ISPC-18 Summer School
Kyoto, Japan

August 24, 2007

Plasma Etching

Kouichi Ono

Department of Aeronautics and Astronautics,
Graduate School of Engineering, Kyoto University,
Yoshida-Honmachi, Sakyo-ku, Kyoto 606-8501, Japan
E-mail: ono@kuaero.kyoto-u.ac.jp

Background

- As integrated circuit device dimensions continue to be scaled down to <0.1 μm, strict requirements are being imposed on plasma etching technology.
- Especially, the precise or nanometer-scale control is indispensable for etched profiles and critical dimensions, together with higher selectivity, higher microscopic uniformity, and less damage.
- Moreover, new materials such as metals and low- and high-*k** dielectrics are being employed for <0.1 μm devices, and so the etching of such new materials are also required in integrating them into device fabrication. **k* : dielectric constant
- This lecture presents the current status of plasma etching technology based on the physical and chemical mechanisms underlying the processing, along with the future prospect towards nano-scale processes.

Outline

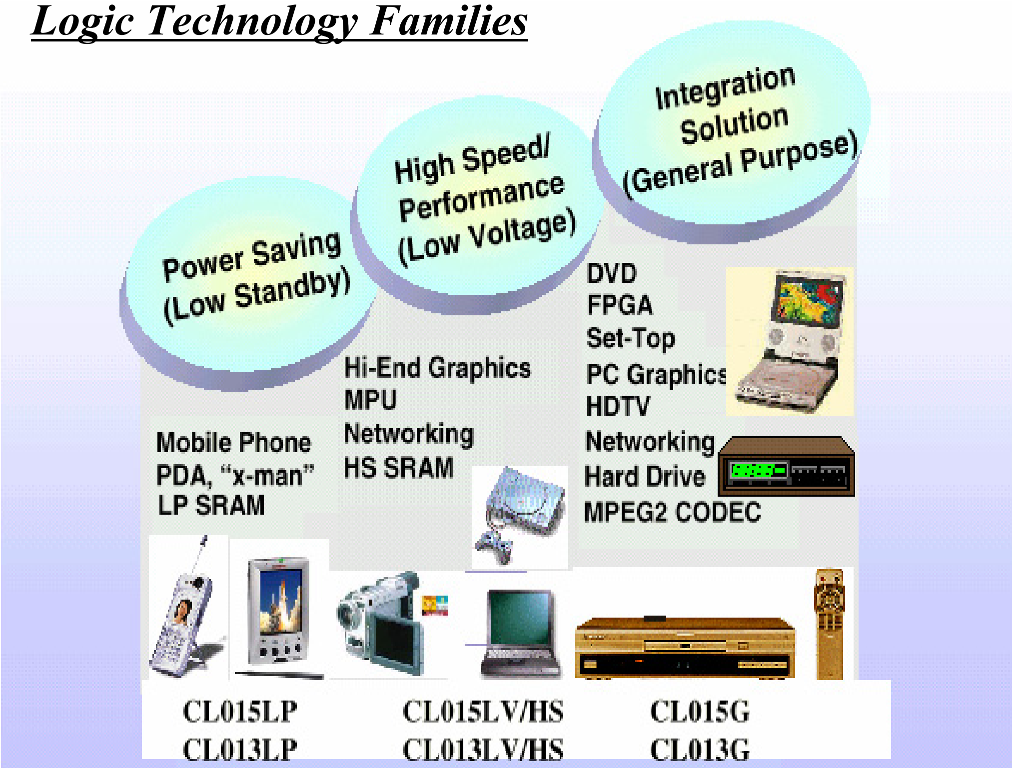
1. Introduction
   •ULSI devices •Requirements for plasma etching technology
2. Fundamentals of Plasma Etching Technology
   •Etching characteristics •Core technology of Plasma Etching
3. Role of Plasma in Plasma Etching
   •Gas-phase reactions •Ion acceleration through the sheath
4. Surface Reaction Processes in Plasma Etching
   •Surface reactions •Ion and neutral transport in microstructures
   •Feature profile evolution •Microscopic uniformity •Charging
5. Current Issues of Plasma Etching Technology
   •Current issues •Poly-Si gate etch •High-*k* gate etch
   •Metal etch •Deep RIE
6. Summary
   •Future prospects

1. Introduction

– Si-ULSI Devices
– Requirements for Plasma Etching

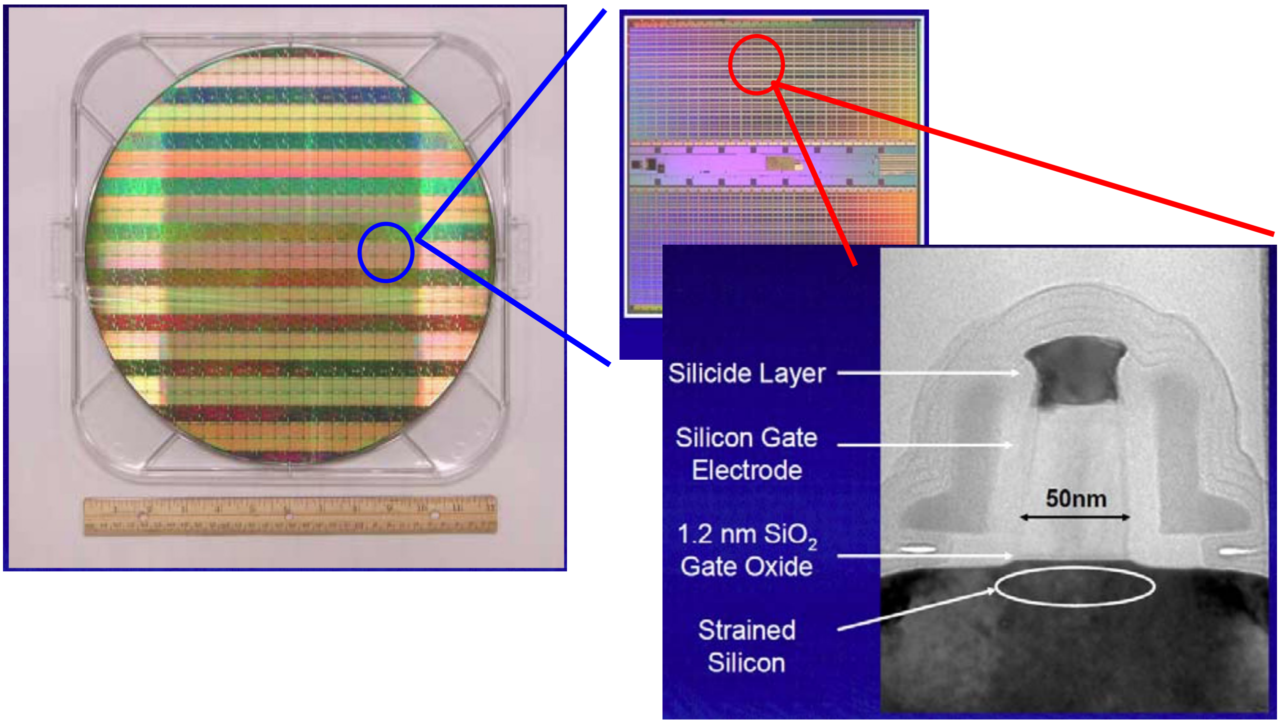
Si- ULSI Devices

Logic Technology Families



http://www.tsmc.com

Si- ULSI Devices *(continued)*



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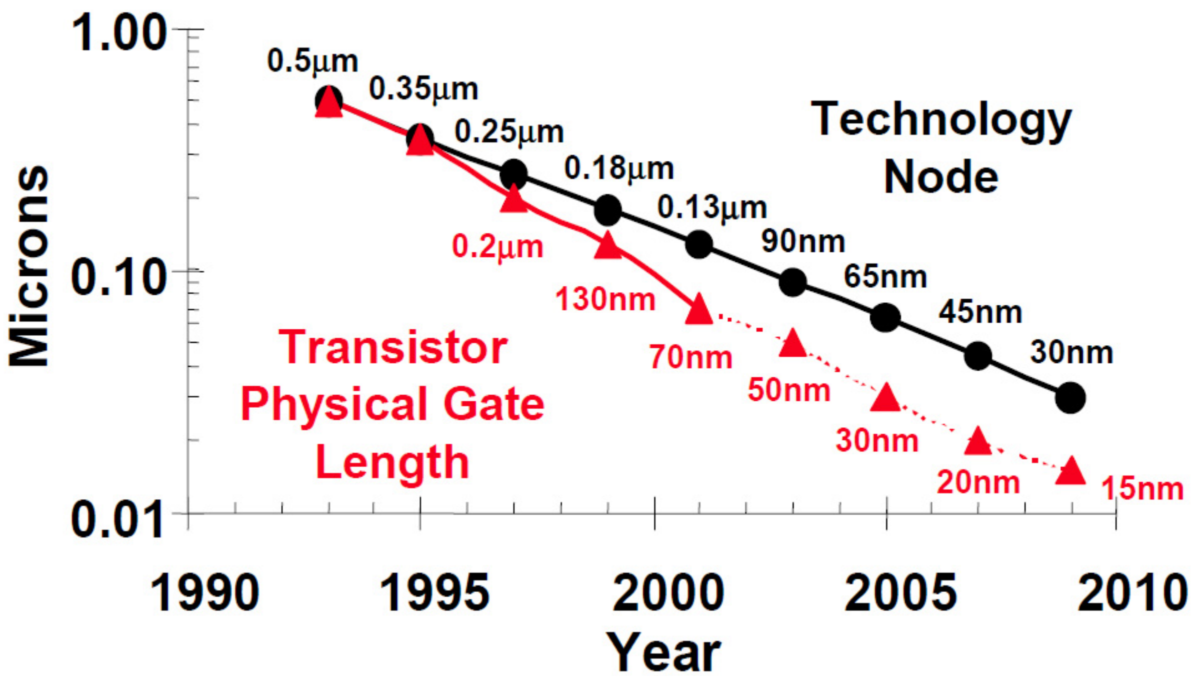
Trends of Si-ULSI Devices (1)



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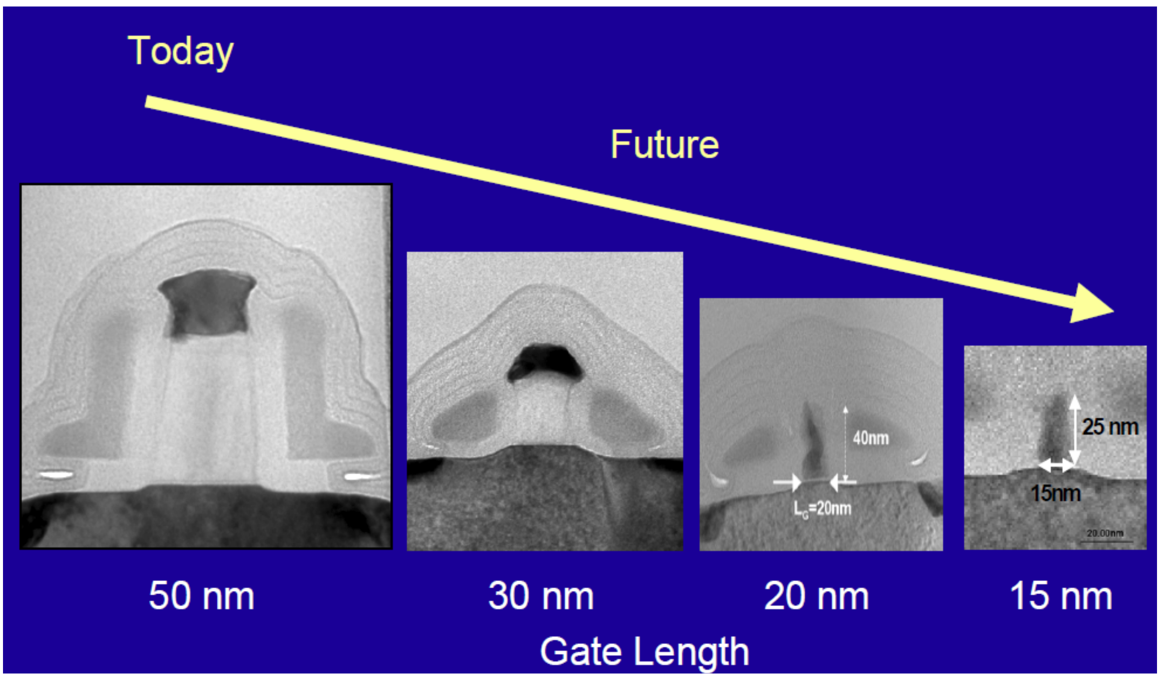
Planar CMOS Transistor Scaling



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Trends of Si-ULSI Devices (2)

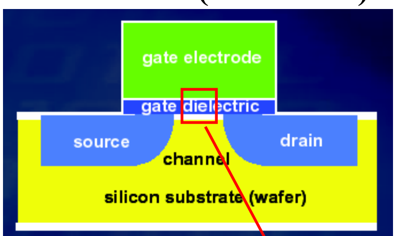
Year (1st production)	1997	1999	2001	2003	2005	2007	2009	2011
Process generation	0.25 μm	0.18 μm	0.13 μm	90 nm	65 nm	45 nm	32 nm	22 nm
Wafer size (mm)	200	200	200/300	300	300	300	300	300
Inter-connect	Al	Al	Cu	Cu	Cu	Cu	Cu	?
Inter-layer dielectric	FSG (k=3.6)	FSG (k=3.6)	FSG (k<3.6)	Low-k (k=2.9)	Low-k (k<2.9)	Ultra Low-k (k=2.5)	Ultra Low-k (k=2.1)	Ultra Low-k (k=1.9)
Gate dielectric	SiO2	SiO2	SiO2	SiO2	SiO2	High-k	High-k	High-k
Gate electrode	Poly-silicon	Poly-silicon	Poly-silicon	Poly-silicon	Poly-silicon	Metal	Metal	Metal

* FSG: high-density plasma fluorinated SiO_2

- As integrated circuit device dimensions continue to be scaled down, increasingly strict requirements are being imposed on plasma processing technology, including the etching and deposition of new materials as well as the more precise control of etching of conventional materials.
- Great attention has recently been placed on integrating high and low dielectric constant (*k*) materials into the fabrication of gate stacks and multi-level interconnections, respectively, for advanced sub-100 nm microelectronic devices.

High-*k* Gate Stack

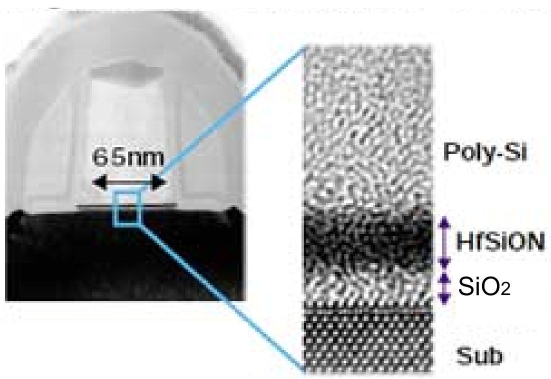
Transistor (Gate stack)



Ultra-thin gate SiO_2

(from AMAT)

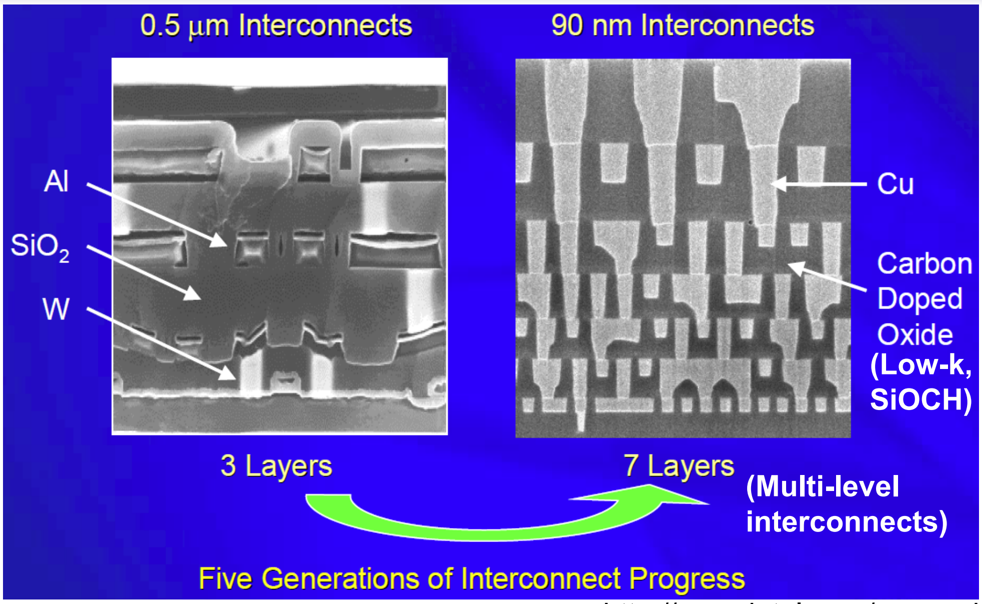
High-*k* gate stack



(from NEC)

- The technological challenge continues for growing ultra-thin SiO_2 film of high quality, to maintain the gate capacitance without increasing the leakage current and reducing the oxide reliability; however, the ultimate solution would rely on high-*k* materials such as HfO_2 and ZrO_2, and their silicates and aluminates.
- Moreover, for gate stacks with high-*k* dielectrics, gate electrodes of conventional Poly-Si are required ultimately to be replaced by metal gates of TiN, TaN, Ru/RuO_2, Pt and Ir.
- Plasma processing is indispensable for the fabrication or etching of gate electrodes, and also for the removal or etching of high-*k* dielectric.

Multi-level Interconnects and Low-*k* Inter-layer Dielectric



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- **Low-*k* inter-layer dielectrics (ILD) are required for reducing the resistance-capacitance time delay, which is getting more conspicuous as the shrinkage of the spacing between metal lines in high-density multi-level interconnections.**
- **Plasma processing is indispensable for chemical vapor deposition (CVD) of ILD, and also for the fabrication or etching of high-aspect-ratio contact (HARC) and via holes through ILD.**

Requirements for Plasma Etching

For ULSI fabrication

(1) Etch anisotropy and selectivity (↑)
– Profile control, Critical dimension (CD) control
– Selectivity over mask and underlying layers

(2) Plasma damage (↓)
– Charging damage
– Physical damage (ion-bombardment, impurity permeation)
– Radiation damage

(3) Microscopic uniformity (on a chip and cell scale) (↑)
– Etch rate, Profile, Selectivity, Damage, etc.
– Dependence on aspect ratio (AR), feature size, and pattern density

(4) Macroscopic uniformity (on a wafer scale) (↑)
– Etch rate, Profile, Selectivity, Damage, etc.

(5) Etching of new materials and device structures
– Low-*k*, High-*k*, Metal, Dual gate, etc.

