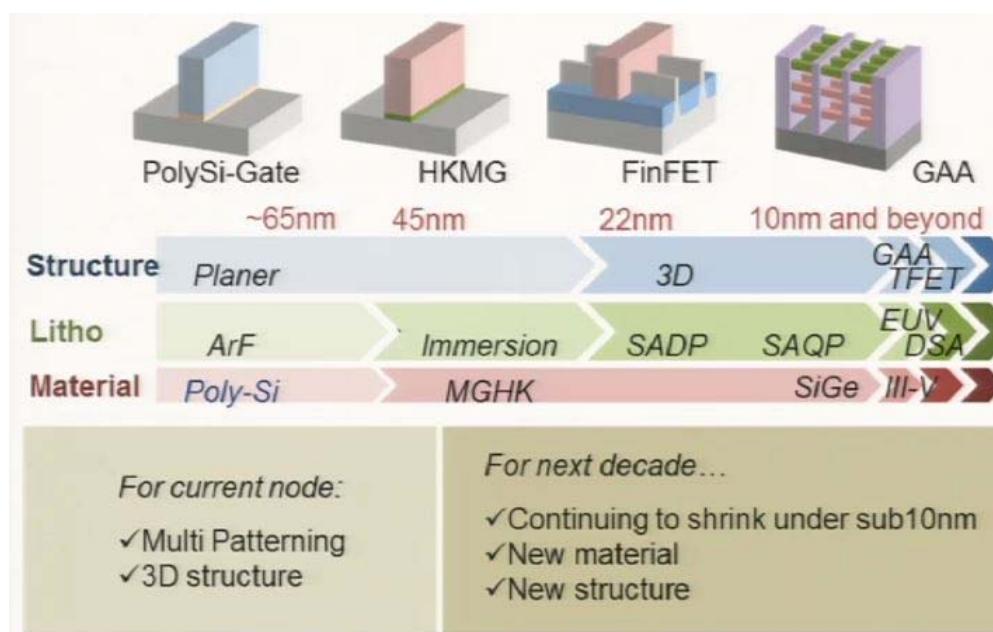
**3**

**Recent Research Trends**

**4**

Summary

# Need for ALE

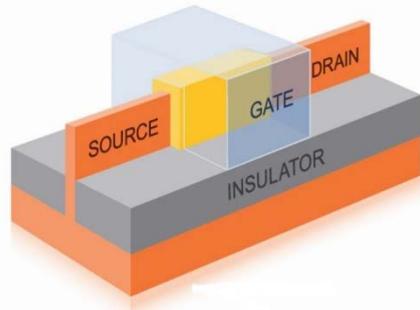
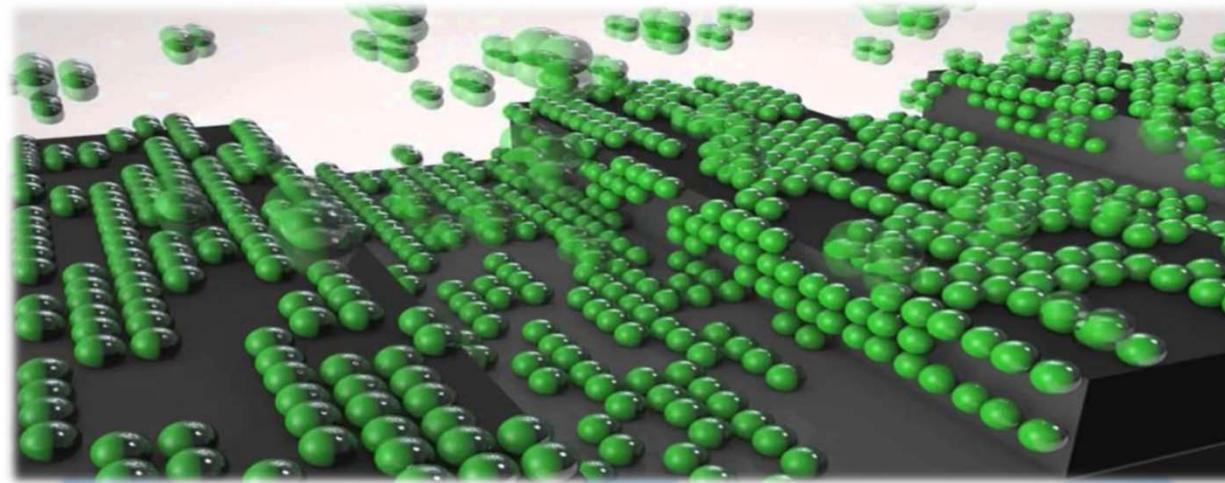
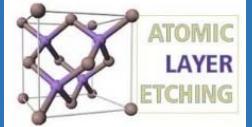


"Atomic Level Etching of Poly-Si in a Microwave Electron Cyclotron Resonance Plasma Etcher"  
Yasushi Sonoda (HITACHI)

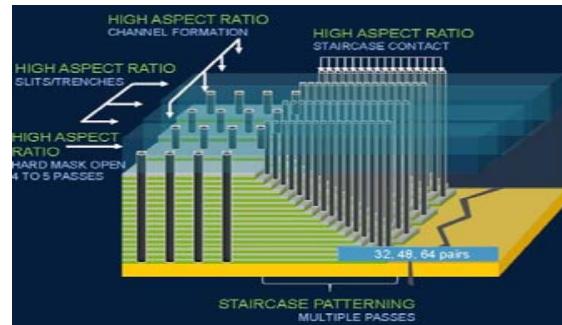
## ◆ Films getting thinner: slow etch rate is not a problem

- High etch selectivity
  - Negligible etching into underlayer
- Low etch damage and contamination
- Precise control of etch depth in atomic scale

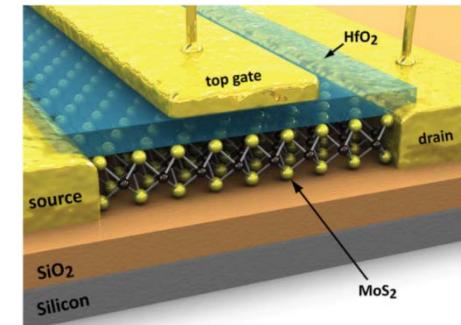
# Possible Application of Anisotropic ALE



Gate etch

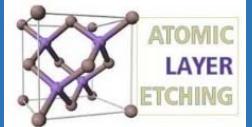


Contact etch      Dummy/Sacrificial  
layer removal



2D-materials

# Logic Challenges for 10 nm Node and Beyond

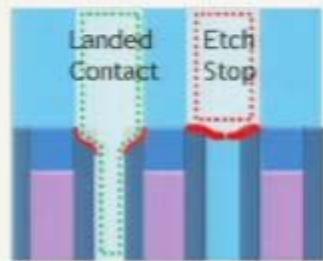


## ◆ Self-aligned contact



### Corner selectivity

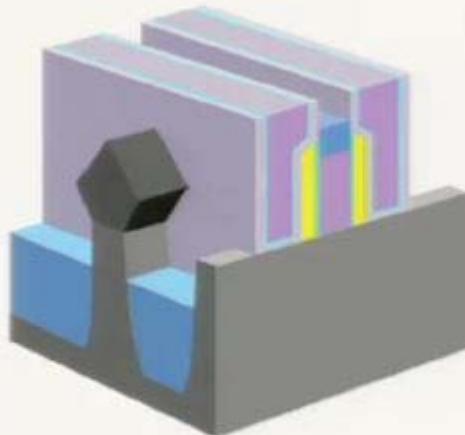
- SiN spacer corner loss increases leakage to gate
- SiN → low-k spacer