- **The ULSI devices are substantially planar (2D), usually 5-10 μm thick, owing to limitations of the traditional fabrication processes for ULSI.**

Requirements for Plasma Etching

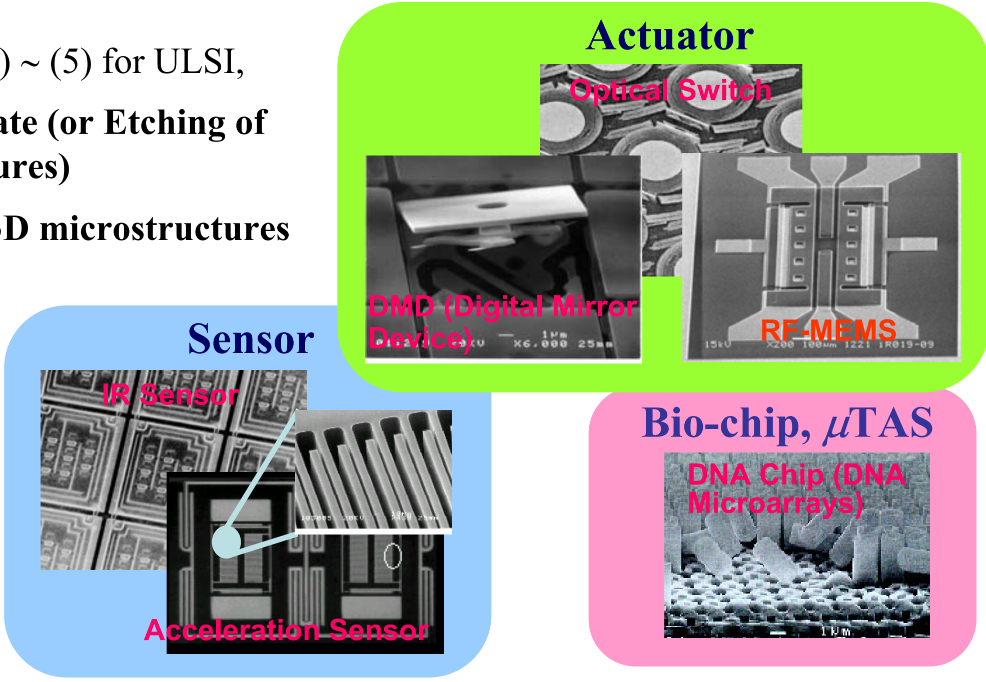
For fabrication of MEMS

*MEMS: Microelectromechanical Systems

In addition to (1) ~ (5) for ULSI,

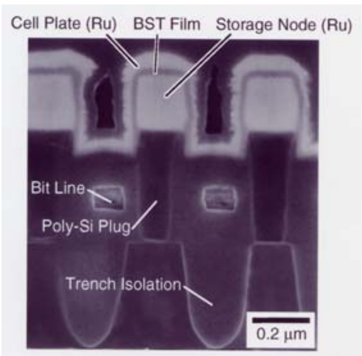
(6) High etch rate (or Etching of deep structures)

(7) Etching of 3D microstructures

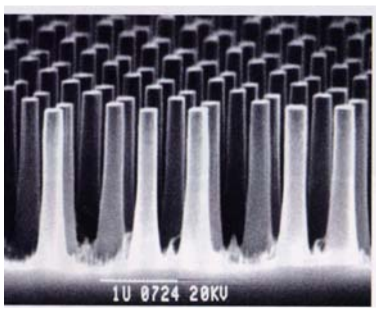


- **MEMS devices are manufactured using processes based on USLI fabrication technologies, and also using emerging technologies to fabricate 3D, deep (up to 1 mm) microstructures with higher throughputs and lower costs.**

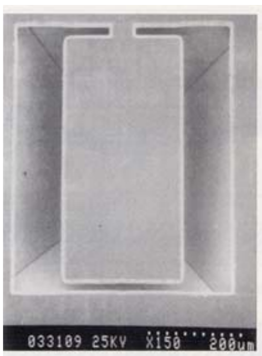
Microfabrication using Etching



DRAM cell — 0.2 μm



Photonic crystal — 1 μm



Micro cantilever — 0.2 mm

Micro turbine — 2 mm

2. Fundamentals of Plasma Etching Technology

– Etching Characteristics
– Core Technology of Plasma Etching
Plasma reactor
Feed gas
Process control

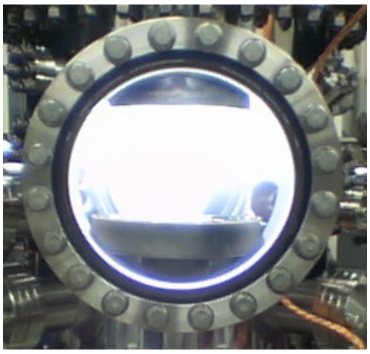
Plasma Etching Technology

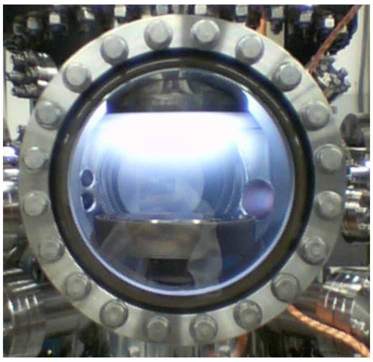
- Etching Characteristics :
  - Etch anisotropy and selectivity
  - Microscopic uniformity
  - Plasma damage

- Plasma etching (or processing) technology consists of three core technologies: (1) Plasma reactor, (2) Reactive Gas, and (3) Process control.

- Plasma plays two roles in plasma processing:
  (1) To generate ions and reactive neutrals from feed gases through electron impact events, which are then transported onto substrate surfaces.
  (2) To form the sheath above substrate surfaces, which accelerates the ions onto substrate surfaces.

Plasma Etching



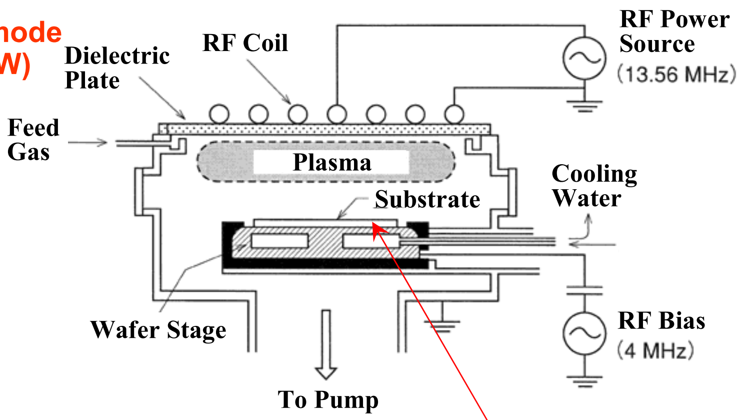


ICP mode (300 W)

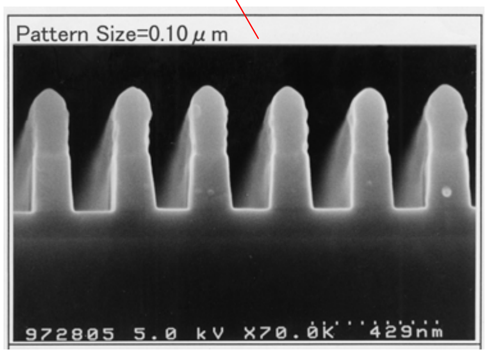
CCP* mode (100 W)

*CCP : Capacitively Coupled Plasma

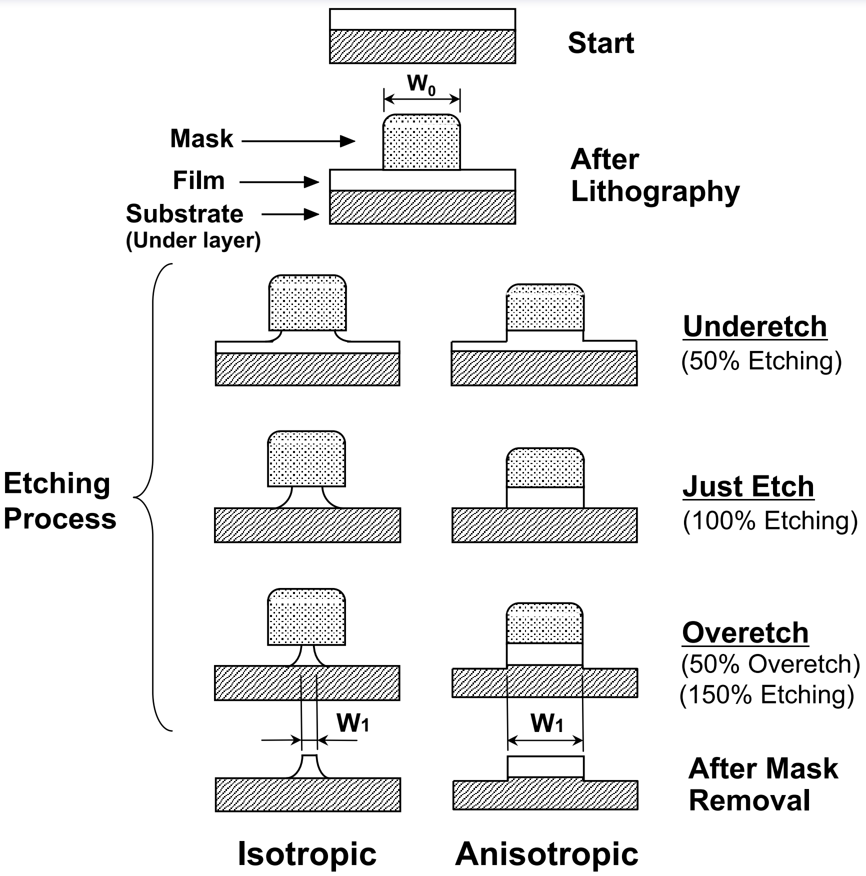
ICP (Inductively Coupled Plasma)



Etched Profile (Poly-Si)



Etch Anisotropy and Selectivity



- **Anisotropy :**

$$A = 1 - \frac{ER_{\text{lateral}}}{ER_{\text{vertical}}}$$

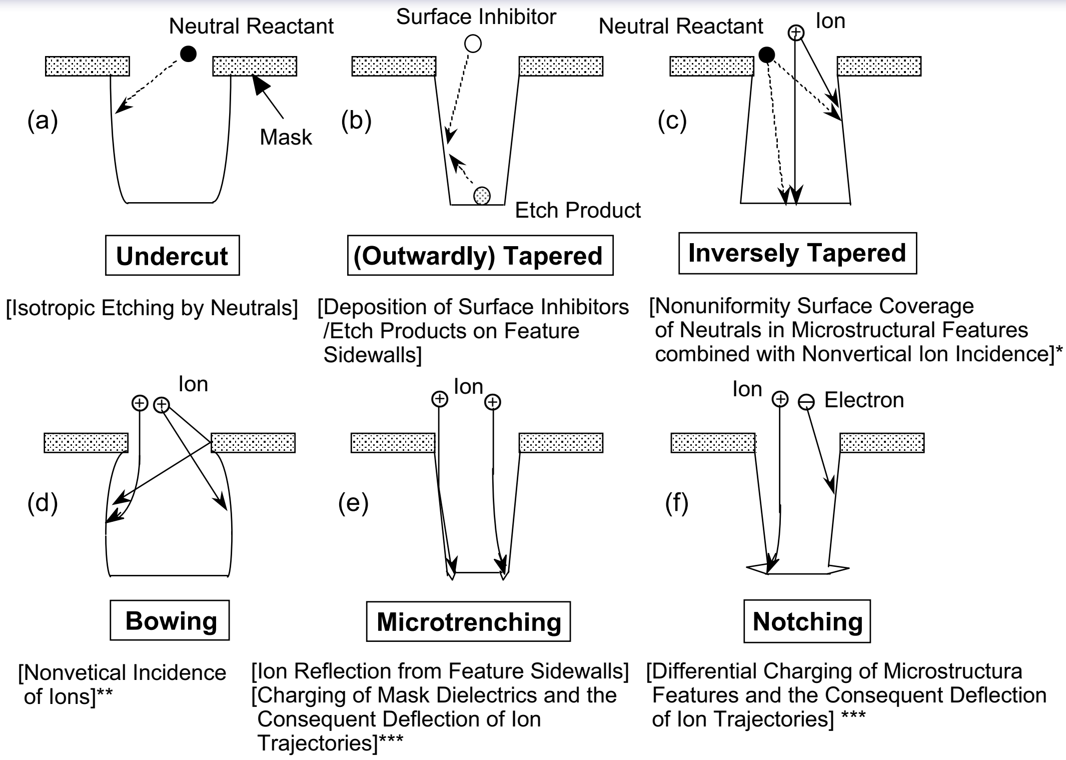
- CD Loss / Gain :

$$\Delta W = W_0 - W_1$$

- **Selectivity :**

$$S = \frac{ER_{\text{film}}}{ER_{\text{mask or under layer}}}$$

Profile Irregularities



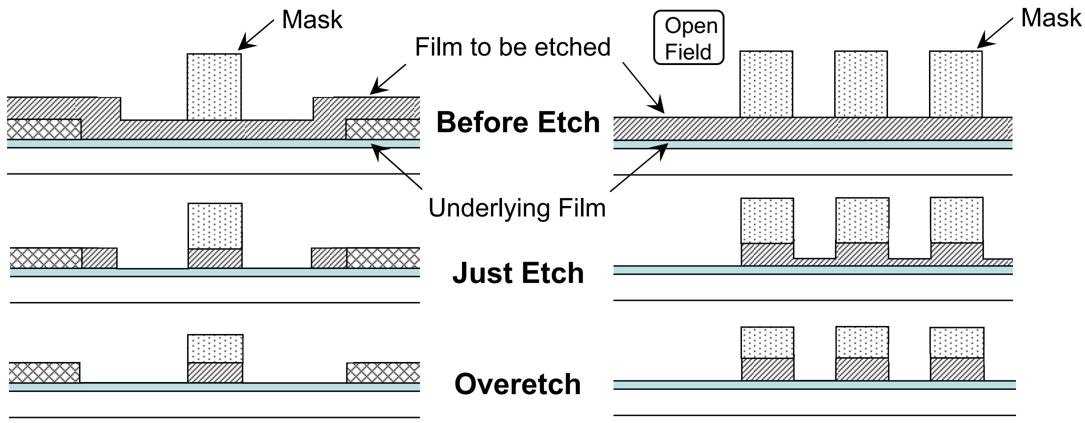
*The nonuniform surface coverage of neutrals results from the difference in anisotropy between incoming ions and neutral reactants.

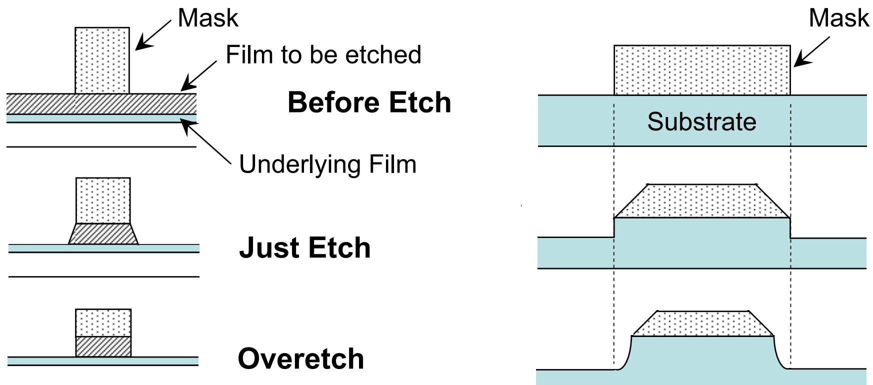
**The nonvertical ion incidence originates from the thermal motion of ions, scattering of ions through collision with neutrals in the sheath, and deflection of ion trajectories due to charging of mask dielectrics.

***The charging results from the difference in anisotropy between incoming Ions and electrons.

Selectivity

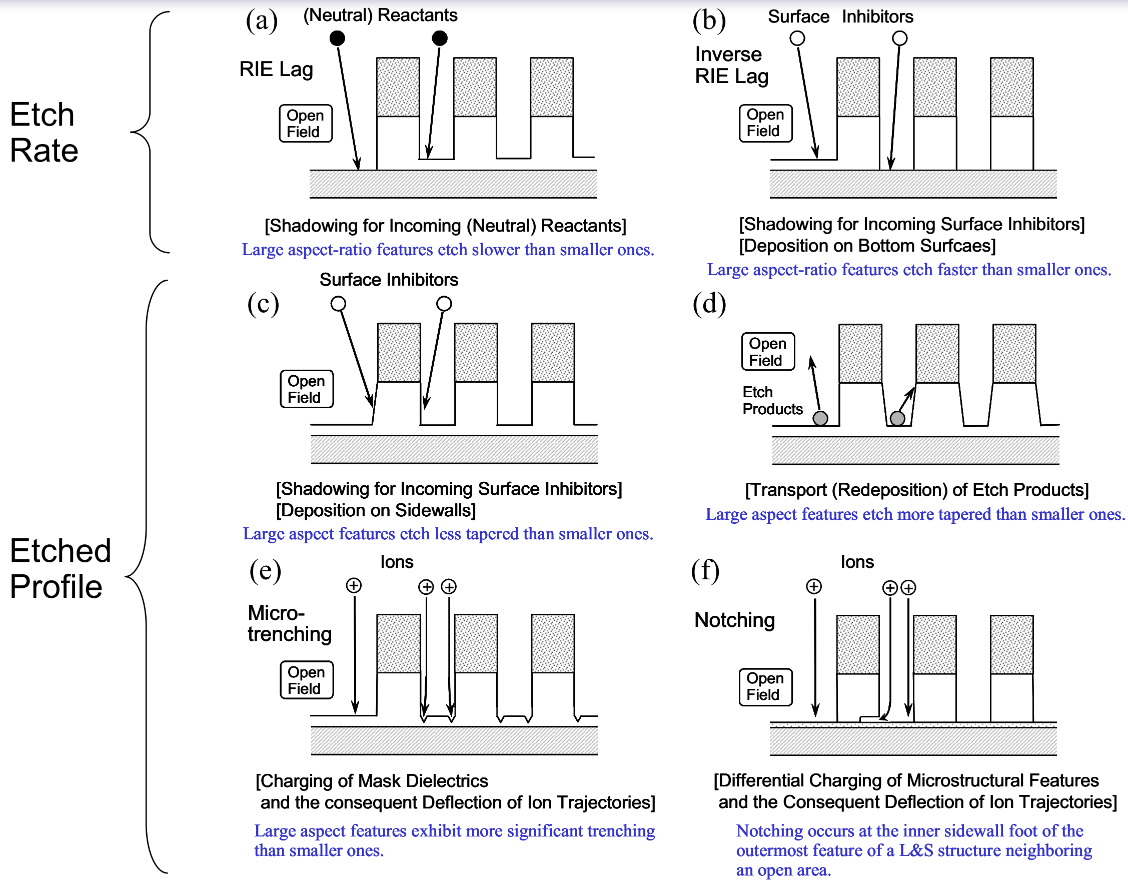
Selectivity over underlying films is required during overetch.



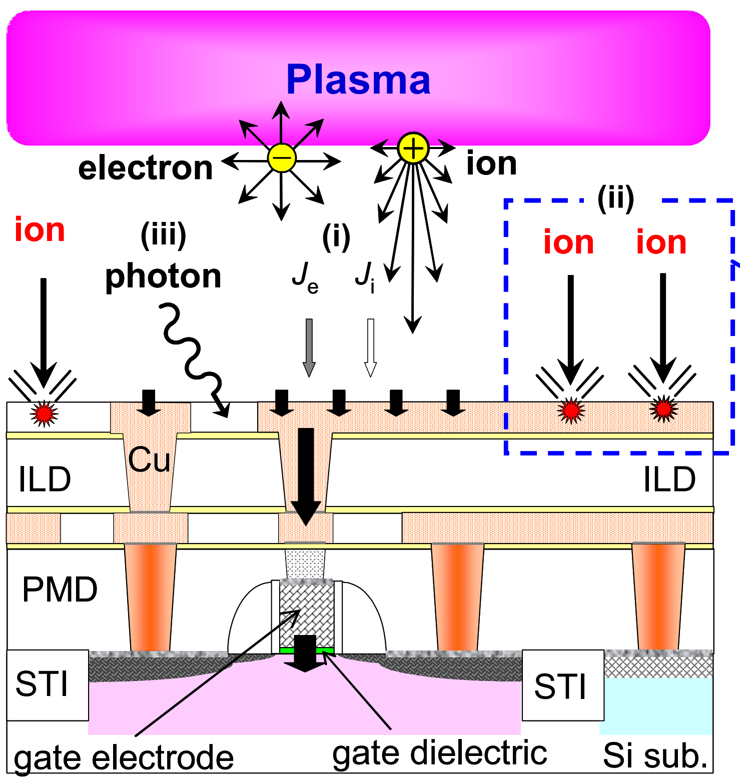


Selectivity over mask is required during main and overetch.