### Etch stop

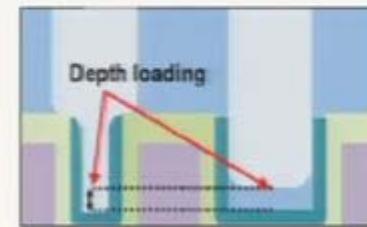
- Polymer pinch off in narrow space etching leading to unlanded contact

### Self Aligned Contact (SAC) on FinFET



### SiGe loss

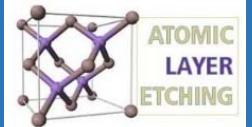
- Increases contact resistance



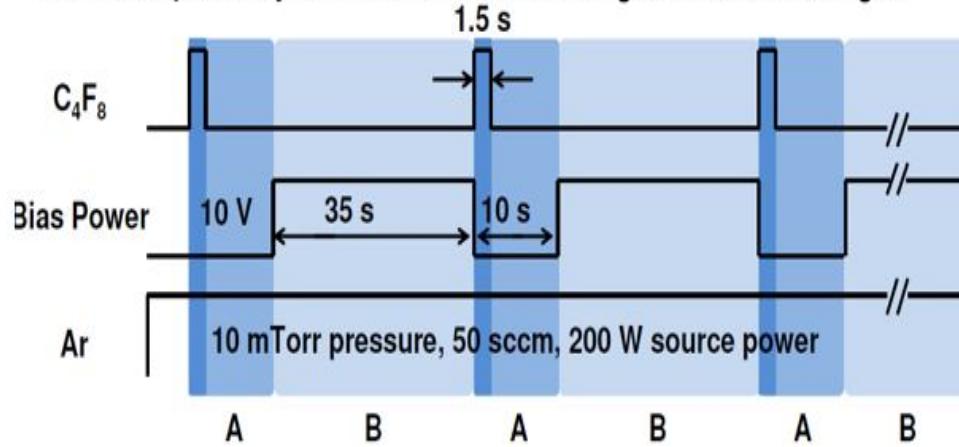
### Etch depth loading

- Due to large vs. small CD (ARDE)

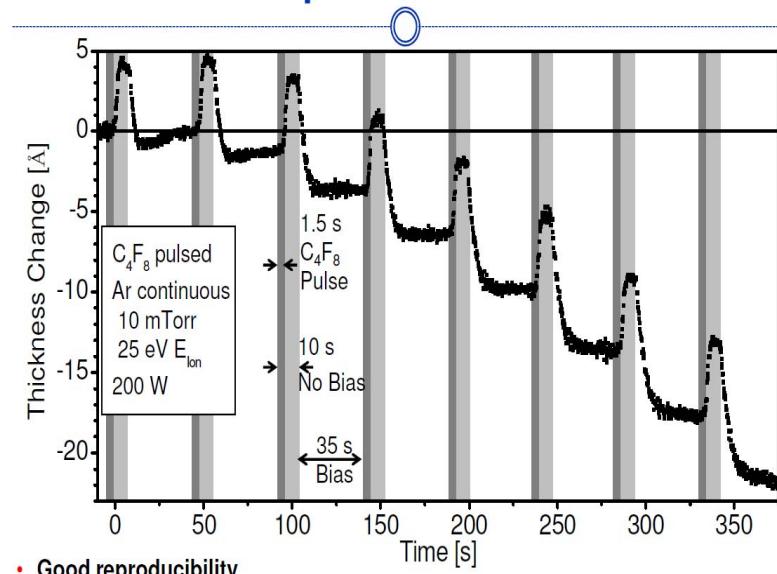
# ALE of SiO<sub>2</sub> using ICP with Pulsing Gases



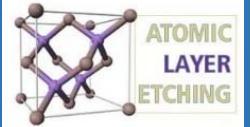
- A. Deposition Step → Short precursor pulse
- B. Etch Step → Removal of modified surface layer
- In-situ ellipsometry allows real-time monitoring of thickness changes



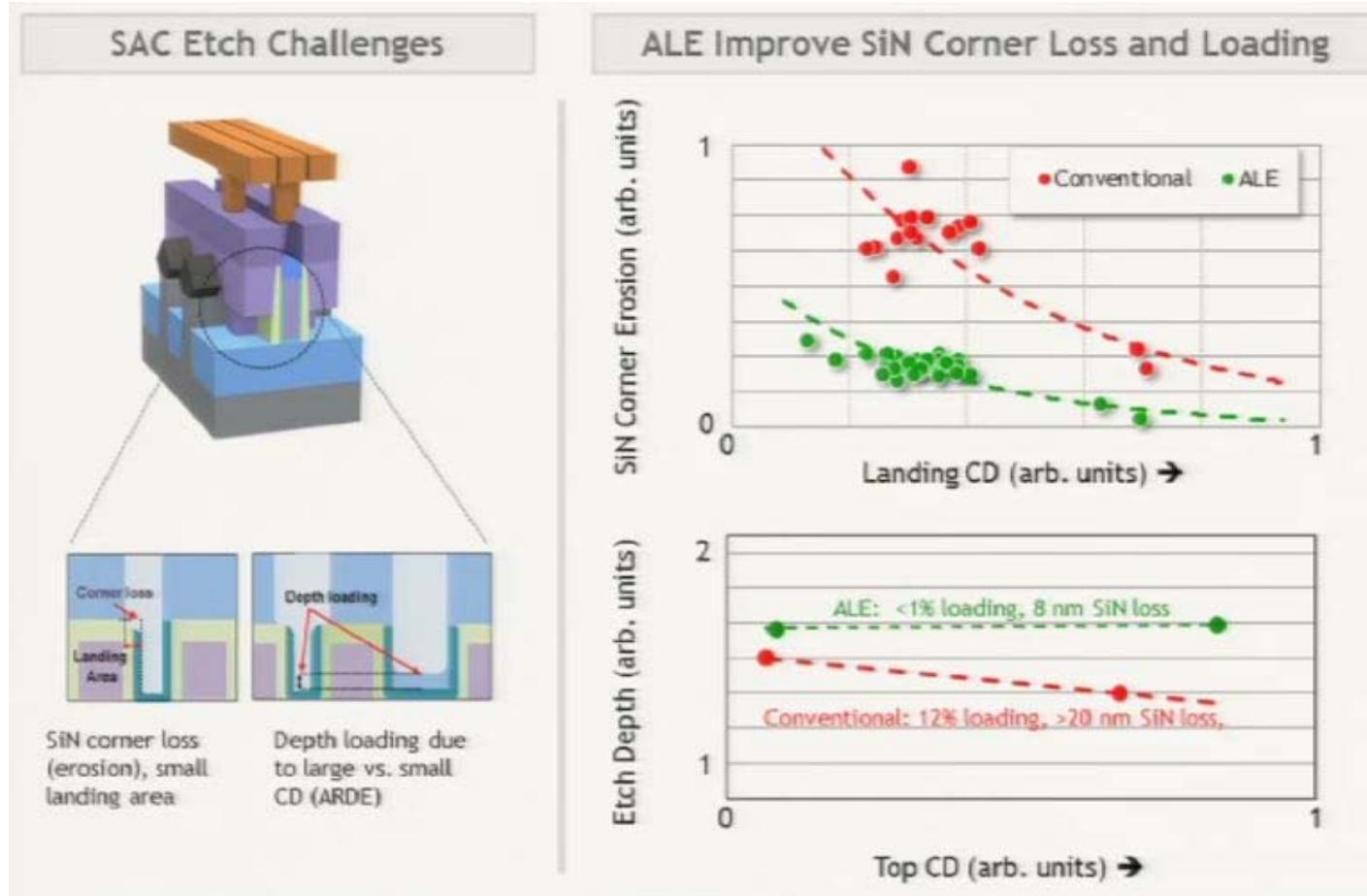
## Time-Dependent Etch Rates



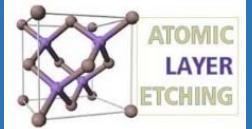
# ALE Tool by Lam Research Inc.