Microscopic Uniformity



Plasma Damage



(i) Charging Damage

"plasma current" : J_i , J_e
(~ mA/cm^2)

(ii) Physical Damage

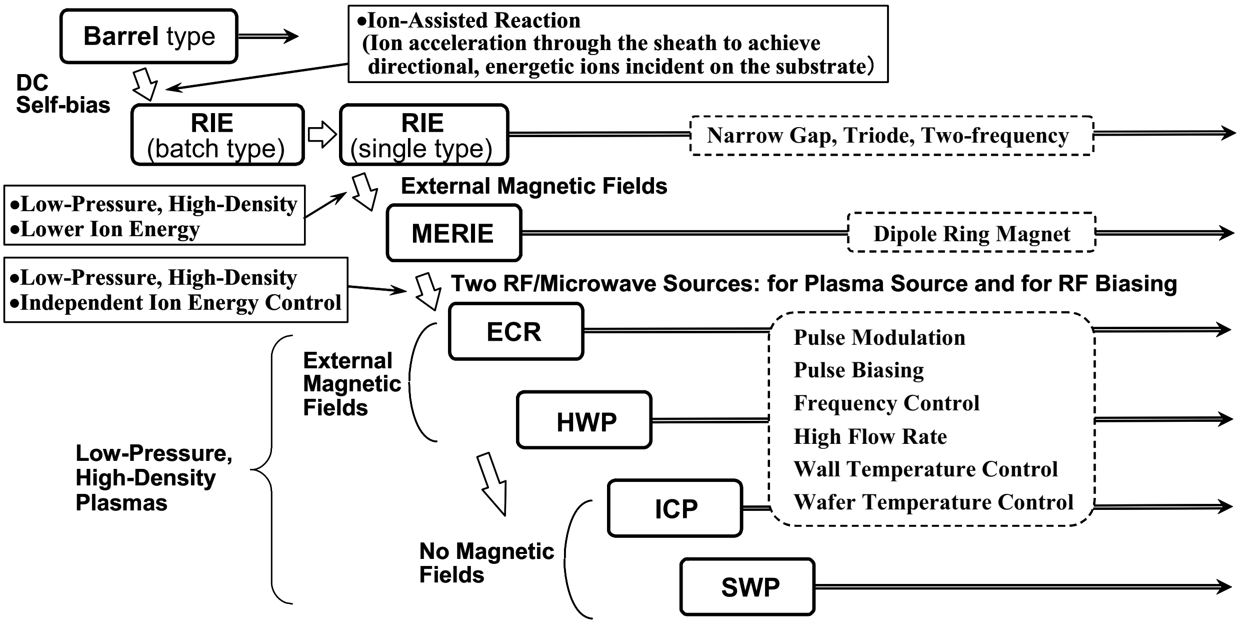
ion with high energy
(E_i ~ 100 eV)

(iii) Radiation Damage

high energy photon
($h\nu$ ~ 10 eV)

Plasma Etching Reactors

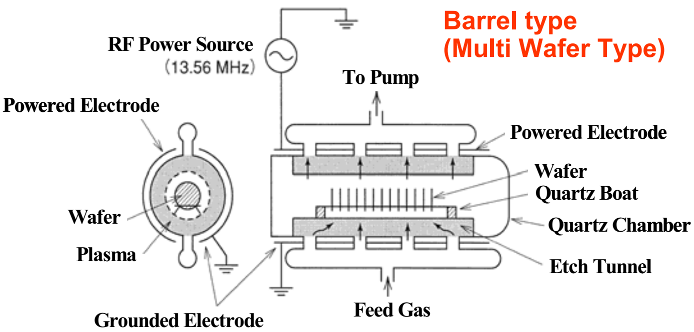
Year	1977	1980	1982	1985	1988	1991	1994	1996	1998	2001	2004	2007
Integration Level	16 K	64 K	256 K	1 M	4 M	16 M	64 M	256 M	1 G	(4 G)	(16G)	---
Feature Size	5 μm	3 μm	2 μm	1.3 μm	0.8 μm	0.5 μm	0.35 μm	0.25 μm	0.18 μm	0.13 μm	90 nm	65 nm
Wafer Diameter	4”	5”		6”		8”			8”/12”			



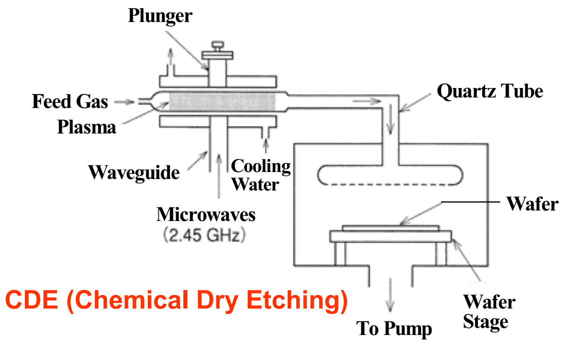
Plasma Sources (1)

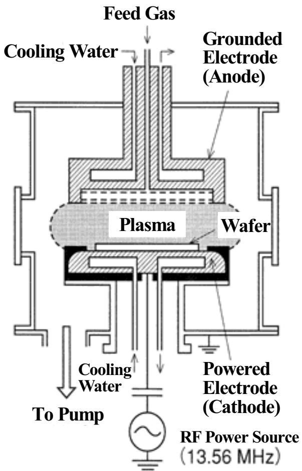
Low and Middle Density

CCP (Capacitively Coupled Plasma)



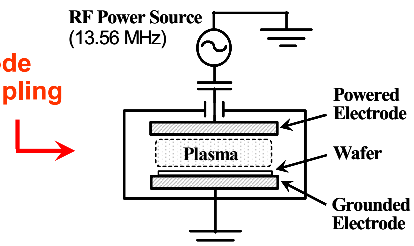
Downstream Plasma



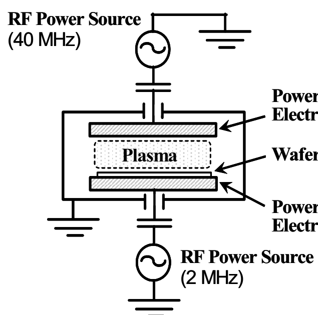


Cathode Coupling RIE (Reactive Ion etching)

Anode Coupling



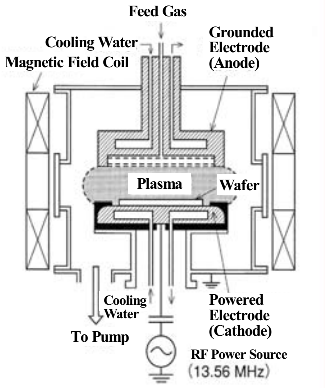
Two-Frequency CCP



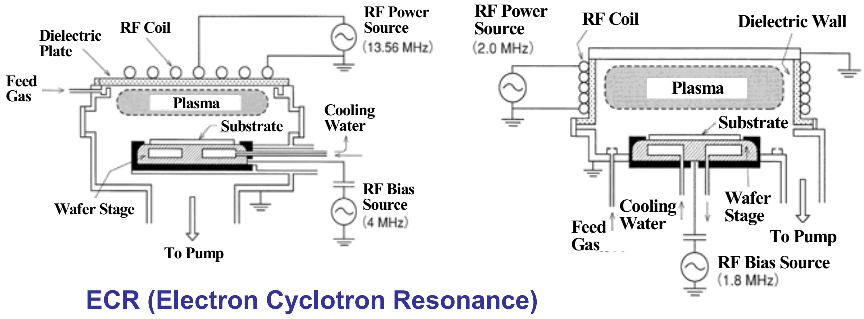
Plasma Sources (2)

Middle and High Density

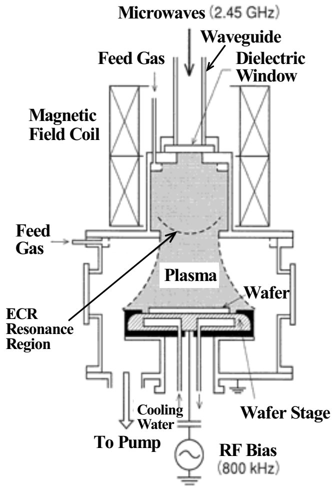
MERIE (Magnetically Enhanced RIE)



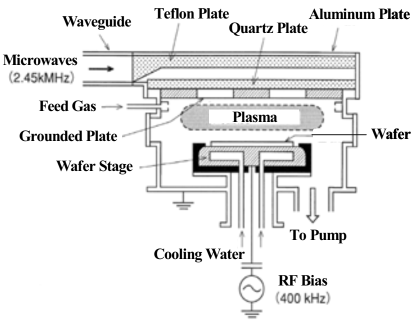
ICP (Inductively Coupled Plasma)



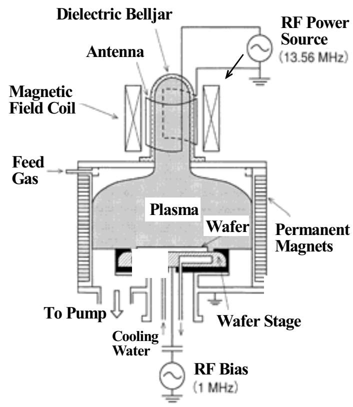
ECR (Electron Cyclotron Resonance)



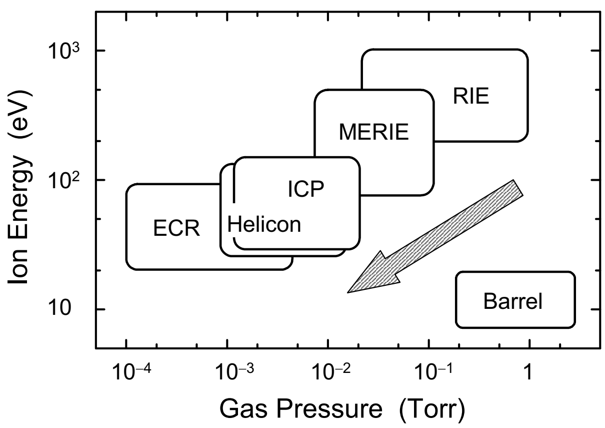
SWP (Surface Wave-excited Plasma)

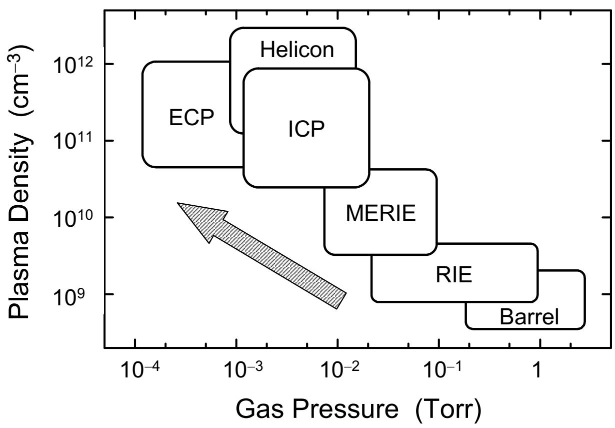


HWP (Helicon Wave-excited Plasma)



Trends of Plasma Etching Reactors





Plasma Properties

- Ion Transport through Collisionless Sheath
- Low Flux of Neutral Reactants
- High Flux of Ions
- Low Ion Incident Energy

Processing

- High Anisotropy
- Little Lateral Etching
- High Selectivity
- Low Damage

Reactive Gases for Plasma Etching

Materials	Reactant	Source Gas	Additive	Profile
Si	F	CF_4	O_2	Isotropic
		C_2F_6	O_2	
		SF_6	—	
		〃	O_2	
		NF_3	—	
		ClF_3	—	
	Cl	Cl_2	—	Anisotropic
		〃	O_2	
		〃	C_2F_6	
		〃	SF_6	
		〃	$SiCl_4$	
		CF_3Cl	—	
		CCl_4 *	O_2	
		$SiCl_4$	O_2	
	Br	HBr	—	
		〃	O_2	
SiO_2	F	CF_4	H_2	Anisotropic
		C_2F_6	H_2	
		C_4F_8	O_2	
		CHF_3	—	
		〃	O_2	
		〃	CO	
		〃	N_2O	
		NF_3	NH_3	Isotropic
		〃	H_2O	
Al	Cl	Cl_2	BCl_3	Anisotropic
		〃	CCl_4 *	
		〃	$CHCl_3$	
		〃	$SiCl_4$	
Resist	O	O_2	—	Isotropic
		〃	CF_4	
		〃	H_2O	

- Halogen-containing gases are primarily employed for plasma etching.
- N_2, O_2, and CH_4 gases are also employed in some cases; e.g., N_2/H_2 for organic low-*k* films, O_2/Cl_2 for Ru, and CH_4/H_2 for ITO.
- Rare gases such as He and Ar are often employed as diluent gases. (Kr and Xe are also employed in some cases.)

* Presently not used owing to toxicity problems.

Reactive Gases for Plasma Etching

(continued)

Bond Strength of Diatomic molecules

Molecule	Bond Strength +	Molecule	Bond Strength	Molecule	Bond Strength +
Si-Si	3.39	Al-Al	1.38	F-F	1.65
Si-Al	2.38	Al-S	3.87	F-Cl	2.66
Si-C	4.68	Al-N	3.08	F-Br	2.90
Si-S	6.46	Al-O	5.30	Cl-Cl	2.51
Si-O	8.29			Cl-Br	2.25
Si-N	4.87	Al-H	2.95	Br-Br	2.00
		Al-F	6.88	H-H	4.52
-Si-Si- *	2.3	Al-Cl	5.30	H-F	5.90
-Si-O- *	4.8	Al-Br	4.45	H-Cl	4.47
				H-Br	3.80
Si-F	5.73	S-S	4.41		
Si-Cl	4.21	S-F	3.55	O-O	5.17
Si-Br	3.81	S-H	3.57	O-H	4.43
Si-H	3.10	S-O	5.41	O-F	2.30
				O-Cl	2.79
C-C	6.29	Cu-Cu	1.83	O-Br	2.44
C-S	7.40	Cu-F	4.28	O-N	6.54
C-H	3.51	Cu-Cl	3.97		
C-F	5.72	Cu-Br	3.43	N-H	3.51
C-Cl	4.11			N-F	3.55
C-Br	2.90	Cu-H	2.88	N-Cl	3.46
C-O	11.16	Cu-O	2.79	N-Br	2.86
C-N	7.82	Cu-Si	2.29	N-N	9.80
W-O	6.96	Pt-Pt	3.70	Ru-C	6.39
W-F	5.68	Pt-C	6.20	Ru-H	2.43
W-Cl	4.38	Pt-H	3.47	Ru-F	4.17
W-Br	3.41	Pt-O	4.06	Ru-O	5.48
		Pt-Si	5.19	Ru-Si	4.11
Ti-O	6.97				
Ti-N	4.93	Ti-Cl	5.12	Ti-H	2.12
Ti-F	5.90	Ti-Br	4.55		

- Feed gases are preferred for etching to give reactive atoms which can break the bond of materials and form etch or reaction products.

From CRC Handbook of Physics and Chemistry

\+ Bond strength in eV

* Bond strength in Materials

Reactive Gases for Plasma Etching

(continued)

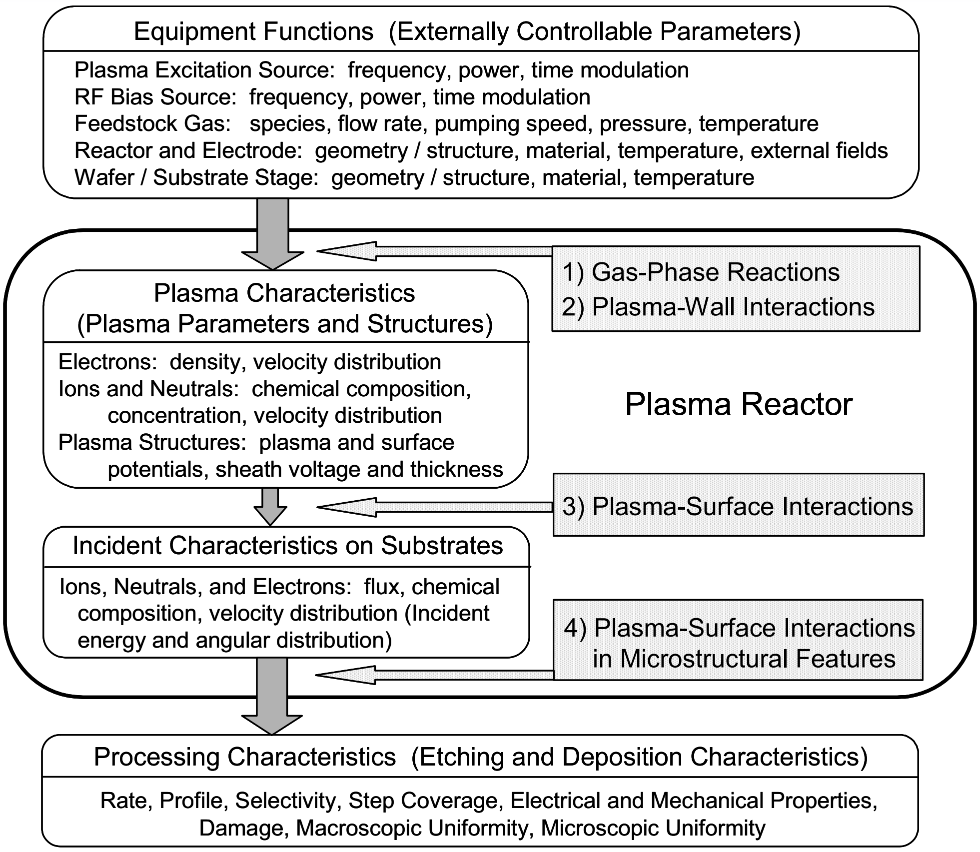
Boiling temperature of Materials (at a vapor pressure of 1 atm)

Material	Temp (℃)	Material	Temp (℃)	Material	Temp (℃)
$AlBr_3$	225	H_2	-252.8	$SiBr_3Cl$	127
$AlCl_3$	180	HBr	-66.3	$SiCl_3F$	12.2
AlF_3	1276	HCl	-85	SF_6	-63.8
BBr_3	91	HF	20	TiF_3	1400
BCl_3	12.6	HI	-35.5	$TiBr_4$	230
BF_3	- 101	H_2O	100	$TiCl_4$	136.4
Br_2	58.8	N_2	-195.7	TiI_4	377
CO	-191.5	N_2O	-88.4	WBr_5	333
CO_2	-78.4	NO	-151.7	WCl_6	346.7
C_3O_2	6.8	NO_2	21.1	WF_6	17
C_2N_2	-21.1	NCl_3	71	$ZrBr_4$	360
Cl_2	-34.0	NF_3	-128.7	$ZrCl_4$	331
ClF_3	11.7	PtF_6	69.1	ZrF_4	912
CuBr	1345	RuF_5	227	ZrI_4	431
CuCl	1400	RuO_4	40	CCl_4	76.8
$CuBr_2$	900	SiH_4	-111.9	CF_4	-128.0
CuF_2	1670	SiF_3Cl	-70.0	CHF_3	-82.1
$FeCl_2$	1023	SiH_2Cl_2	8.3	C_2F_6	-78.1
$FeCl_3$	316	$SiCl_2F_2$	-32	C_3F_8	-36.6
F_2	-188.1	$SiBr_4$	154	C_2F_4	-75.9
$GeBr_4$	186.3	$SiCl_4$	57.6	C_4F_8	-5.9
$GeCl_4$	86.5	SiF_4	-86	CH_4	-161.4
GeF_4	-36.5	SiI_4	287.3	C_2H_4	-103.7

- Feed gases are preferred for etching to give reaction or etch products having lower boiling temperatures (or higher vapor pressures).

From CRC Handbook of Physics and Chemistry

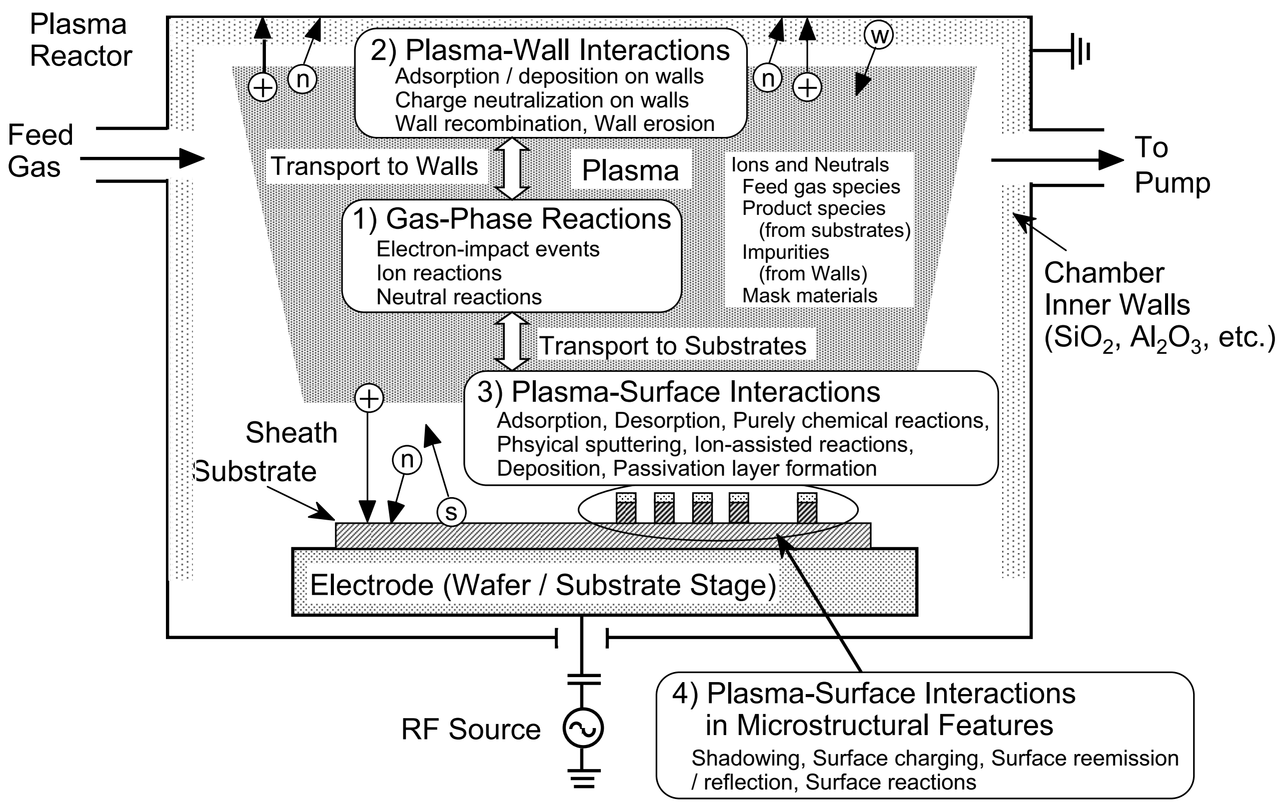
Process Control in Plasma Processing



3. Role of Plasma in Plasma Etching Technology

– Gas-phase Reactions
(to generate ions and neutrals)
– Ion Acceleration through the Sheath
(DC self-bias voltage)

Reaction Processes in Plasma Reactor



Gas-Phase Reactions

Cl/Cl2 Reaction Processes in Chlorine Plasmas

Reaction	Process	E_{th} (eV)	Cross section (cm^2)	Rate coefficient[a] (cm^3/s)
Electron-impact reactions:				
Molecular ionization	$e + Cl_2 \rightarrow Cl_2^+ + e + e$	11.48	σ_1	k_1
Dissociative ionization	$e + Cl_2 \rightarrow Cl^+ + Cl + e + e$	15.48	σ_2	k_2
Ion-pair formation	$e + Cl_2 \rightarrow Cl^+ + Cl^- + e$	11.87	σ_3	k_3
Dissociative attachment	$e + Cl_2 \rightarrow (Cl_2^-)^* \rightarrow Cl^- + Cl^*$	0	σ_4	k_4
Dissociative excitation	$e + Cl_2 \rightarrow (Cl_2)^* + e \rightarrow Cl + Cl^* + e$	3.12	σ_5	k_5
Atomic ionization	$e + Cl \rightarrow Cl^+ + e + e$	13.01	σ_6	k_6
	$e + Cl^+ \rightarrow Cl^{++} + e + e$	23.80	σ_7	k_7
Electron detachment	$e + Cl^- \rightarrow Cl + e + e$	3.62	–	$k_8 = 2.6\times10^{-8}\exp(-5.3/T_e)$
Dissociative recombination	$Cl_2^+ + e \rightarrow Cl + Cl^*$	0	–	$k_9 = 9.1\times10^{-7}/T_e^{0.6}$
Atomic recombination	$Cl^+ + e \rightarrow Cl^*$	0	–	$k_{10} = 3.2\times10^{-11}/T_e^{1/2}$
	$Cl^+ + e + e \rightarrow Cl^* + e$	−13.01	–	$k_{11} = 7.1\times10^{-7}/T_e^{9/2}$ cm^6/s
	$Cl + e \rightarrow Cl^-$	0	–	$k_{12} = 9.1\times10^{-12}/T_e^{1/2}$
	$Cl + e + e \rightarrow Cl^- + e$	−3.12	–	$k_{13} = 7.1\times10^{-7}/T_e^{9/2}$ cm^6/s
Ion reactions:				
Ion-ion recombination	$Cl_2^+ + Cl^- \rightarrow Cl_2 + Cl$	....		$k_{14} = 5.0\times10^{-8}$
	$Cl^+ + Cl^- \rightarrow Cl + Cl$	....		$k_{15} = 5.0\times10^{-8}$
Charge exchange	$Cl^+ + Cl_2 \rightarrow Cl + Cl_2^+$	....		$k_{16} = 5.4\times10^{-10}$
	$Cl^- + Cl_2 \rightarrow Cl + Cl^- + Cl$	....		$k_{17} = 1.0\times10^{-10}$
Neutral reactions:				
Volume recombination	$Cl + Cl + M(Cl_2) \rightarrow Cl_2 + M(Cl_2)$	....		$k_{18} = 2.8\times10^{-32}$ cm^6/s
Wall recombination	$Cl + Cl + wall \rightarrow Cl_2 + wall$	....		$\gamma_1 = 0.005$ for stainless steel **or $\gamma_1 = 0.007$ ***
Surface reaction	$Cl + wafer \rightarrow (0.25)SiCl_4 + wafer$	....		$\gamma_2 = 0.05$ for silicon

[a] In k_7-k_{13}, the electron temperature T_e is in eV. Coefficients γ_1 and γ_2 are reactive sticking probabilities.

Rate coefficients k_{13}-k_{17} are values at T=300 K.

*** For anodized aluminum $\gamma_1 = 0.1$ or 0.15**

* Total Ionization Cross Section: $Q_i = \sigma_1 + \sigma_2 + \sigma_3$

$\sigma_1 = Q_i - (\sigma_2 + \sigma_3)$

$\sigma_2 = Q_i (E_e - 4.0)/4$

Total Cross section for Negative Ion Formation: $Q_a = \sigma_3 + \sigma_4$

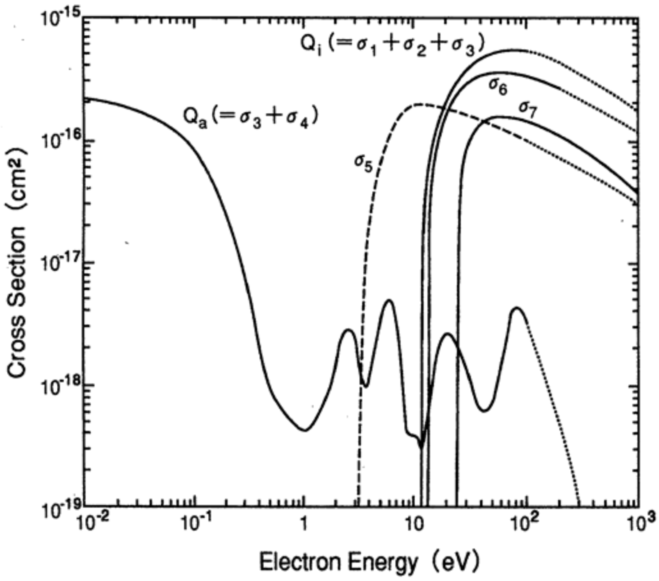
$\sigma_3 = Q_a$ for $E_e > 11.87$ eV

$\sigma_4 = Q_a$ for $E_e < 11.87$ eV

Gas-Phase Reactions *(continued)*

Electron-Impact Reactions for Cl/Cl2

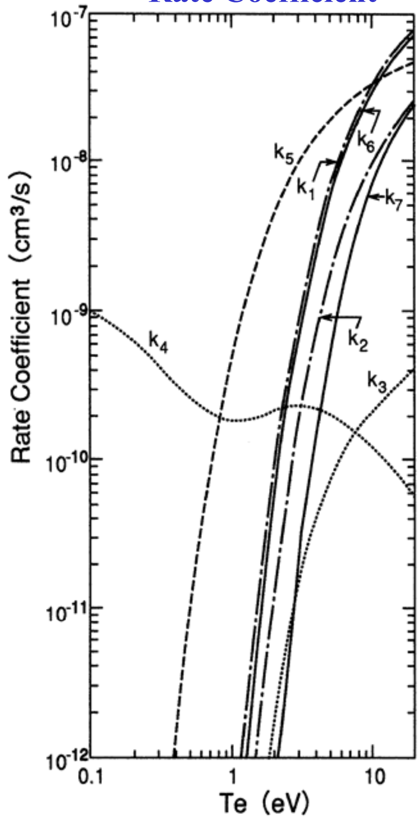
Collision Cross Section



$$k = \langle \sigma v_e \rangle_e = \int d\mathbf{v}_e f_e(\mathbf{v}_e)\sigma(v_e)v_e$$

$$= \langle \sigma \varepsilon_e \rangle_e = \int d\varepsilon_e f_e(\varepsilon_e)\sigma(\varepsilon_e)\sqrt{\varepsilon_e}$$

Rate Coefficient

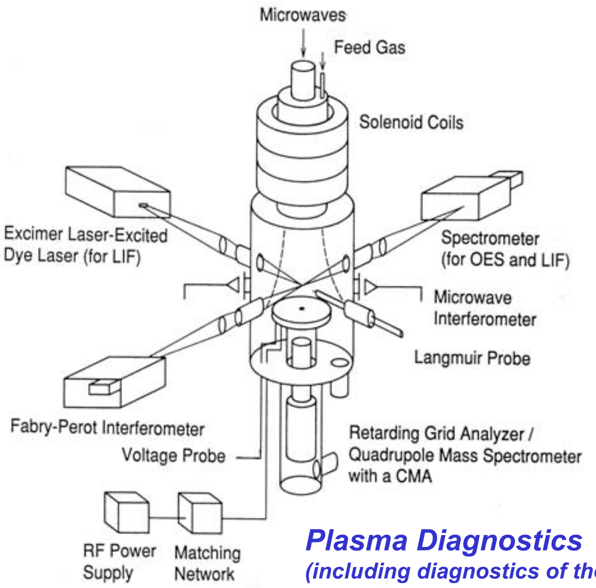


Reactants and Products

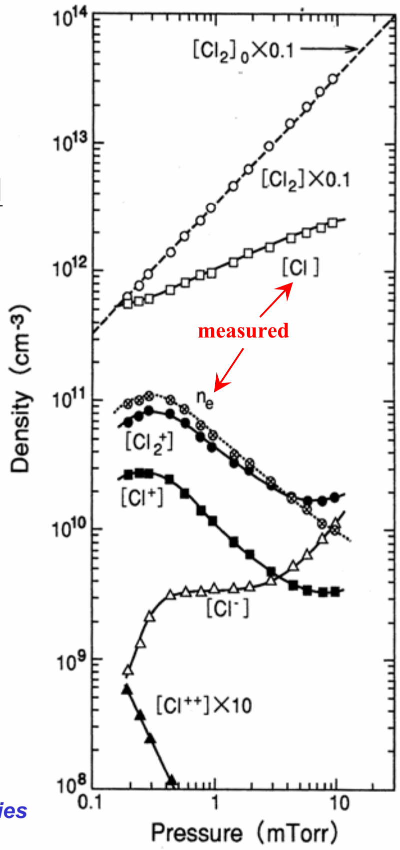
Reactants

***0-dimensional Calculation* – Cl2 Plasma –**

$$\frac{d[\mathrm{Cl}]}{dt} = (k_2 + k_4 + 2k_5)\, n_e n_g - k_6 n_e [\mathrm{Cl}]$$
$$+ (k_8[\mathrm{Cl}^-] + k_9[\mathrm{Cl}_2{}^+] + k_{10}[\mathrm{Cl}^+] + k_{11} n_e [\mathrm{Cl}^+]) n_e - (k_{12} + k_{13} n_e) n_e [\mathrm{Cl}]$$
$$+ (k_{14}[\mathrm{Cl}_2{}^+] + 2k_{15}[\mathrm{Cl}^+])[\mathrm{Cl}^-] + (k_{16}[\mathrm{Cl}^+] + 2k_{17}[\mathrm{Cl}^-]) n_g - \frac{[\mathrm{Cl}]}{\tau_n} - \frac{[\mathrm{Cl}]}{\tau_r}$$



Plasma Diagnostics
(including diagnostics of the fluxes and energies of ions and neutrals incident on the surface).



Reactants and Products *(continued)*

Flux of Ions and Neutrals Incident on Substrate Surfaces

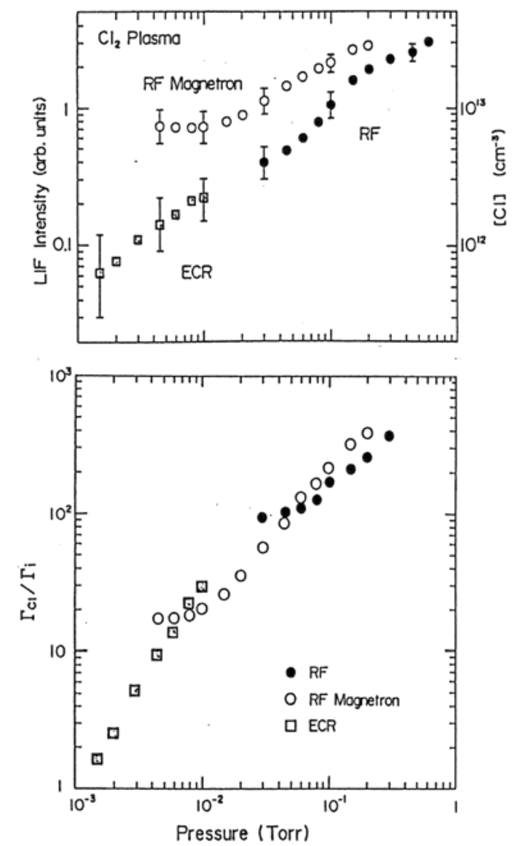
Neutral Flux :

$$\Gamma_n \approx (n_n/4)\,(8kT_n/\pi m_n)^{1/2}$$

Ion Flux :

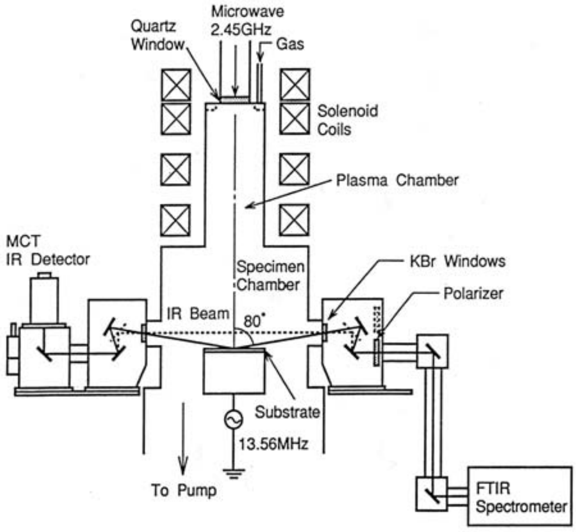
$$\Gamma_i \approx 0.6 n_i\,(kT_e/m_i)1/2$$

- **The neutral-to-ion flux ratio Γ_{Cl}/Γ_i is of the order of 10 at 10 mTorr, decrease wit decreasing pressure.**
- **The neutral-to-ion flux ratio Γ_{Cl2}/Γ_i is about one order of magnitude higher than Γ_{Cl}/Γ_i.**



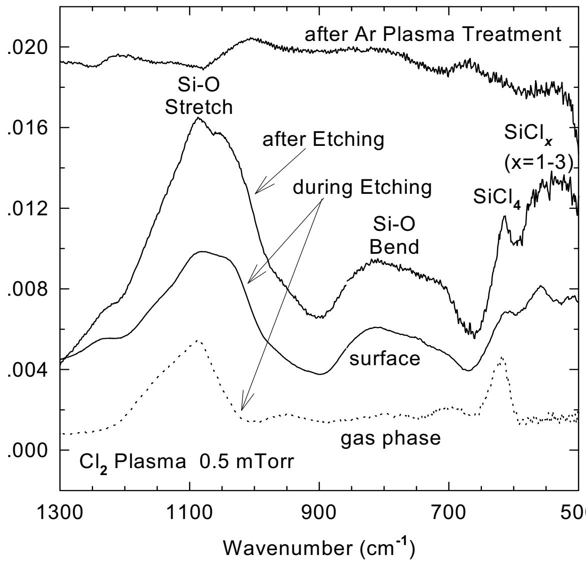
Reactants and Products *(continued)*

Reaction Products (or Etch Products)



Plasma and Surface Diagnostics
(by using FTIR absorption spectroscopy)

Si etching in Cl2 plasma



- **Silicon tetrachloride $SiCl_4$ was the only IR-absorbing etch product species detected in the gas phase, while unsaturated $SiCl_x$ (x=1–3) as well as $SiCl_4$ were observed on the surface.**
- **$[SiCl_4] \sim 1\times10^{13}$ cm^{-3} $\sim [Cl_2]$ in the gas phase.**
- **A broad absorption feature due to Si–O vibrations or silicon oxides was found to occur both in the gas phase and on the surface, where oxygen came from the dielectric windows and chamber walls.**

Reactants and Products *(continued)*

Electron-Impact Reactions and Neutral reactions for Product Species

Electron-Impact Reactions

$$e^- + SiCl_4 \rightarrow Cl^- + SiCl_3 \qquad [k_1]$$
$$e^- + SiCl_4 \rightarrow Cl^- + SiCl_2 + Cl \qquad [k_2]$$
$$e^- + SiCl_4 \rightarrow Cl^- + SiCl + Cl_2 \qquad [k_3]$$
$$e^- + SiCl_4 \rightarrow Cl_2^- + SiCl_2 \qquad [k_4]$$
$$e^- + SiCl_4 \rightarrow Cl_2^- + SiCl + Cl \qquad [k_5]$$