## ◆ Oxide ALE for SAC etch : Better selectivity and loading

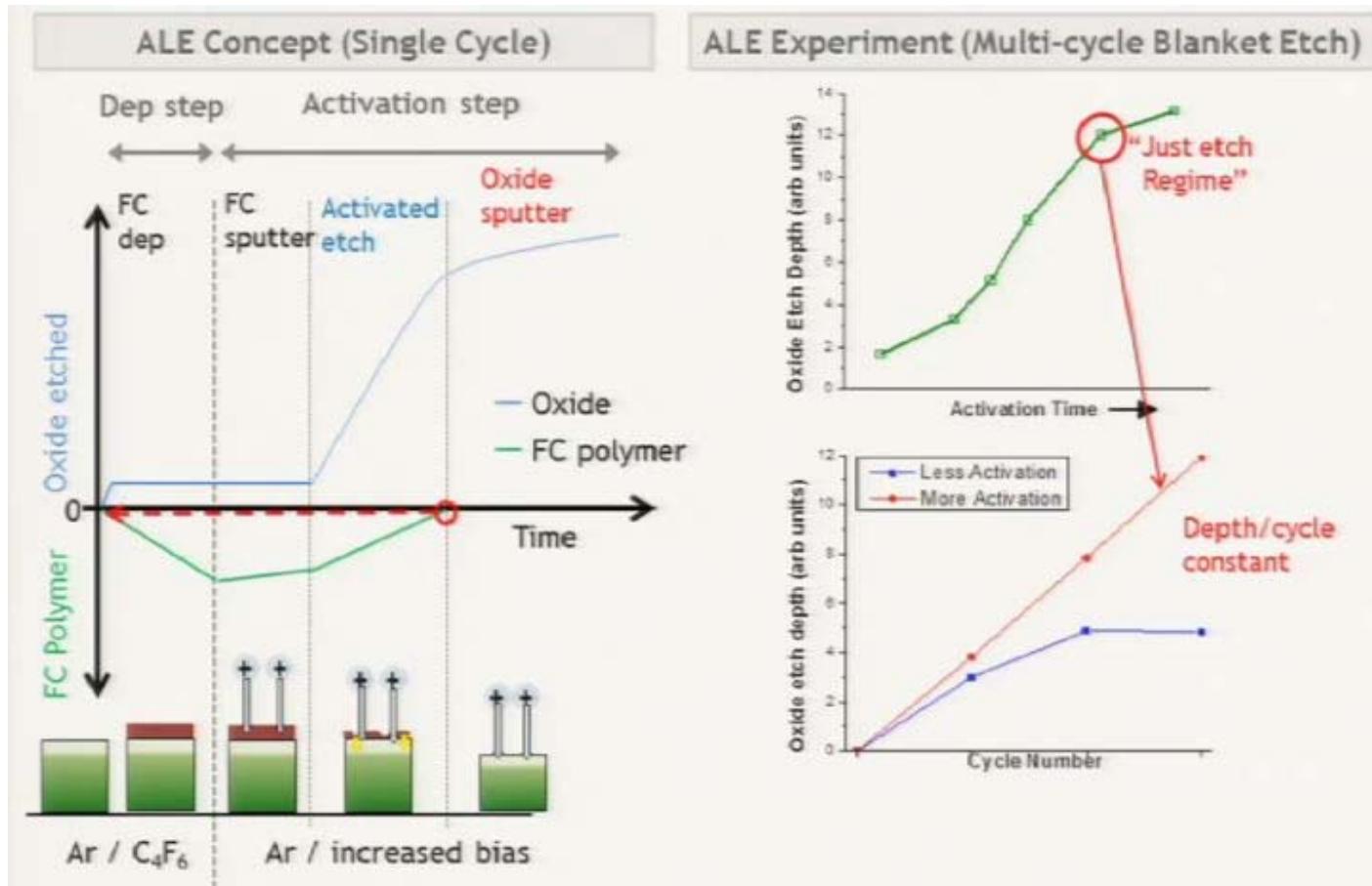


# ALE Tool by Lam Research Inc.

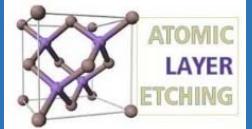


## ◆ Deposition + Activation cyclic process

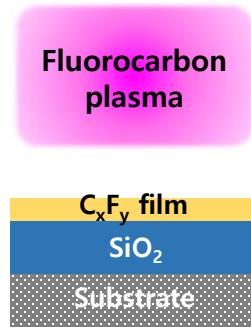
: Concept vs. Experiment



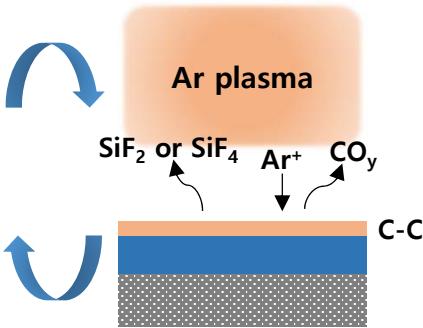
# $\text{SiO}_2$ ALE using $\text{O}_2$ as Desorption Gas