At E_e<10 eV, $k_1 \sim 10^{-7}$, $k_2 \sim 10^{-7}$, $k_3 \sim 10^{-9}$, $k_4 \sim 10^{-9}$, and $k_5 \sim 10^{-10}$ cm^3/s

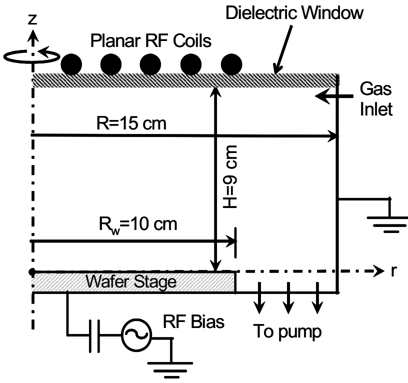
Neutral Reactions

$$SiCl + O_2 \rightarrow SiO + ClO \qquad [k_6]$$
$$SiCl_2 + O_2 \rightarrow SiO + ClO + Cl \qquad [k_7]$$
$$SiCl_3 + O_2 \rightarrow SiO + ClO + Cl_2 \qquad [k_8]$$
$$SiCl_4 + O_2 \rightarrow SiO + ClO + Cl_2 + Cl \qquad [k_9]$$

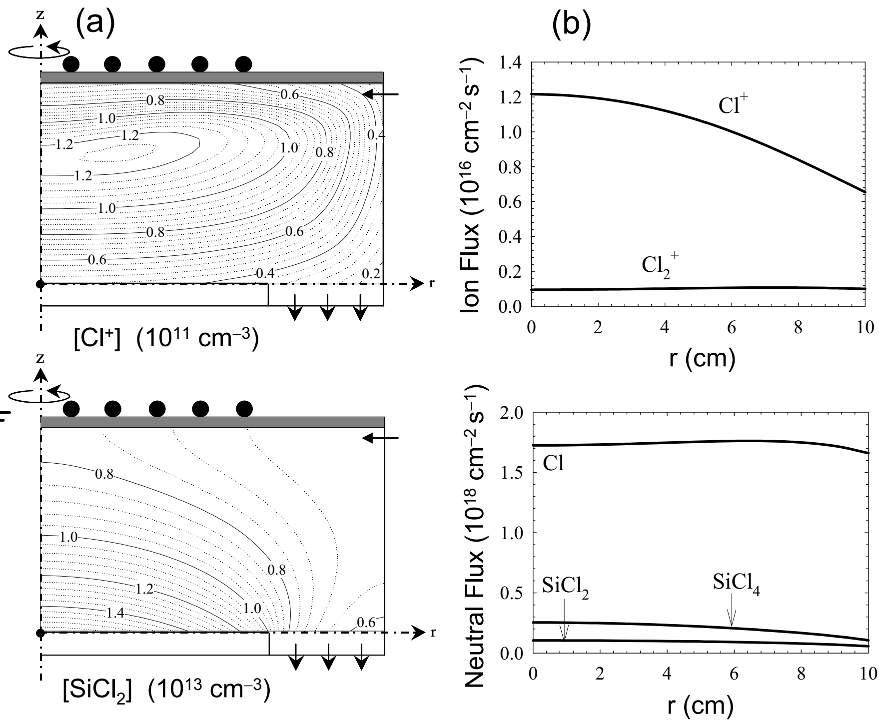
At T~300 K, $k_6 \sim 10^{-12}$, $k_7 \sim 10^{-15}$, $k_8 \sim 10^{-12}$, and $k_9 \sim 10^{-17}$ cm3/s

Reactants and Products *(continued)*

Si etching in Cl_2 Plasma



Two-dimensional Fluid Simulation
– Cl_2 Plasma (10 mTorr) –



Reactive Species in Real Etching Environments

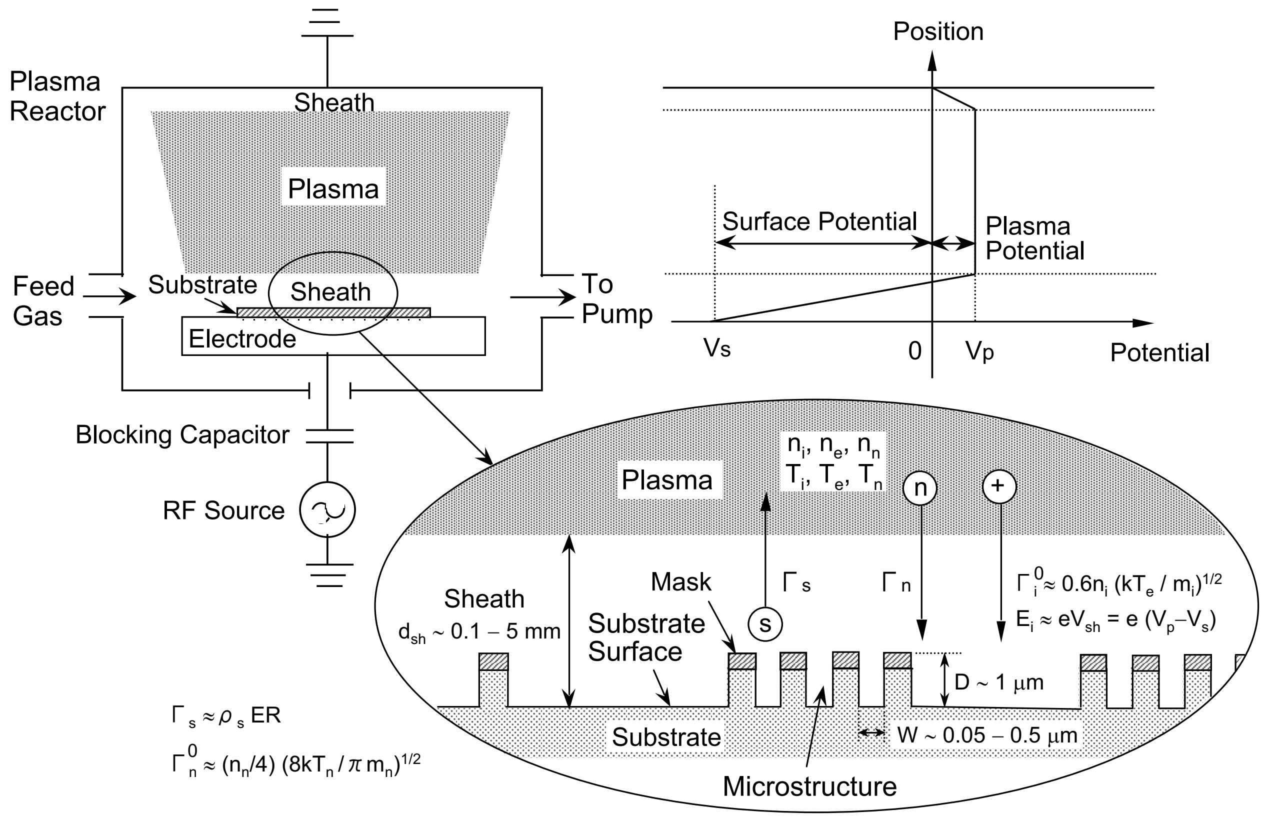
During Si etching in Cl_2 plasmas [a)]

Role in Surface Reactions \ Source		Feed Gas	Reaction Product	Impurity from Walls and Windows	Mask Material
Neutral Reactant		Cl_2, Cl			
Ion		Cl_2^+, Cl^+		O_2^+, O^+	
Surface Inhibitors	Depositing Species		$SiCl_x$, SiO_xCl_y [b)]		C_xH_y [c)]
	Reactive species			O_2, O	

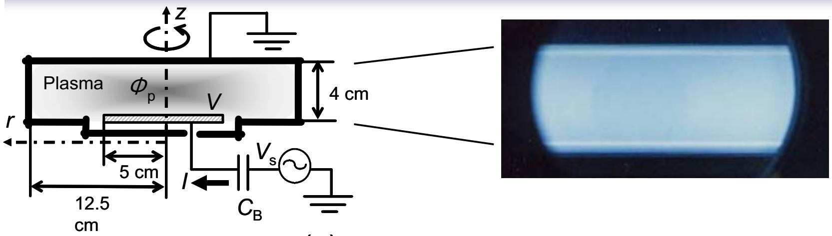
a) The situation is similar to Si etching in Cl_2/O_2 plasmas.
b) Silicon oxides SiO_x would also occur.
c) In case of photoresist mask.
In case of hard mask (or SiO2 mask), Si and/or O would occur.

- **In real etching environments, reactive species responsible for etching surface reactions come not only from feed gases but also reaction products, impurities from walls and/or windows, and mask materials.**

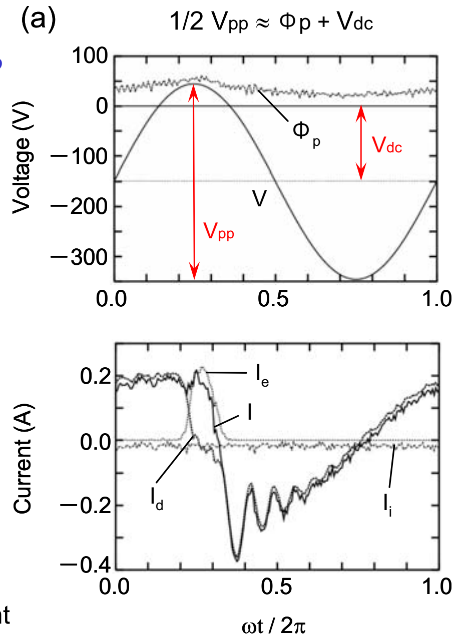
Plasma Reactor

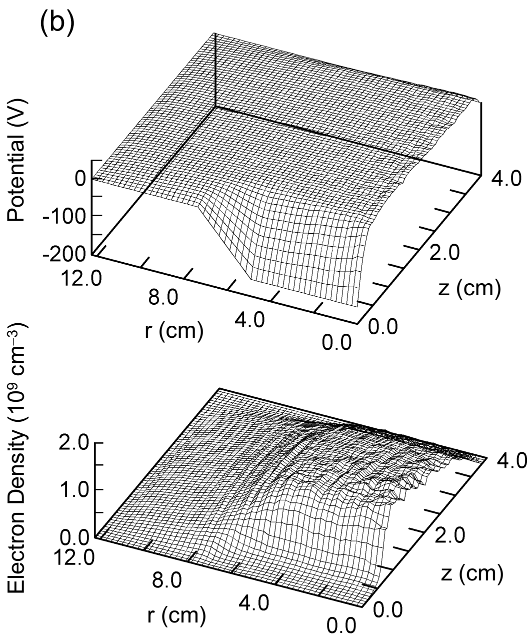


DC Self-bias Voltage



Two-dimensional Particle-in-cell/Monte Carlo (PIC/MC) Simulation
– Ar Plasma (200 mTorr) –

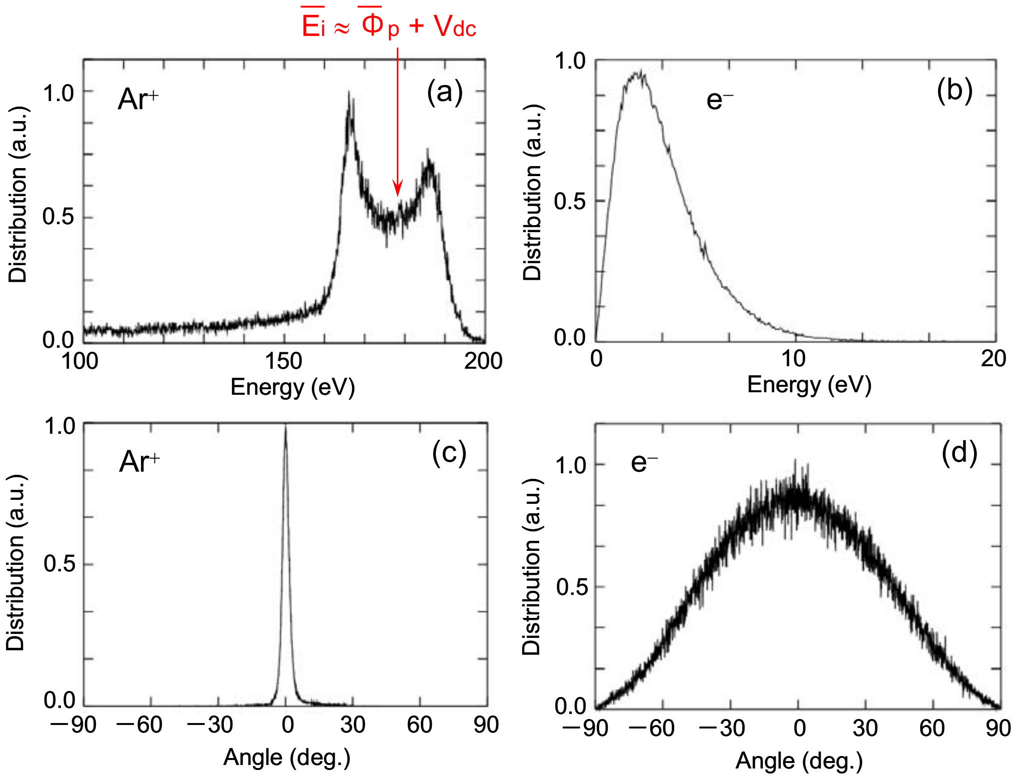




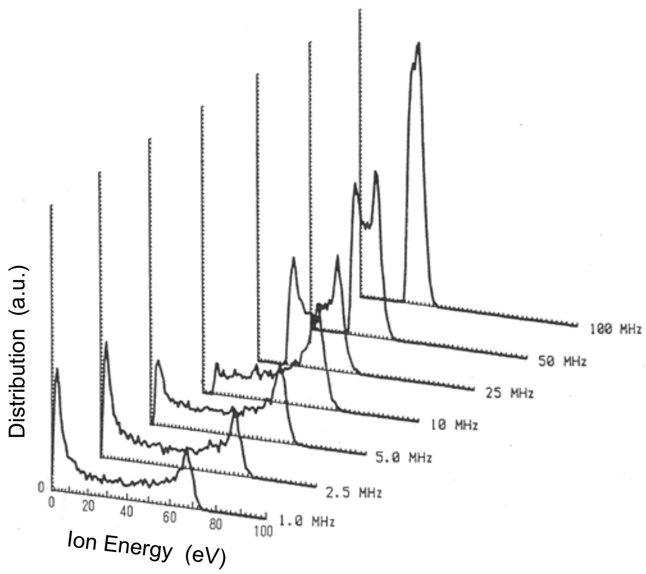
Total current :
$I = I_i + I_e + I_d$

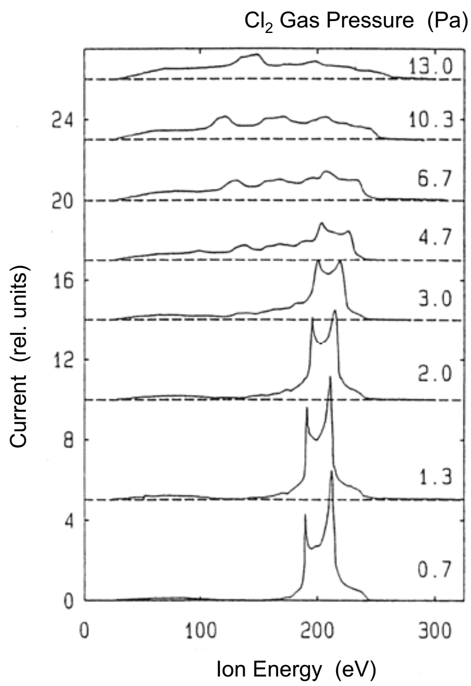
I_i : Ion current
I_e : Electron current[
I_d : Displacement current

Incident Ions and Electrons



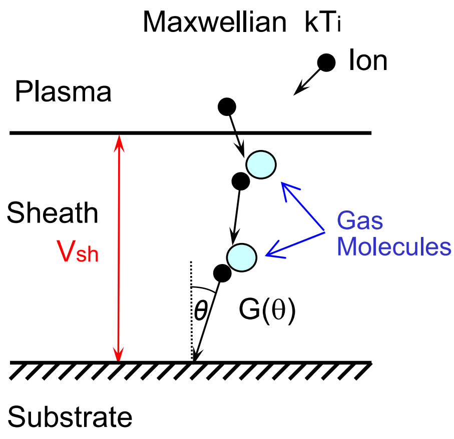
Energy Distribution of Incident Ions



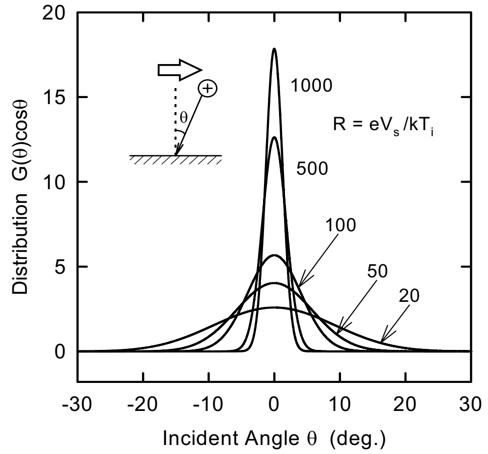


*** Incident ion energy (or IEDF) depends on rf frequency, voltage, sheath width, ion mass, and pressure.**

Angular Distribution of Incident Ions



Incident Angle Distribution G(q) of Ion Fluxes
In Collisionless Sheath



Low-Pressure, High-Density Plasmas
(Typically, $kT_i \sim 0.5$ eV, $V_{sh} \sim 50$ V)

$R = eV_{sh}/kT_i \sim 100$

- **Incident angular distribution of ion fluxes (or IADF) depends on sheath voltage, sheath width, ion mass, and pressure.**

4. Surface Reaction Processes in Plasma Etching

(Plasma-Surface Interactions)

- Surface Reactions
- Transport of Ions and Neutrals in Microstructural Features
- Feature Profile Evolution
- Microscopic Uniformity
- Surface Charging

Etching Surface Reactions

- **Etching occurs through surface reactions with ions and neutrals incident on surfaces from the plasma, where the positive ions are incident on surfaces after been accelerated through the sheath, while the neutrals are incident isotropically on surfaces.**

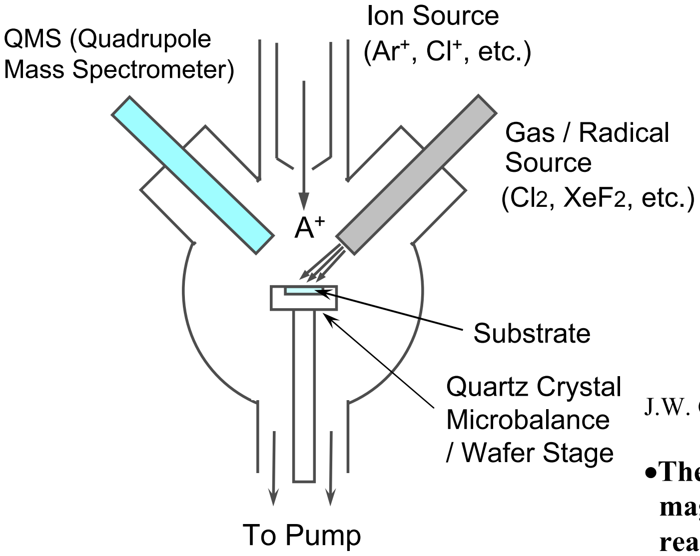
  (High-energy electrons are also incident on surfaces after being decelerated through the sheath, playing an important role in differential charging of feature surfaces.)