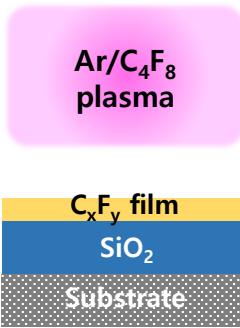
## Step 1



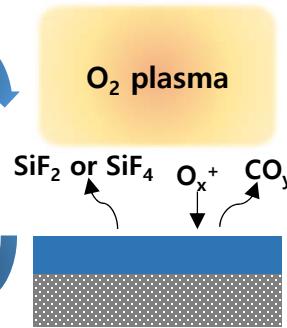
## Step 2



## Step 1

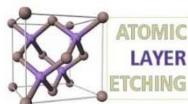
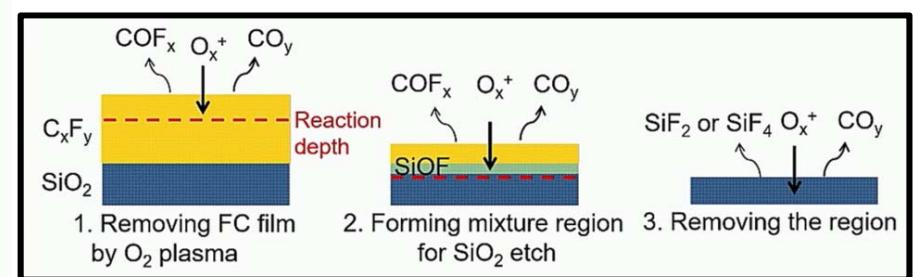
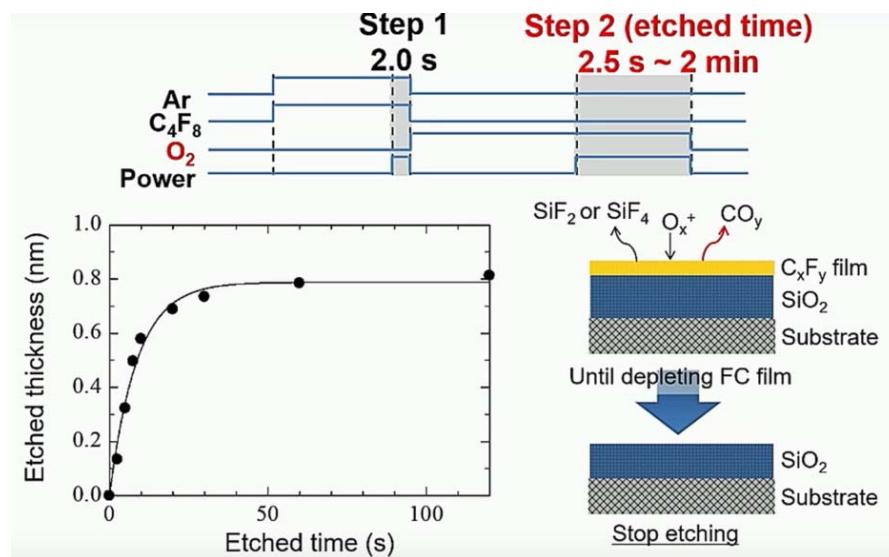


## Step 2



### ◆ Advantage

- To remove extra carbon such as  $\text{CO}$  or  $\text{CO}_2$ ,  $\text{COF}_x$  during ALE
- To maintain clean chamber by  $\text{O}_2$  plasma process



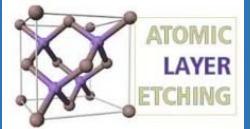
ALE 2016 Ireland

3rd International Workshop on Atomic Layer Etching  
24th - 25th July 2016, Dublin, Ireland

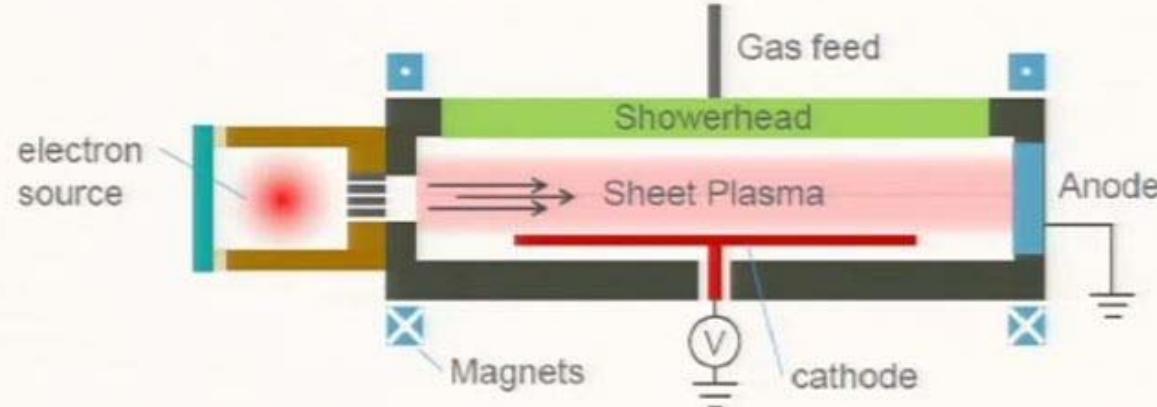
"A novel atomic layer etching of  $\text{SiO}_2$  with alternating  $\text{O}_2$  plasma with fluorocarbon film deposition"  
Takayoshi Tsutsumi (Nagoya Uni.), Masaru Zaitsu, Akiko Kobayashi, Hiroki Kondo,  
Toshihisa Nozawa, Nobuyoshi Kobayashi, Masaru Hori

ALD 2017  
17th International Conference on Atomic Layer Deposition

# Low Energy E-beam Etch Tool of Applied Materials for ALE



## ◆ Electron beam-generated plasma etch tool



Typical beam energy: 1500 – 2500 V

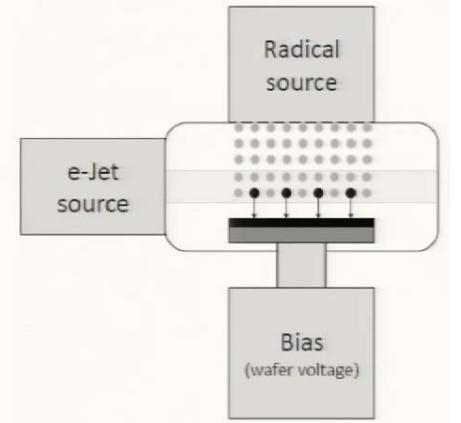
Argon / Nitrogen plasma

Typical beam current: 120 – 180 mA

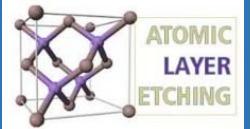
Oxygen plasma



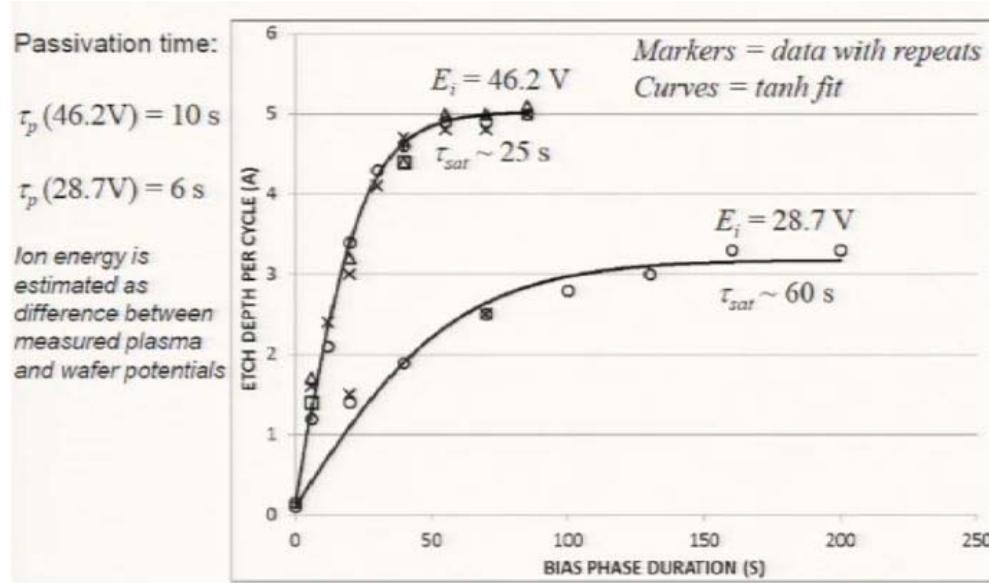
We have demonstrated a robust electron beam-generated plasma with stable and reproducible operation at 5 – 80 mT in all relevant etch chemistries



# Low Energy E-beam Etch Tool of Applied Materials for ALE

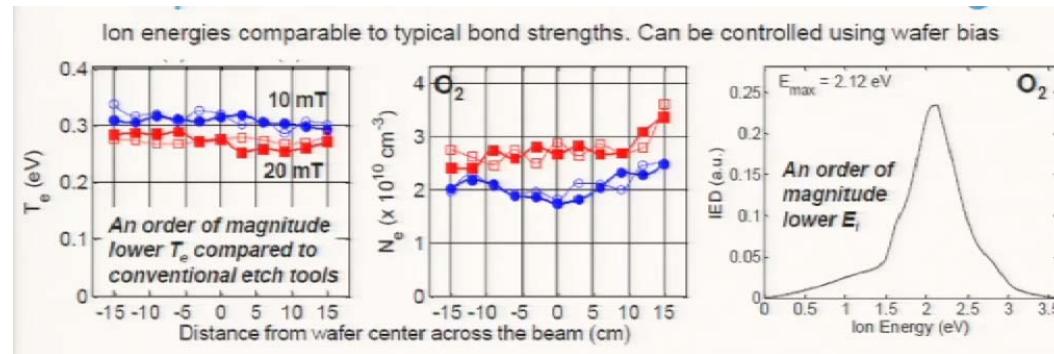
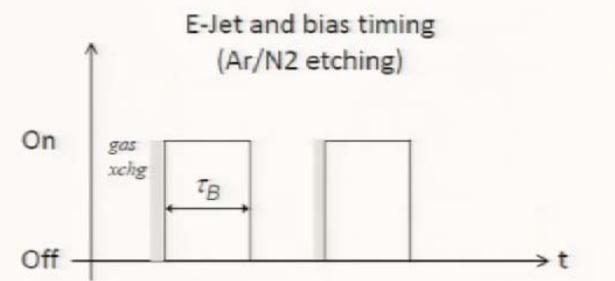
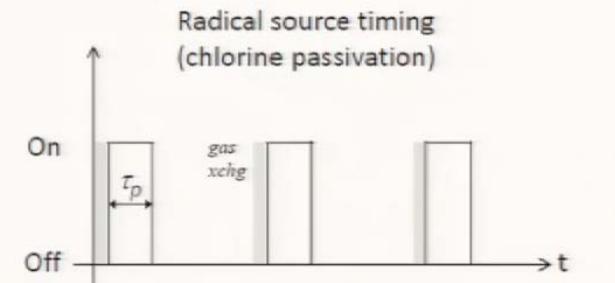


## ◆ Si ALE in chlorine at different ion energies



$P = 5 \text{ mT}$

Saturation is limited by Ar-only etch rate of  $\sim 1 \text{ A/min}$

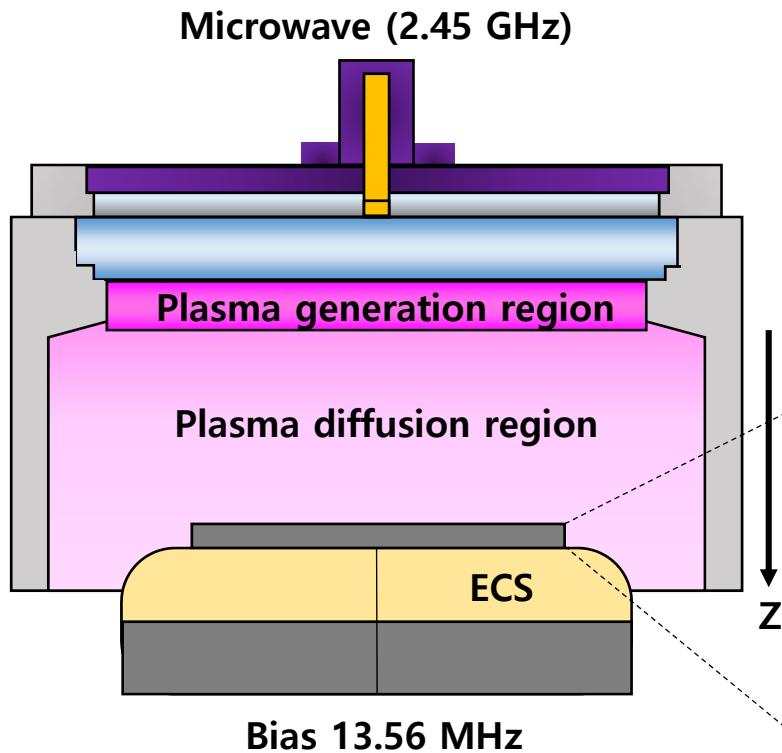


# Cyclic Etch Tool by TEL

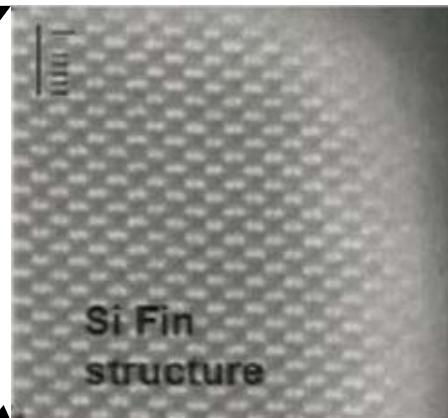


## ◆ One way

: Spatial pulsing with microwave plasma processes



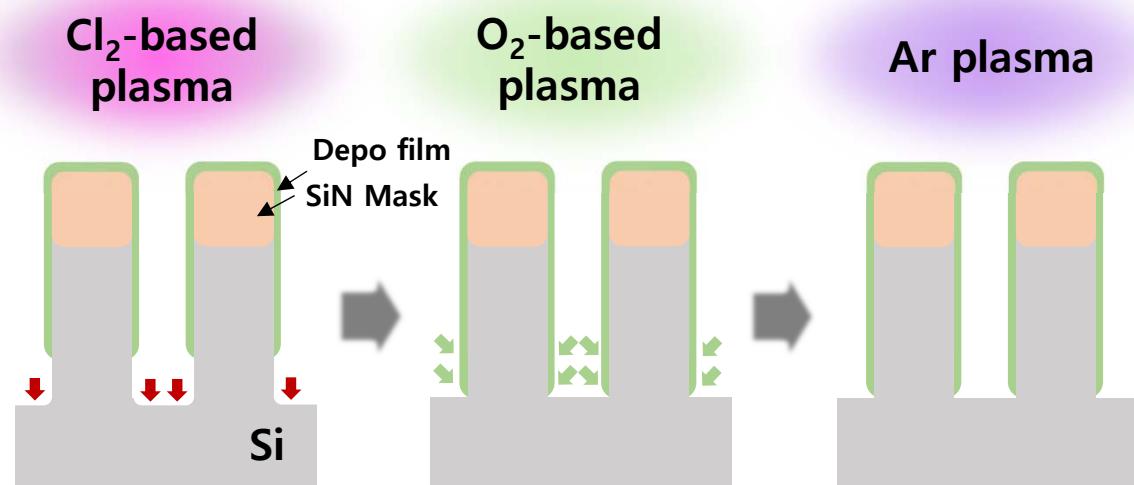
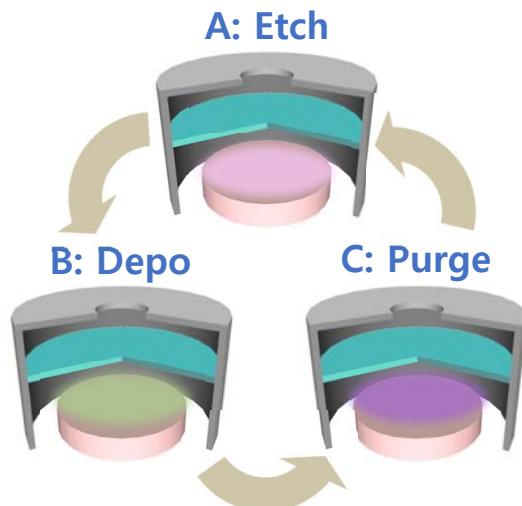
- Allows access to an energy range where chemistry can be done on a surface and the sub-surface left pristine