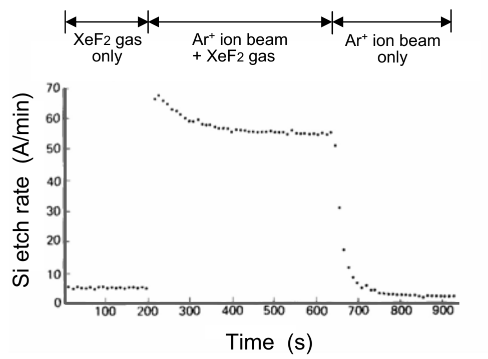
- **Etching characteristics achieved depends primarily on the chemical constituent of ions and neutrals incident on surfaces, flux and energy and angular distributions of incident ions and neutrals, and surface temperature.**

- **Moreover, the etching of patterned features (or the feature profile evolution during etching) are determined also by the transport of ions and neutrals in microstructural features, because the etching reactions occur in feature surfaces in microstructures**

Study of Etching Surface Reactions

- **Surface reactions responsible for etching have been investigated by using : Beam experiments (including surface diagnostics)**
  Plasma experiments (including plasma and surface diagnostics, plasma simulation*)   *Particle model and Fluid model
  Process simulation (semi-empirical profile simulation, molecular dynamics (MD) simulation)

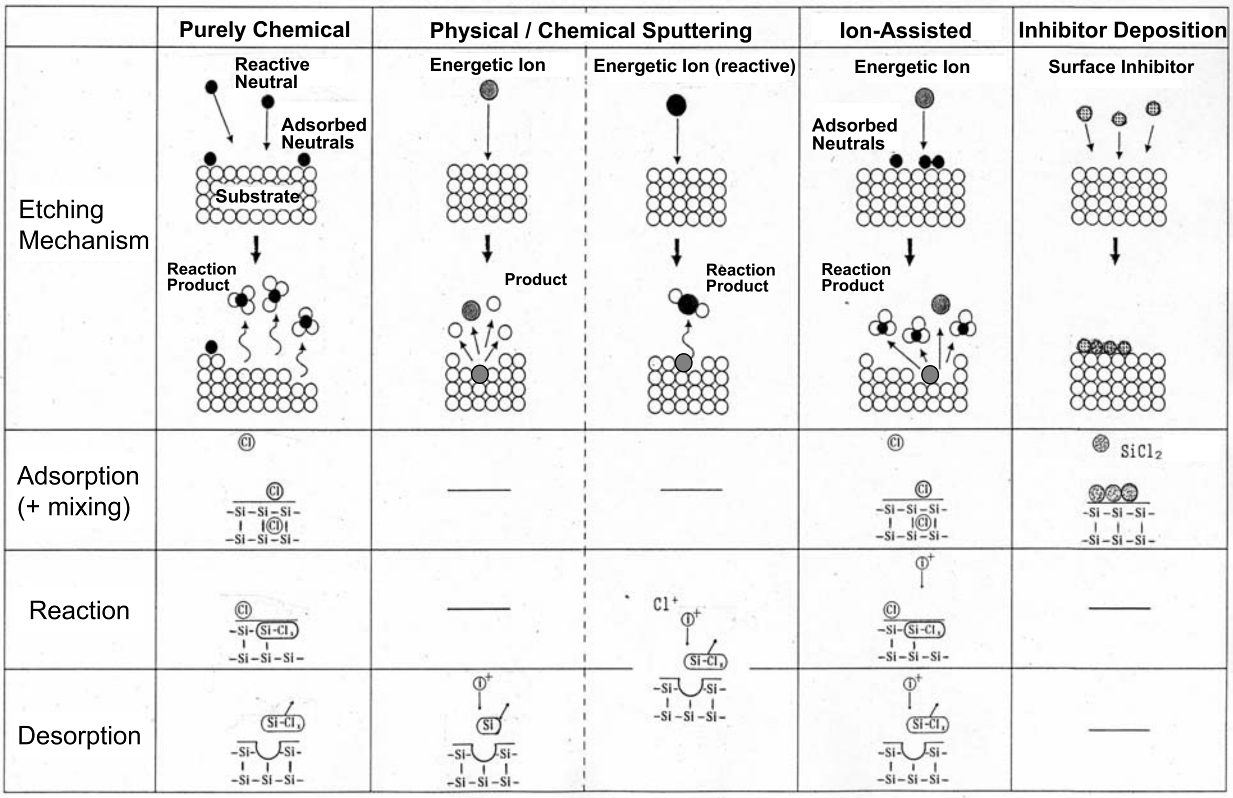




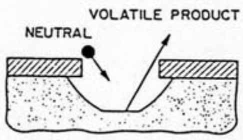
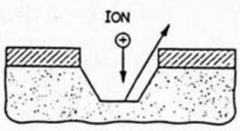
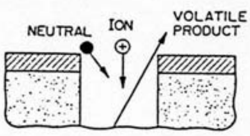
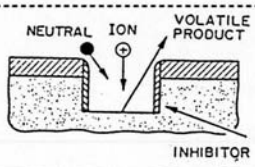
J.W. Coburn and H.F. Winters, J. Appl. Phys. **50**, 3189 (1979).

- **The etch rate is enhanced by about an order of magnitude by simultaneous exposure of ions and reactive neutrals.**

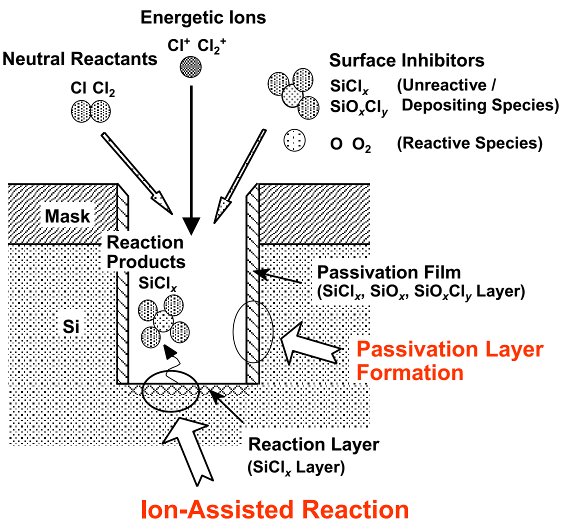
Etching Mechanisms



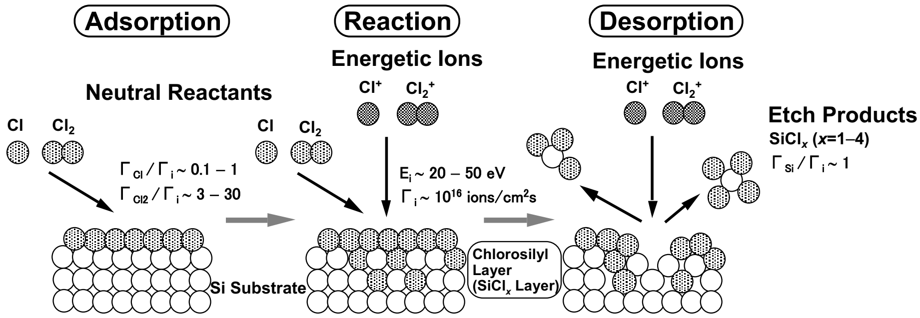
Etching Mechanism vs. Characteristics

Etching Mechanism		Aniso-tropy	Selec-tivity	Dam-age	Rate
	Chemical $F+Si \rightarrow SiF_4\uparrow$	×	○	○	○
	Sputtering $A^+ + Si \rightarrow Si\uparrow$ $(A^+ + Si \rightarrow ASi\uparrow)$	○	×	×	×
	Ion-Assisted $Cl+Si \rightarrow SiCl_x$ $B^+ + SiCl_x \rightarrow SiCl_4\uparrow$	△	△	△	△
	(Ion-Assisted) Inhibitor Deposition	↑	↑		↓

Mechanism for Anisotropic Etching



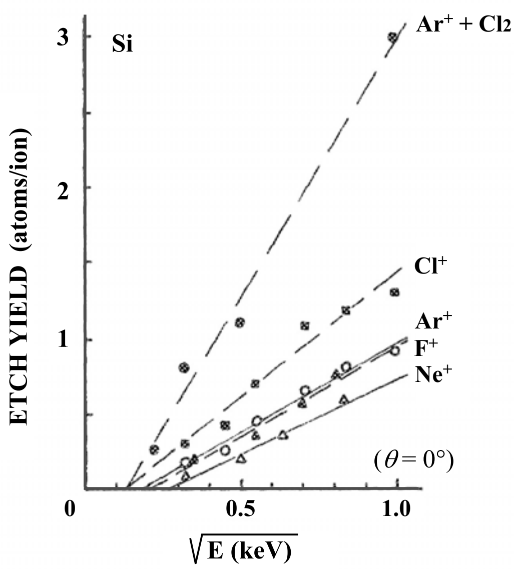
- The etch anisotropy relies primarily on the ion-assisted reaction at the bottom of the feature and the passivation layer formation on feature sidewalls.
- There are two mechanisms for the formation of passivation layers on feature surfaces:
  - (i) Inhibitor deposition.
  - (ii) Inhibitor adsorption or surface oxidation.
- There are two mechanisms for ion-assisted (or ion-enhanced) reaction:
  - (i) Chemical sputtering (or Physically enhanced chemical sputtering), where energetic ions enhance the step of Reaction.
  - (ii) Chemically enhanced physical sputtering (or Physical sputtering), where energetic ions enhance the step of Desorption



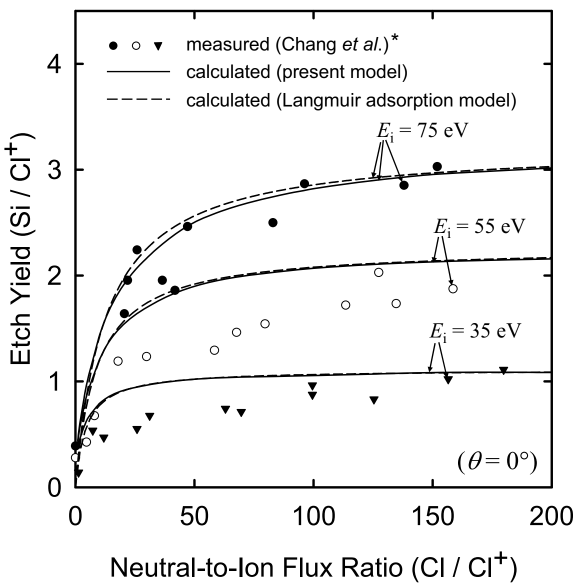
Ion-Assisted Reaction

Beam Experiments

Etch Yield $Y(E_i, \theta)$ vs. Incident Ion Energy E_i



Ch. Steinbrucel, Appl. Phys. Lett. **55**, 1960 (1989).



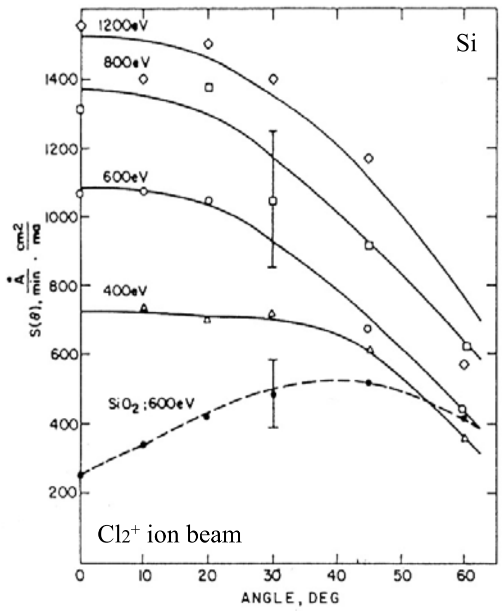
* J.P. Chang and H.H. Sawin, J. Vac. Sci. Technol. A **15**, 610 (1977).

- The etch yield depends on ion energy as $Y(E_i)=A(E_i^{1/2}-E_{th}^{1/2})$ at $E_i < 1$ keV, where A is a constant, in physical sputtering as well as ion-assisted etching reaction.
- In ion-assisted etching, the etch yield depends also on neutral-to-ion flux ratio.

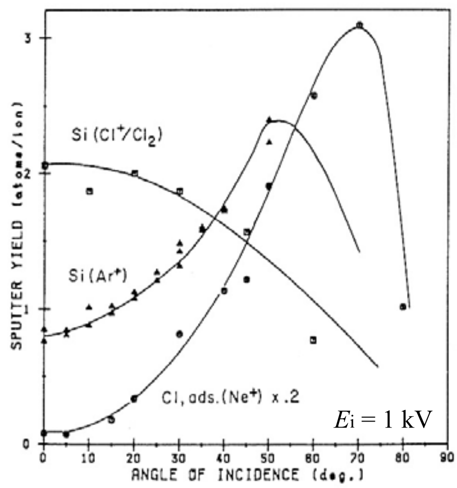
Ion-Assisted Reaction

(continued)

Beam Experiments **Etch Yield $Y(E_i, \theta)$ vs. Ion Incidence Angle θ**



T.M. Mayer, R.A. Baker, and L.J. Whitman, J. Vac, Sci. Technol. **18**, 349 (1981).



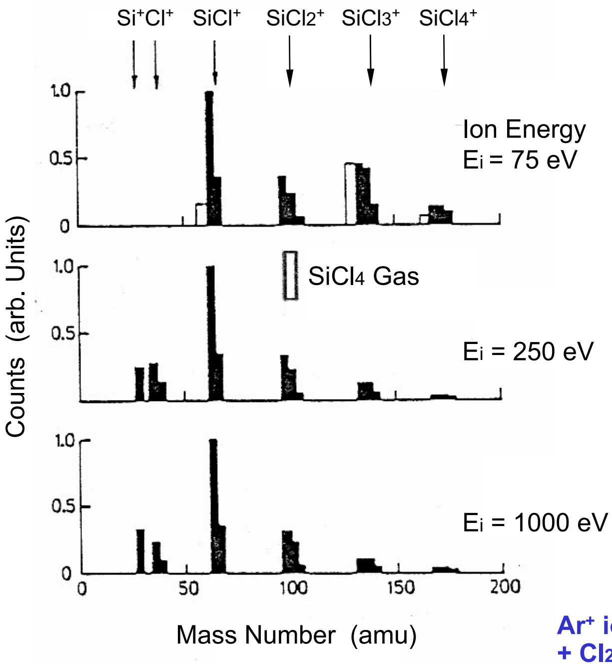
T. Mizutani *et al*., Nucl. Instrum. Methods, **B7/8**, 825 (1985).

- **The etch yield peaks at normal incidence ($\theta = 0°$) in ion-assisted etching reaction, while it peaks at around $\theta \approx 65°$ in physical sputtering.**

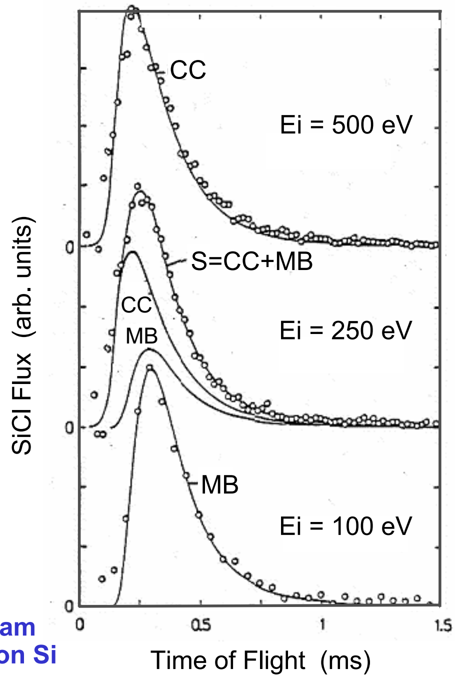
Ion-Assisted Reaction

(continued)

Beam Experiments **Reaction Products**



Ar^+ ion beam + Cl_2 gas on Si



D.J. Oosatra et al., J. Apl. Phys. **63**, 315 (1988)

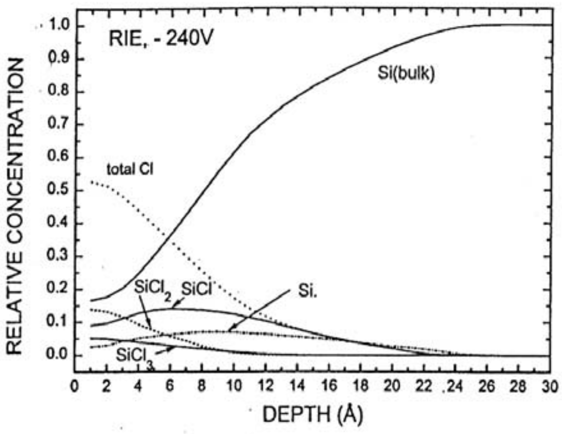
*MB: Maxwell-Boltzmann *CC: Collision Cascade

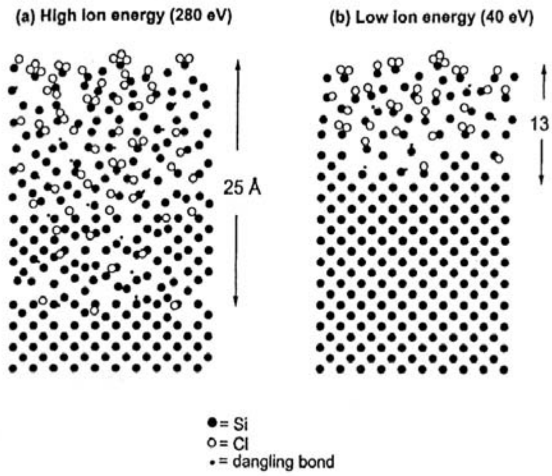
- **The amount of lower chlorinated $SiCl_x$ species increases with increasing ion energy.**
- **The velocity distribution of etch product species desorbed from surfaces changes from MB to CC, as the ion energy is increased.**

Ion-Assisted Reaction *(continued)*

Si etching in Cl_2 plasmas

Surface Reaction Layer (Chlorinated Surface Layer ($SiCl_x$ Layer)