## ◆ Gas pulsing process

: Tri-time modulation

- Tri-TM is triadic combination of pulsing techniques, bias plasma and gas pulsing
- Tri-TM process is demonstrated for Fin etching of Si



### A: Etch

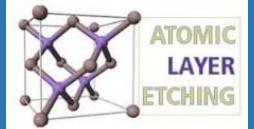
- Cl<sub>2</sub>-based Si etch step
- Bias & Plasma pulsing

### B: Depo

- O<sub>2</sub>-based passivation step

### C: Purge

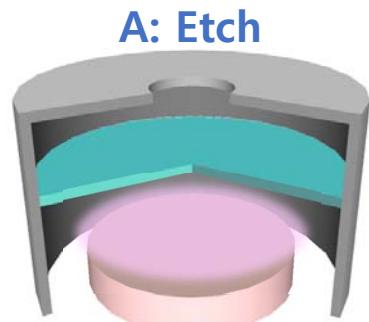
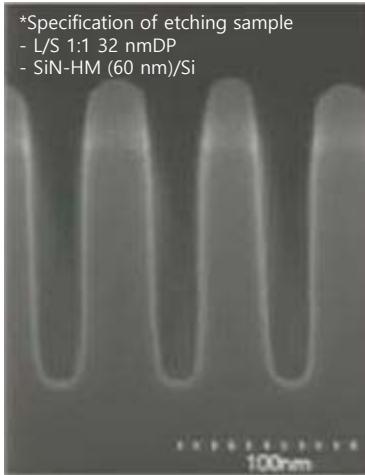
- Ar purge step



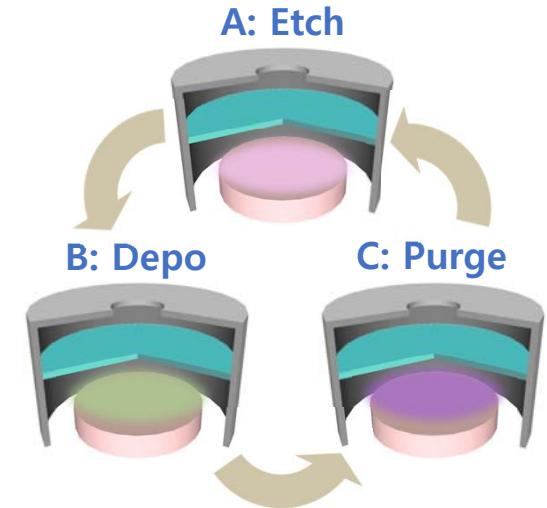
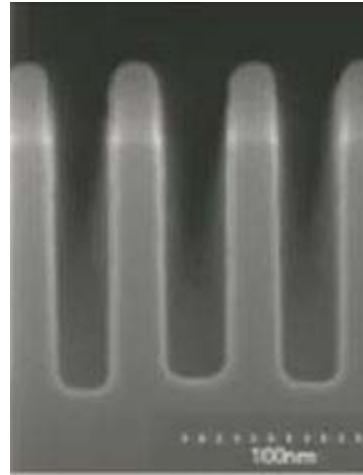
## ◆ Results: Gas pulsing process

: Gas pulsing enables to realize the vertical profile and higher selectivity

### Single step process



### Gas pulsing process



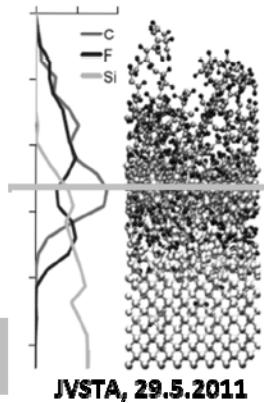
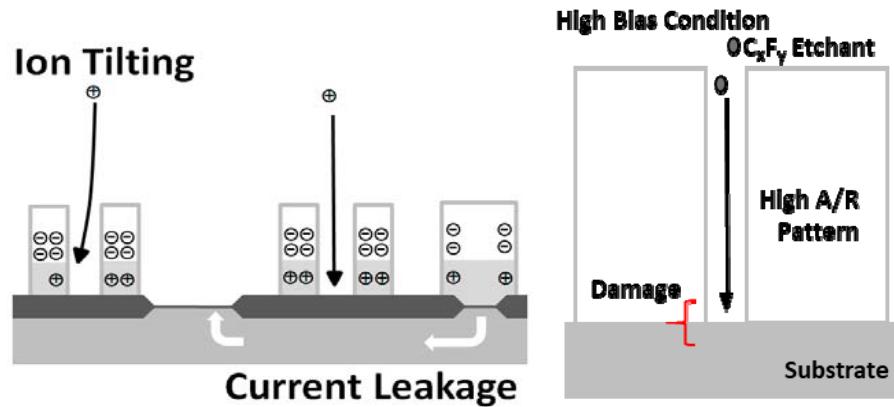
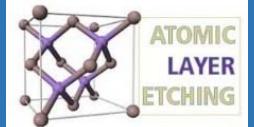
#### Continuous process:

- Tapered profile
- Lower selectivity
- Rounding etch front

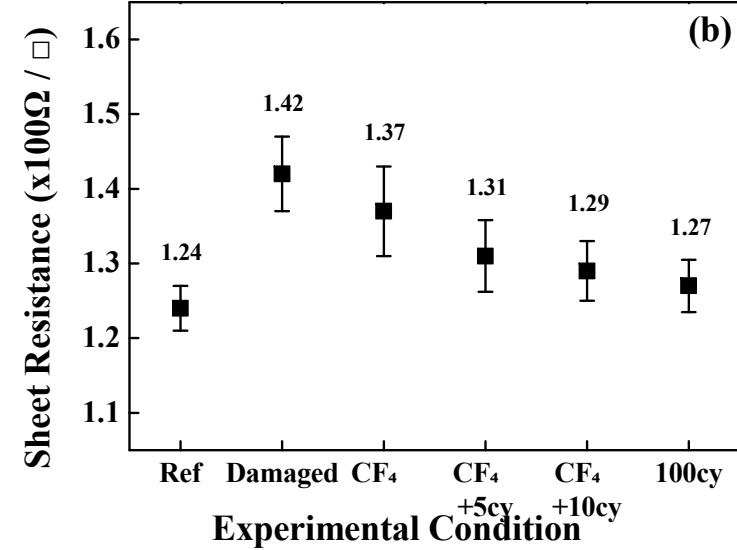
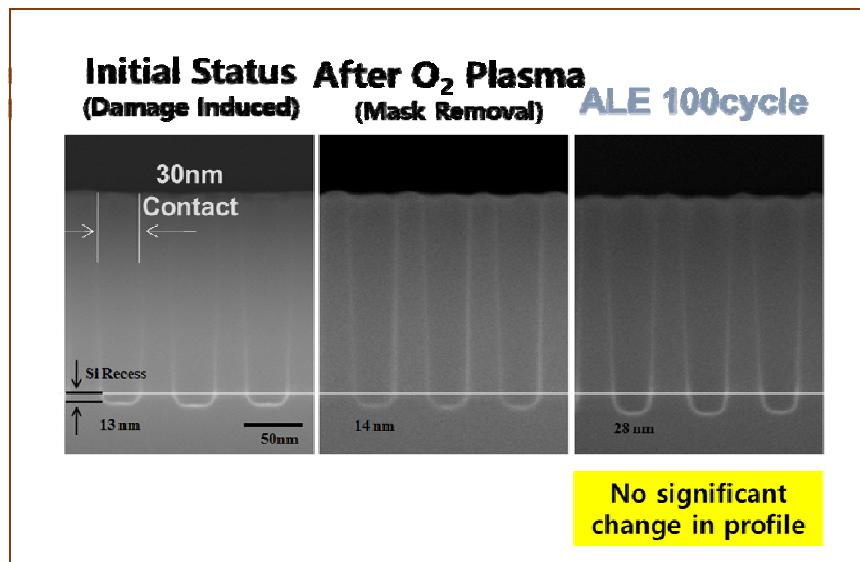
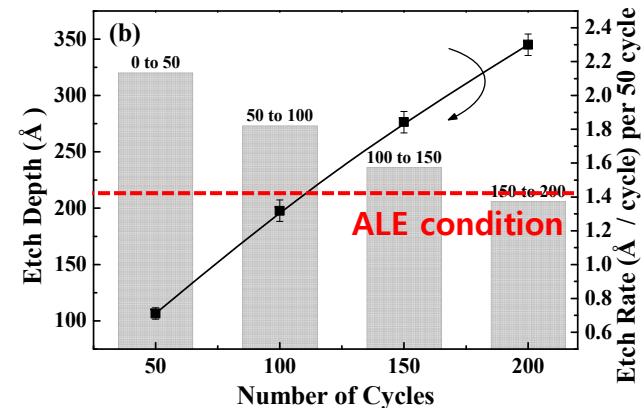
#### Gas pulsing process achieves:

- Vertical profile
- Higher selectivity
- Flat etch front

# Possible Advantage of Neutral Beam instead of Ar Ion Beam?



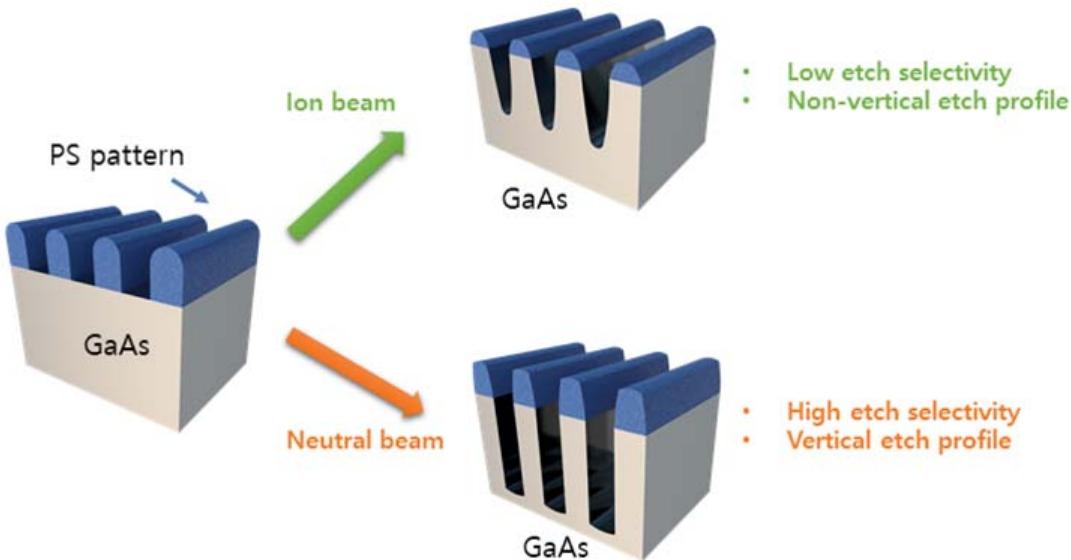
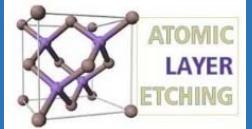
JVSTA, 29.5.2011



"Damaged silicon contact layer removal using atomic layer etching for deep-nanoscale semiconductor devices"  
Jong Kyu Kim, Sung Il Cho, Sung Ho Lee, Chan Kyu Kim, Kyung Suk Min, Seung Hyun Kang, and Geun Young Yeom  
Journal of Vacuum Science & Technology A 31, 061310 (2013)

"Atomic layer etching removal of damaged layers in a contact hole for low sheet resistance"  
Jong Kyu Kim, Sung Il Cho, Sung Ho Lee, Chan Kyu Kim, Kyung Suk Min, and Geun Young Yeom  
Journal of Vacuum Science & Technology A 31, 061302 (2013)

# Possible Advantage of Neutral Beam instead of Ar Ion Beam?



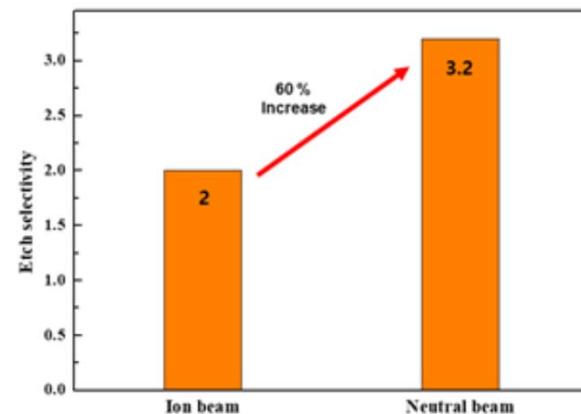
Ion Beam	Ref.	흡착
Etch profile		
Etch depth		110~126 nm

Neutral Beam	Ref.	흡착
SEM		
Etch depth		190~210 nm

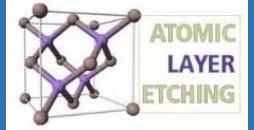
Power	200W
Cl <sub>2</sub>	1.5mTorr
Ar	2mTorr
Cycle(time)	500cycle(10-10-10-10)
Grid	10V, -250 V

Power	200W
Cl <sub>2</sub>	1.5mTorr
Ar	2mTorr
Cycle(time)	500cycle(10-10-35-10)
Grid	10V, -250 V



Etch selectivity improved by over 60 % with low-damage plasma source

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Introduction of Atomic Layer Etching (ALE) with Ion/Neutral Beam