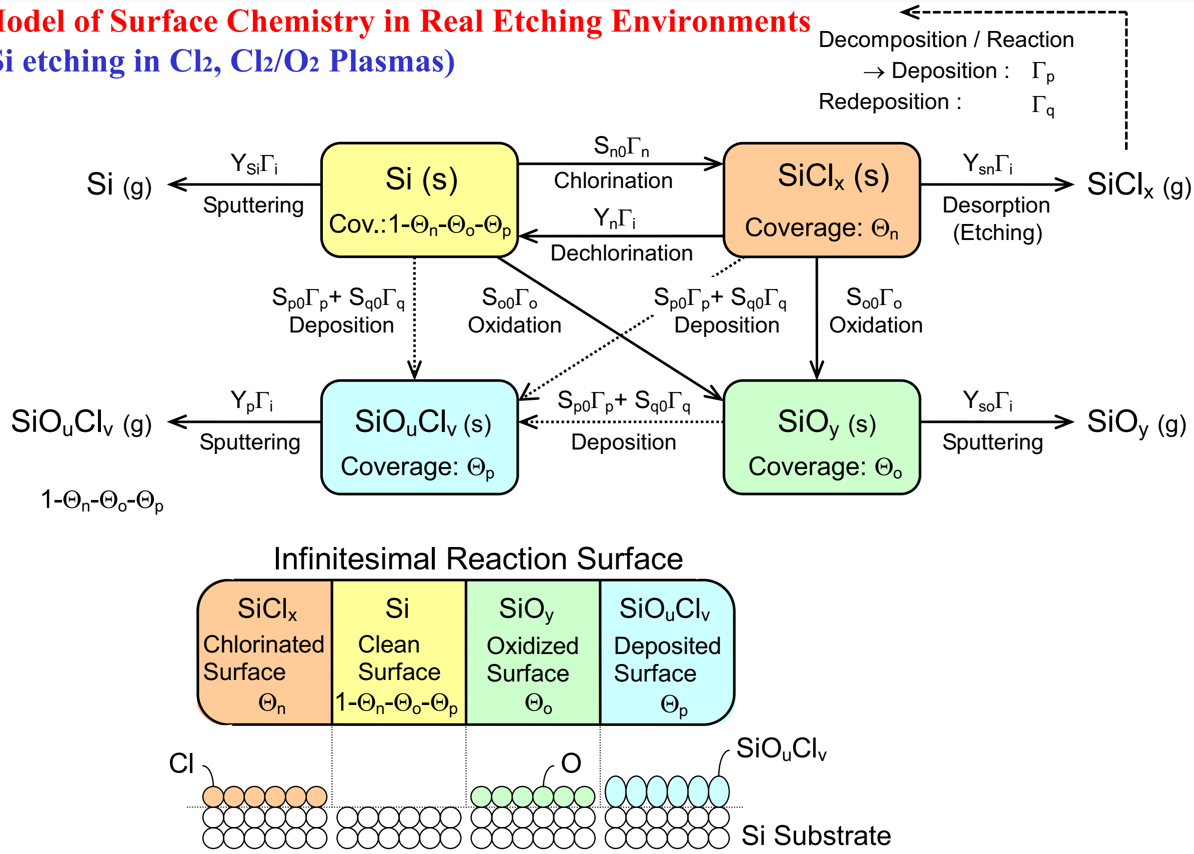


N. Layadi, V.M. Donnelly, and J.T.C. Lee, J. Appl. Phys. **81**, 6738 (1977).

- **The chlorinated surface layer consists of $SiCl_x$ (x=1-3)**
- **The thickness of $SiCl_x$ layer increases with increasing ion incident energy.**

Surface Reaction Processes

Model of Surface Chemistry in Real Etching Environments
(Si etching in Cl_2, Cl_2/O_2 Plasmas)



Surface Reaction Processes *(continued)*

Langmuir Adsorption Kinetics Model (monolayer adsorption)

Temporal Change of the Coverage of Infinitesimal Reaction Surfaces :

$$
\begin{cases}
\sigma_s \dfrac{\partial \Theta_n}{\partial t} = S_{n0}\Gamma_n\left(1-\Theta_n-\Theta_o-\Theta_p\right) - (xY_{sn}+Y_n)\Gamma_i\Theta_n - S_{o0}\Gamma_o\Theta_n - \left(S_{p0}\Gamma_p+S_{q0}\Gamma_q\right)\Theta_n \\[2ex]
\sigma_s \dfrac{\partial \Theta_o}{\partial t} = S_{o0}\Gamma_o\left(1-\Theta_o-\Theta_p\right) - Y_{so}\Gamma_i\Theta_o - \left(S_{p0}\Gamma_p+S_{q0}\Gamma_q\right)\Theta_o \\[2ex]
\sigma_s \dfrac{\partial \Theta_p}{\partial t} = \left(S_{p0}\Gamma_p+S_{q0}\Gamma_q\right)\left(1-\Theta_p\right) - Y_p\Gamma_i\Theta_p
\end{cases}
$$

Etch and Deposition Rates :

$$
\begin{cases}
ER = \dfrac{1}{\rho_s}\Gamma_i\left[Y_{sn}\Theta_n + Y_{so}\Theta_o + Y_s\left(1-\Theta_n-\Theta_o-\Theta_p\right)\right] \\[2ex]
DR = \dfrac{1}{\rho_p}\left[\left(S_{p0}\Gamma_p+S_{q0}\Gamma_q\right) - Y_p\Gamma_i\Theta_p\right]
\end{cases}
$$

Infinitesimal Reaction Surfaces :

Chlorinated $SiCl_x$ Surface	Θ_n
Oxidized SiO_y Surface	Θ_o
Deposited SiO_uCl_v Surface	Θ_p
Clean Si Surface	$1-\Theta_n-\Theta_o-\Theta_p$

Surface Coverage : $0 \le \Theta_n,\ \Theta_o,\ \Theta_p \le 1$

Interface Evolution Rate :

$$
\left\{\; v = ER - DR \right.
$$

Surface Reaction Processes *(continued)*

Parameters for Surface Reaction Processes (Si etching in Cl_2, Cl_2/O_2 Plasmas)

- Ion-Enhanced Etch Yield of Si : $Y_{sn} = 0.4$ ($E_i = 50$ eV, maximum at $\theta \approx 0°$)
  from a Cl^+/Cl_2^+ ion beam study [M. Balooch *et al*, JVST A**14**, 229 (1996)].

- Total Removal Yield of Cl Adsorbed : $(xY_{sn} + Y_n) = 3$ ($E_i = 50$ eV, maximum at $\theta \approx 0°$)
  determined by comparing an ion-neutral synergy model with aspect-ratio dependence data on etch rate obtained in ECR Ar/Cl_2 plasmas [A.D. Bailey III *et al*, JVST B**13**, 2133 (1995)].

- Sputter Yields of Si and SiO_y : Y_s ($\theta=0°$) = 0.06 (maximum at $\theta \approx 60°$)
  Y_{so} ($\theta=0°$) = 0.02 (maximum at $\theta \approx 60°$)
  from Cl^+/Cl_2^+ ion beam study [D.J. Oostra *et al.*, Appl. Phys. Lett. **50**, 1506 (1987)].
  [S. Tachi *et al.*, JVST A**9**, 796 (1991)].

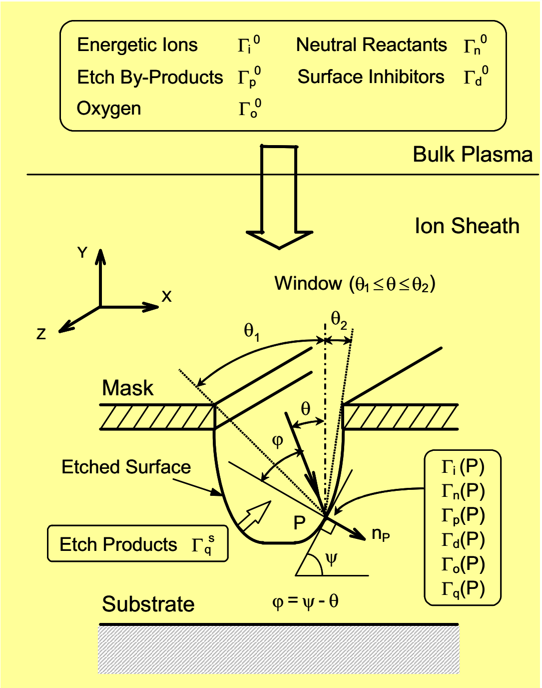
- Sputter Yield of Surface Inhibitors $Si_uCl_vO_w$: Y_p ($\theta=0°$) = Y_{sn} (maximum at $\theta \approx 60°$)
  assumed.

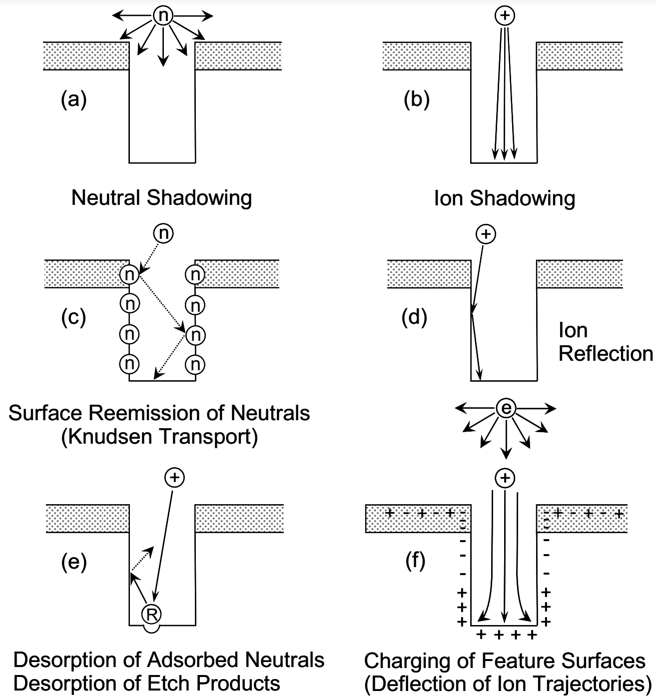
- Sticking Coefficient of Neutral Reactants on Si : $S_{n0} = 0.55$
  from beam study of Cl_2 on Si [D.J.D.Suullivan *et al.*, J. Phys. Chem. **97**, 12051 (1993)].
  * ~ 0.001 for Cl on Si.

- Sticking Coefficient of O on Si and $SiCl_x$: $S_{o0} = 1$
  from beam study [J.R. Engstrom *et al.*, Phys. Rev. B**41**, 1038 (1990)].
  * ~ 0.001 for O_2 on Si from beam study [J.R. Engstrom *et al.*, Phys. Rev. B**41**, 1038 (1990)].

- Sticking Coefficient of Etch Products on Si, $SiCl_x$, and SiO_y : S_{p0} , S_{q0} = 0.1 ~ 0.5 (assumed)
  * ≤ 0.002 for $SiCl_4$ on Si from beam study [L.J. Whitman *et al.*, Surf. Sci. **232**, 297 (1990)].
  * ~ 0.1–0.5 for $SiCl_x^+$ (x=1,2; E_i=30 eV) from beam study [T. Sakai *et al.*, **32**, 3089 (1993)].
  * ~ 1 for products on themselves.

Transport of Ions and Neutrals in microstructures





- **Ions and neutrals coming from the plasma onto substrate surfaces are further transported onto sidewalls and bottom surfaces in microstructural features. Here, neutrals include reactants, etch products and by-products, surface inhibitors, and oxygen.**

Transport of Ions and Neutrals *(continued)*

Ion Flux Incident on Feature Surfaces :

$$\Gamma_{\mathrm{i}}(P) = \underbrace{\Gamma_i^0 \int_{\theta_1}^{\theta_2} G_{\mathrm{i}}(\theta)\cos(\theta-\psi)\,\mathrm{d}\theta}$$

(b) Direct incidence (Ion shadowing)

Neutral Flux Incident on Feature Surfaces :

$$\Gamma_{\mathrm{n}}(P) = \underbrace{\Gamma_{\mathrm{n}}^0 \int_{\theta_1}^{\theta_2} (1/2)\cos(\theta-\psi)\,\mathrm{d}\theta}$$

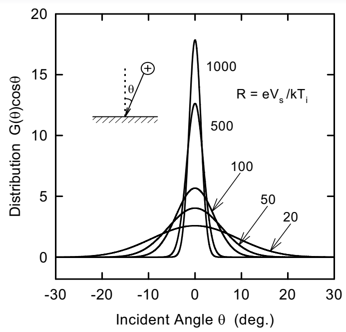
(a) Direct incidence (Neutral shadowing)

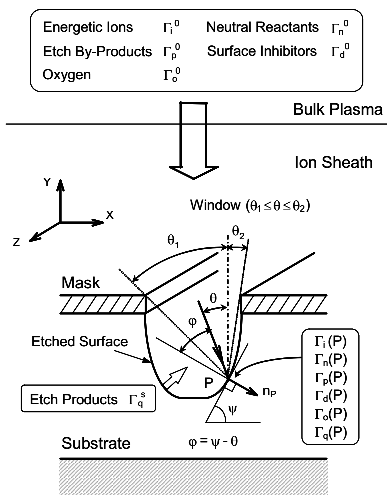
$$+ \underbrace{\int_{\mathrm{Profile}} (1/2r)\left\{Y_{\mathrm{n}}\Gamma_{\mathrm{i}}(Q)\Theta_{\mathrm{n}}(Q)\right.}$$

(e) Incidence through desorption from feature surfaces

$$\underbrace{\left. + \left[1 - S_{\mathrm{n}}(Q)\right]\Gamma_{\mathrm{n}}(Q)\right\}\cos\phi_{\mathrm{P}}\cos\phi_{\mathrm{Q}}\,\mathrm{d}s}$$

(c) Incidence through surface reemission

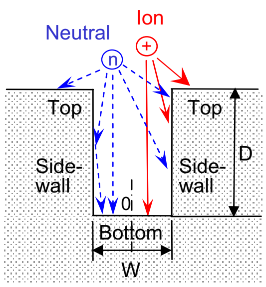




Transport of Ions and Neutrals *(continued)*

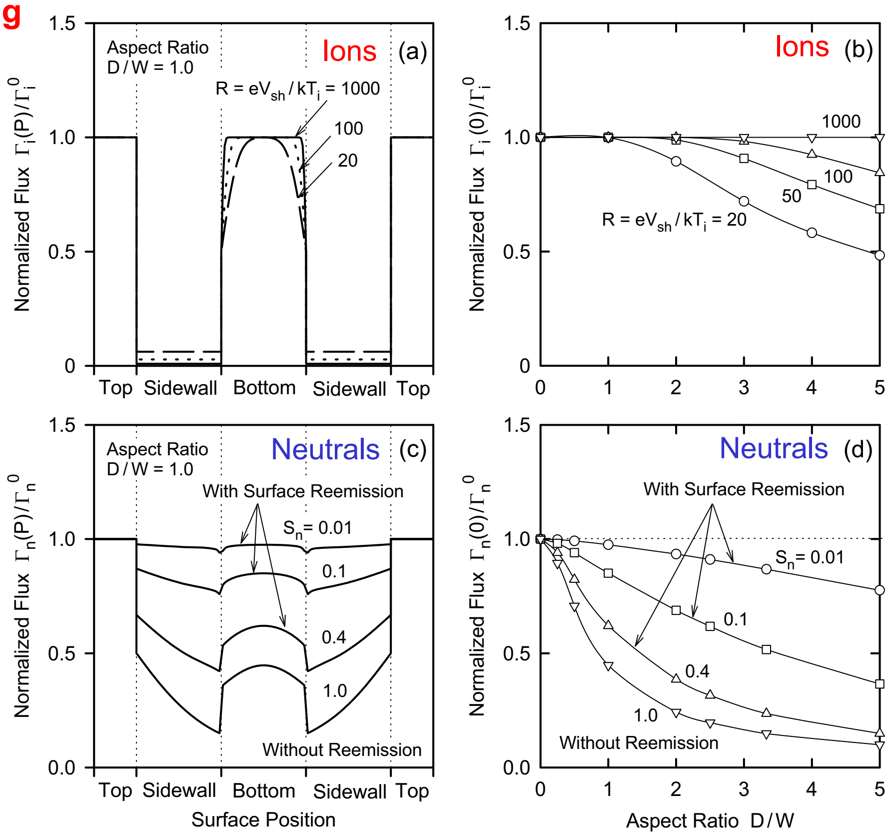
Geometrical Shadowing of Ions and Neutrals

Rectangular Trench



Geometrical Shadowing

- **Ion shadowing**
- **Neutral shadowing with surface reemission**

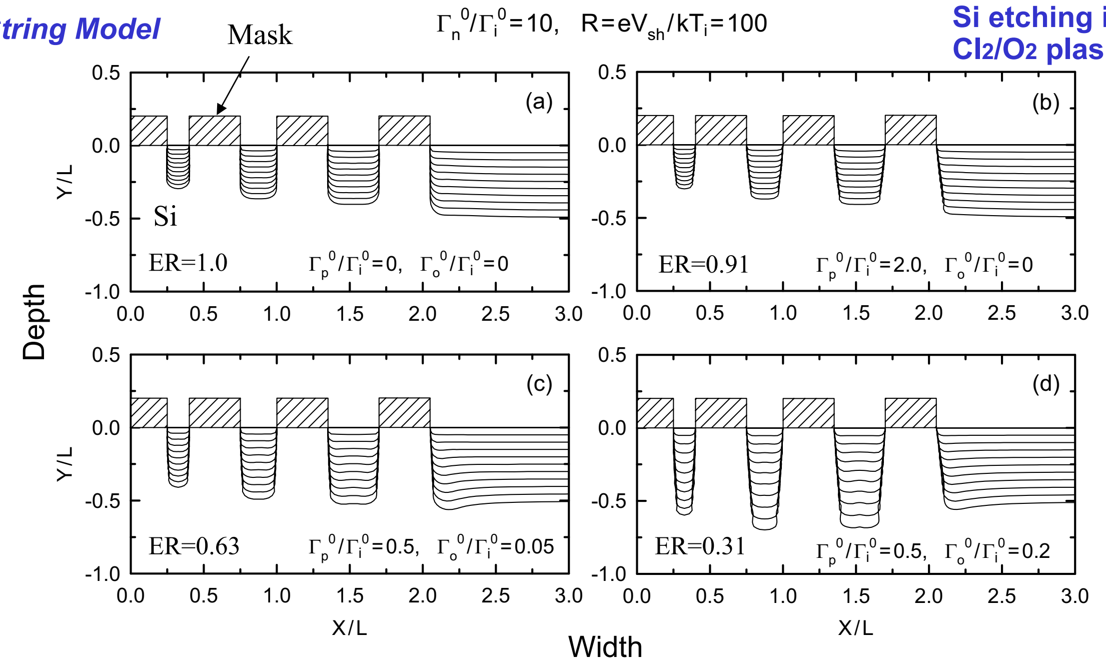


Feature Profile Evolution

— Etched profiles are simulated through modeling the transport of ions and neutrals in microstructures along with surface reaction kinetics thereat. —

String Model

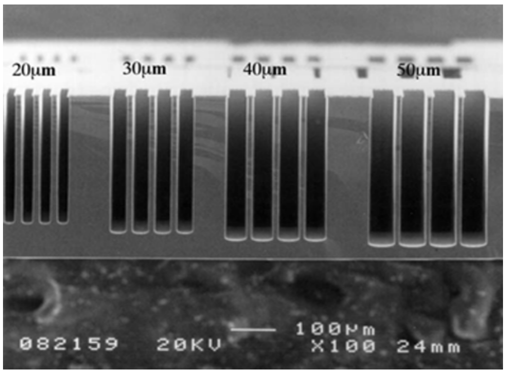
Si etching in Cl_2/O_2 plasmas



- **RIE lag occurs in (a) and (b), being suppressed in (c) with increasing oxygen flux from the plasma.**
- **Inverse RIE lag occurs in (d) at high oxygen flux.**
- **Sidewall tapering occurs in (b), (c), and (d) where surface inhibitors come from the plasma.**

Microscopic Uniformity *(continued)*

<Example 1>



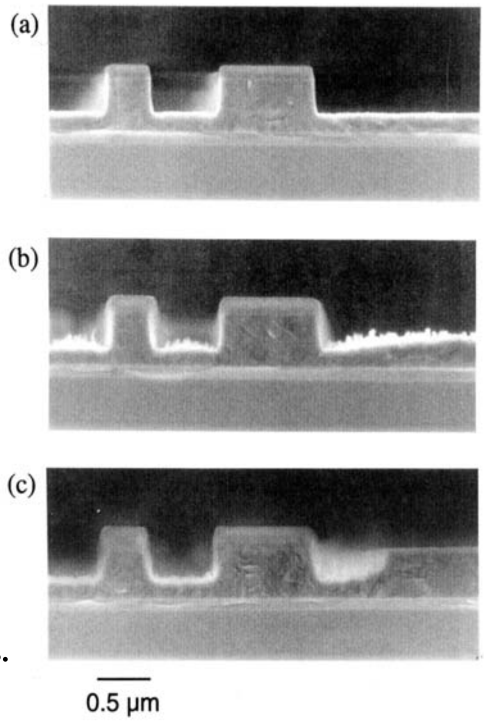
Si etching in SF_6/Ar plasmas

↑ RIE lag (reactive-ion-etching lag) :

- Large aspect-ratio features etch slower than smaller ones. (Narrow space features etch slower than wider ones.)