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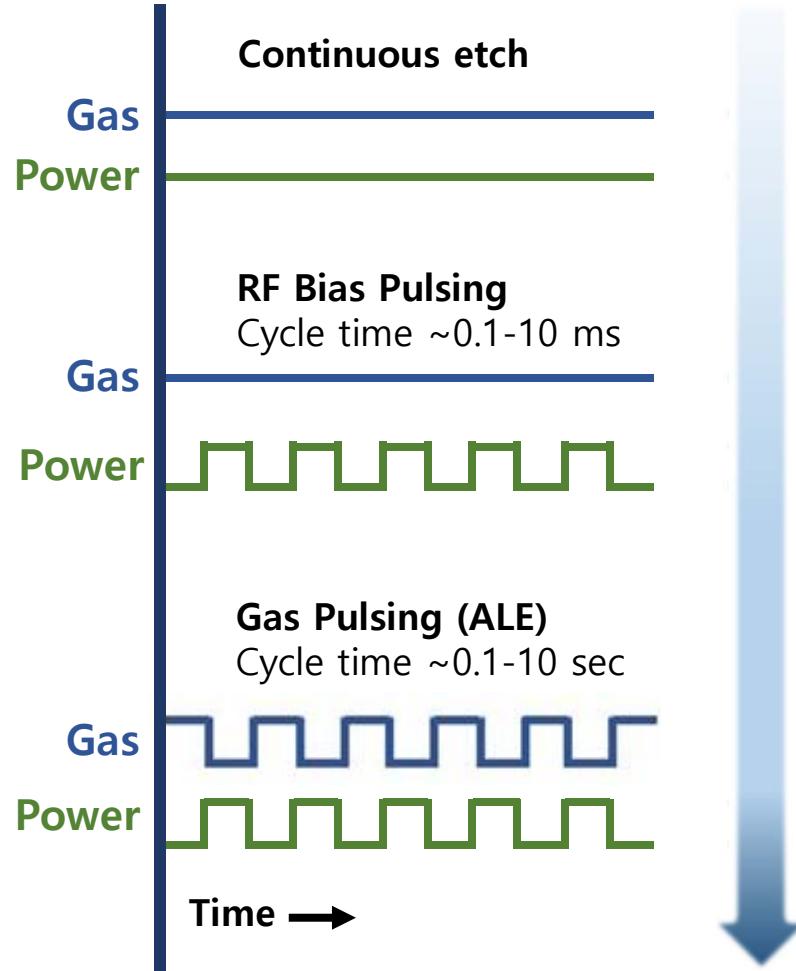
ALE of Various Materials  
(III-V Compounds, High-k Dielectirics)

**3**

Recent Research Trends

**4**

**Summary**



## ◆ Continuous Etch

- Maintain constant gas and RF power
- Recipe steps typically >10 sec

## ◆ RF Pulsing

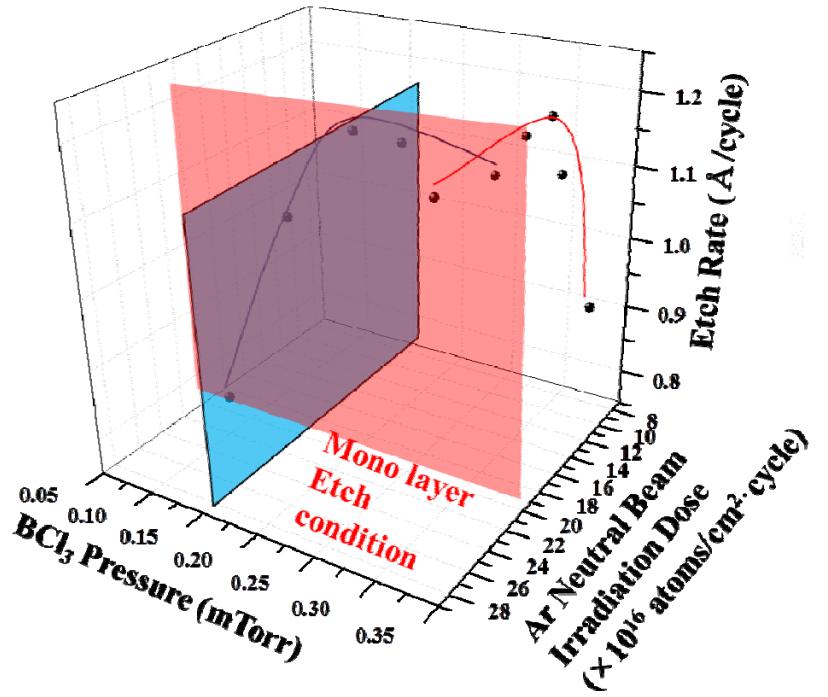
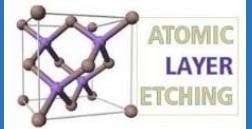
- Rapid variation in RF power to plasma
- Many different process benefits
- Bias pulsing modulates ion energy, effectively decouples ion energy control from gas neutral chemistry

## ◆ Gas Pulsing

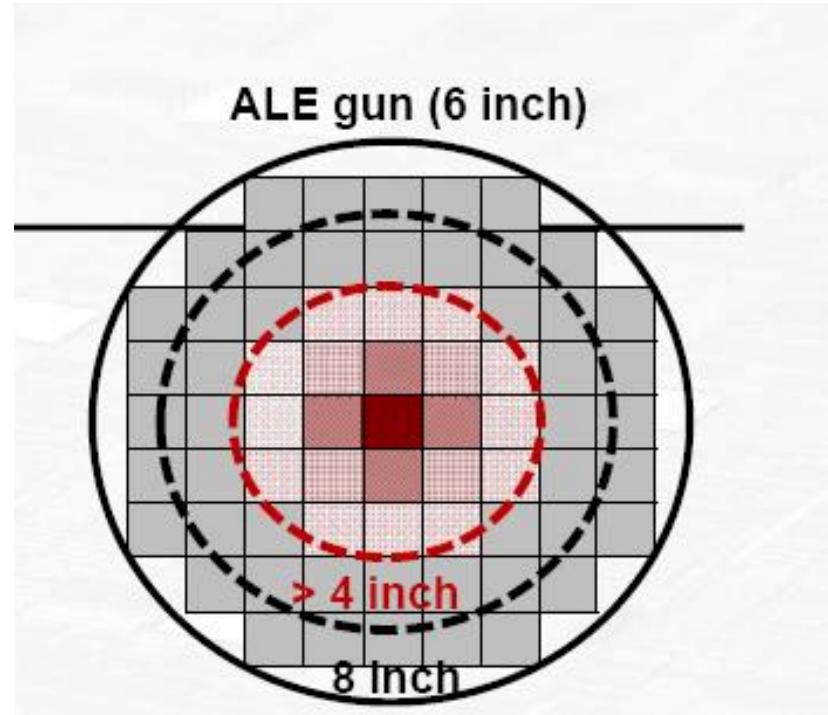
- Rapid variation of gas mixture delivered to reactor
- Generally slower than RF pulsing
- Synchronize gases to RF power (bias) to enable processes of atomic layer etching

## ◆ *Neutral Beam ? What else ?*

# Properties of ALE



Wide process window



Theoretical Uniformity : 0.0 %