Inverse RIE lag : →

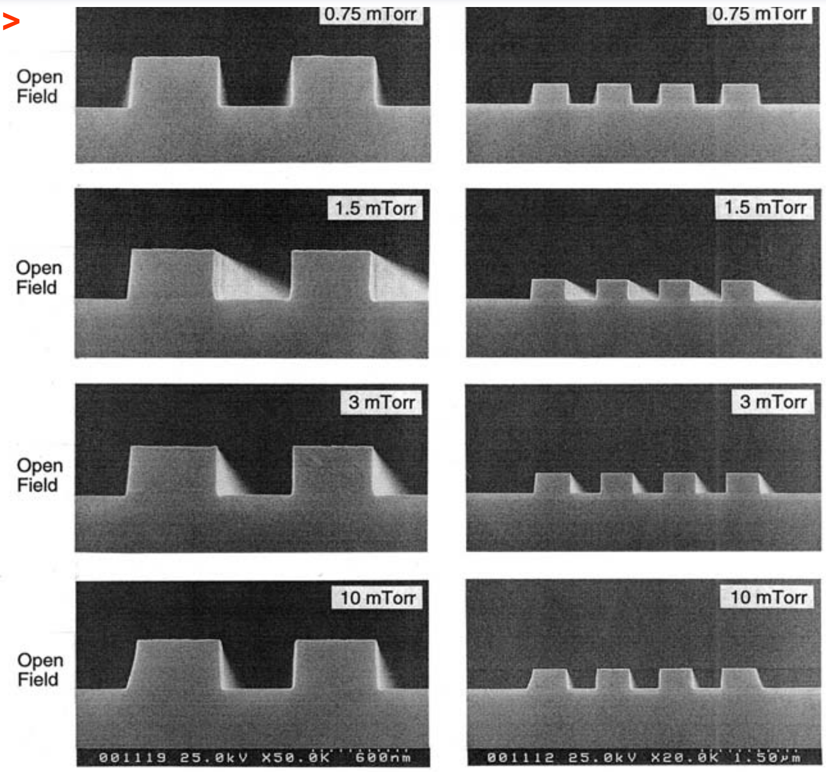
- Large aspect-ratio features etch faster than smaller ones. (Narrow space features etch faster than wider ones.)
- The degree of inverse RIE lag increases with increasing O_2 concentration in Cl_2/O_2 plasmas.



Poly-Si etching in Cl_2/O_2 plasmas

Microscopic Uniformity *(continued)*

<Example 2>



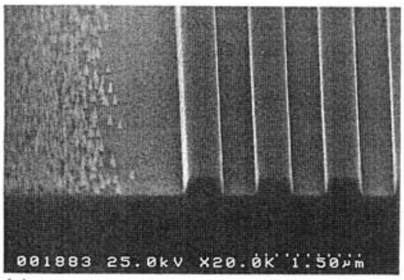
Outwardly tapered sidewall :

Poly-Si etching In Cl_2 plasmas

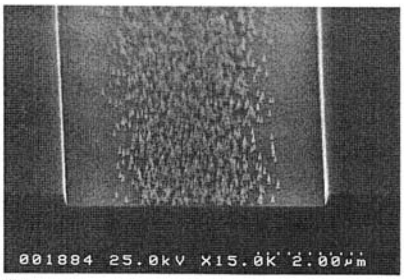
- Large aspect-ratio features etch less tapered than smaller ones. (Narrow space features etch less tapered than wider ones.)
- The degree of sidewall tapering increases with increasing pressure in Cl_2 plasmas.

Microscopic Uniformity *(continued)*

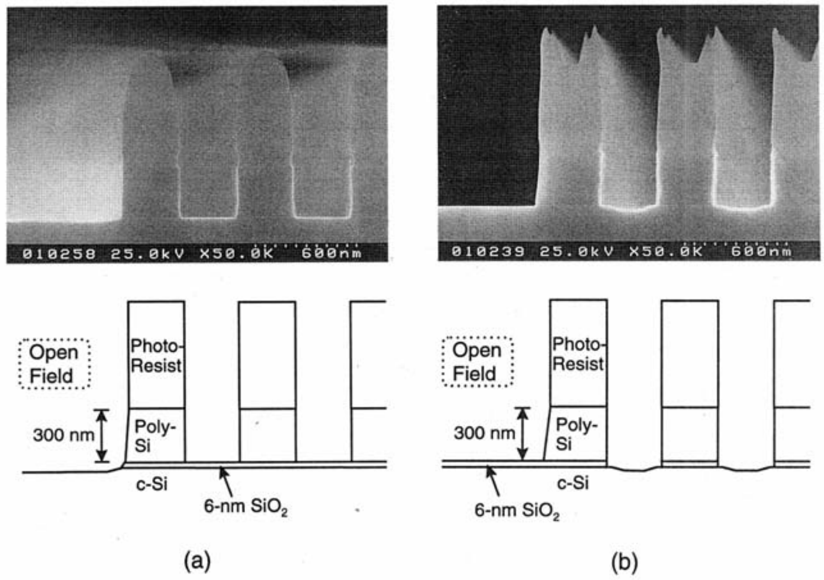
<Example 3> **Poly-Si etching in Cl_2/O_2 plasmas**



(a)



(b)



↑ Micropillar:

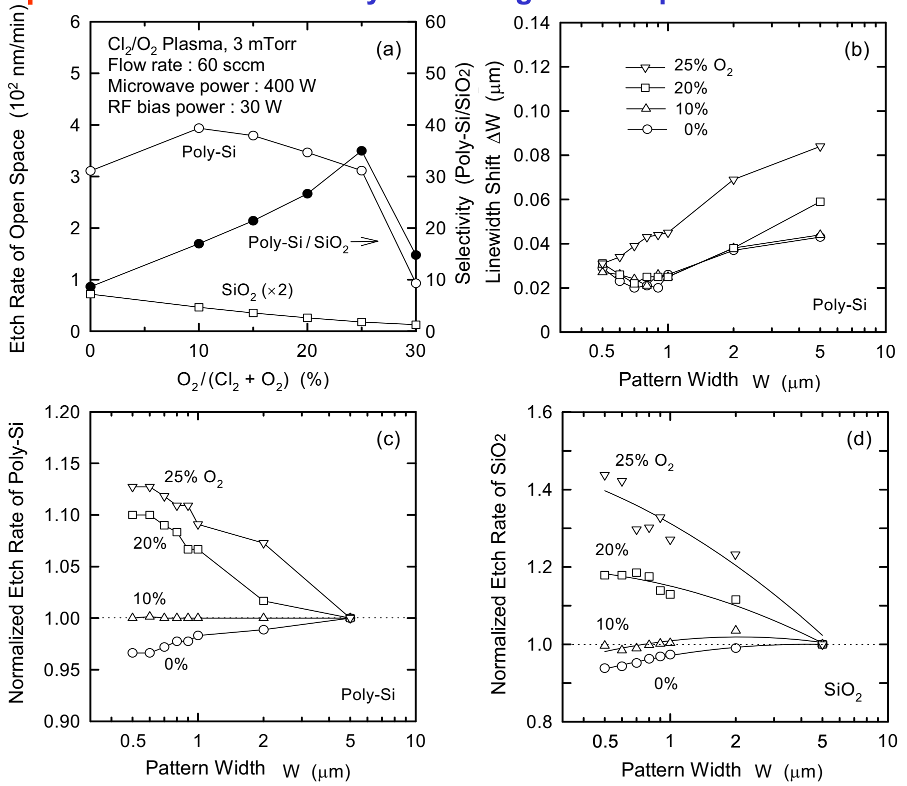
- Miropillars often occurs in wide space features (or small aspect-ratio features).

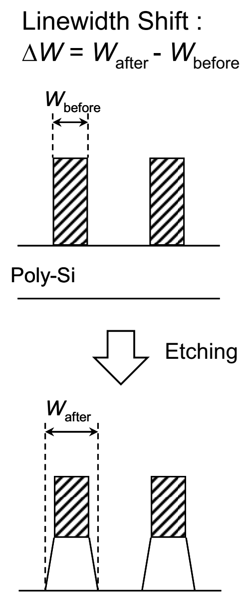
↑ Microscopic uniformity during overetch:

- The thinning and breaking of thin gate oxides during overetch step occurs preferentially in large open spaces in pure Cl_2 plasmas, while in dense areas at high level O_2 addition in Cl_2/O_2 plasmas.

Microscopic Uniformity *(continued)*

<Example 4> **Poly-Si etching in Cl_2O_2 plasmas**

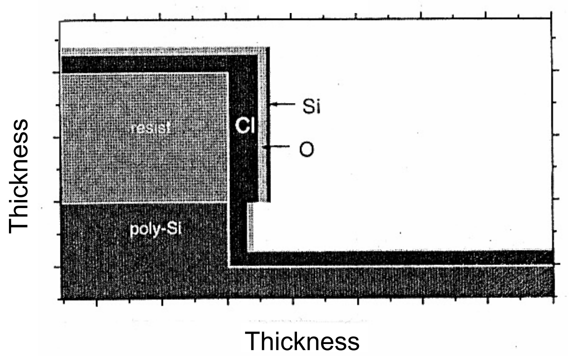




*Microscopic uniformity (etch rate, sidewall profile) is achieved at ~10% O_2 addition in Cl_2/O_2 plasmas.

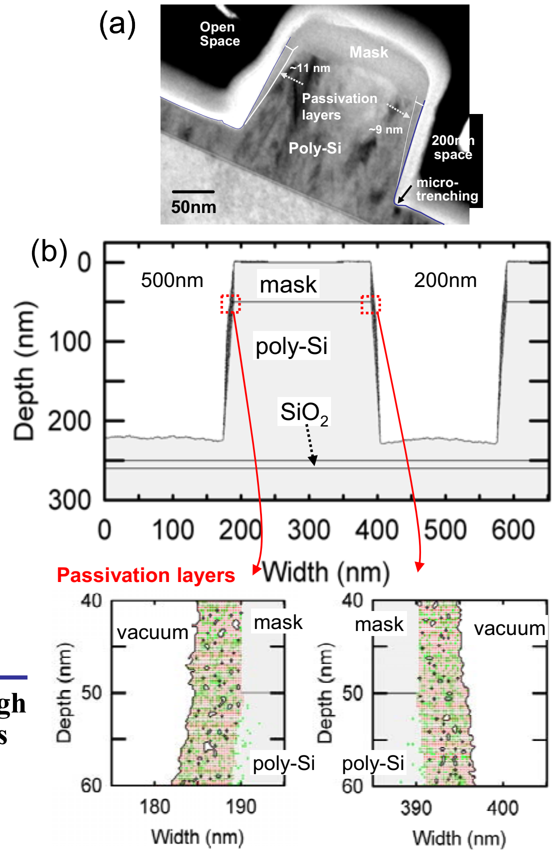
Passivation Layer Formation

Si etching in Cl_2/O_2 plasmas



↑ **XPS Analysis**

K.V. Guinn, C.C. Cheng, and V.M. Donnelly,
J. Vac. Sci. Technol. B**13**, 214 (1995).



Etched Profile and Profile Simulation →

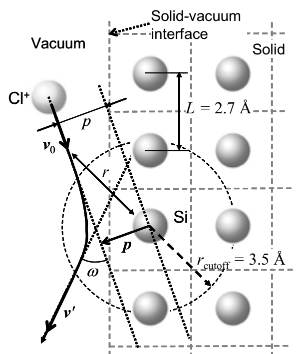
– Atomic-scale Cellular Model –

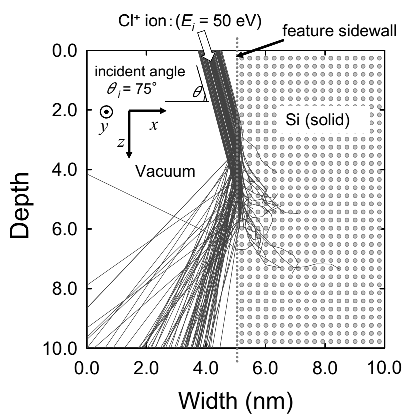
Y. Osano *et al*., Jpn. J. Appl. Phys. **45**, 8157 (2006).

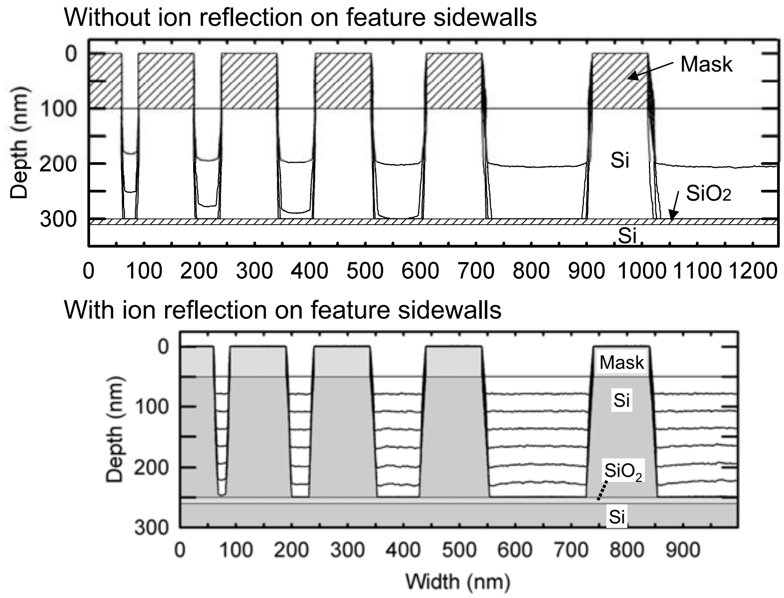
- **Passivation layers are formed on feature surfaces through deposition of surface inhibitors (primarily etch products and by-products) and/or surface oxidation.**
- **The thickness of passivation layers is significantly large on feature sidewalls.**

Ion Reflection

Si etching in Cl_2/O_2 plasmas





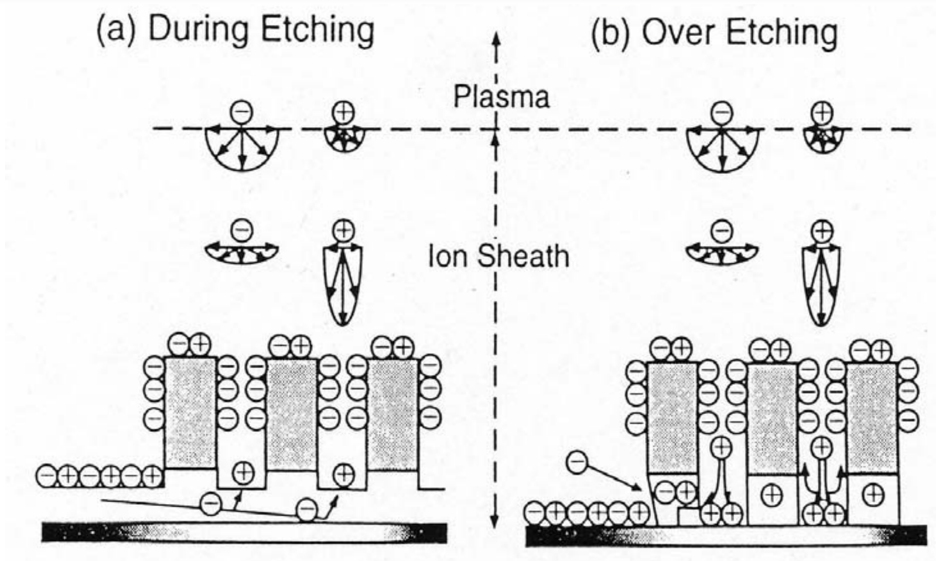


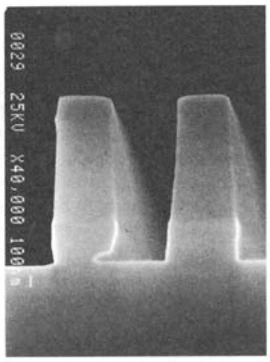
Etched Profile Simulation ↑ ***– Atomic-scale Cellular Model –***

Y. Osano *et al*., Jpn. J. Appl. Phys. **45**, 8157 (2006).

- **Ion reflection on feature sidewalls is responsible for profile anomalies such as microtrenching and footing on sidewalls near the feature bottom and thereat, which are also affected by deposition of etch products and by-products and surface oxidation.**

Surface Charging





- Notch is a sharp undercut that occurs on feature sidewalls near the bottom of the feature.
- In etching of conducting films on dielectrics (e.g., poly-Si gate etch), notching occurs during overetch step, at the inner sidewall foot of the outermost feature of a L&S structure neighboring an open area.

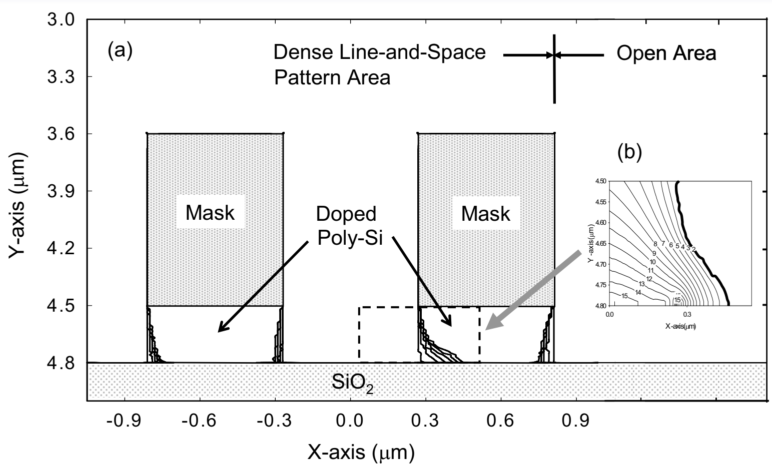
- The notch is caused by the deflection of ion trajectories in microstructural features due to the localized charging of feature surfaces, which in turn originates intrinsically from the difference of the velocity distribution between ions and electrons incident on substrate surfaces.
- Such a phenomena is known as "electron shading effect", which causes charging damage as well as profile anomalies.

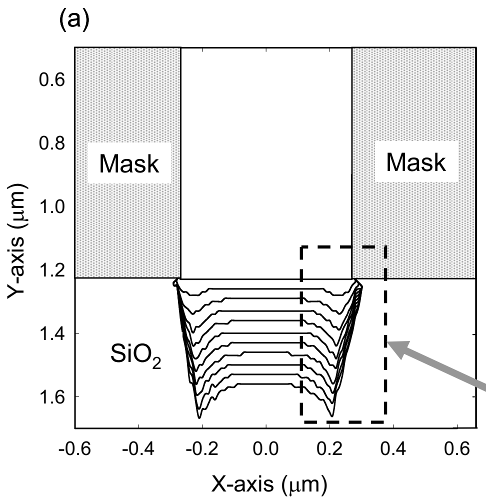
Surface Charging *(continued)*

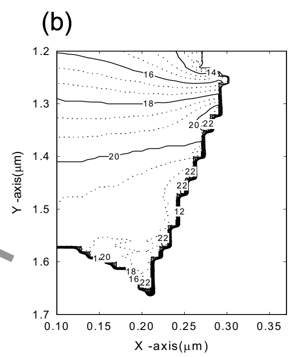
Profile Simulation

–String Model–

Charging (1): Conductor feature surfaces (during overetch)







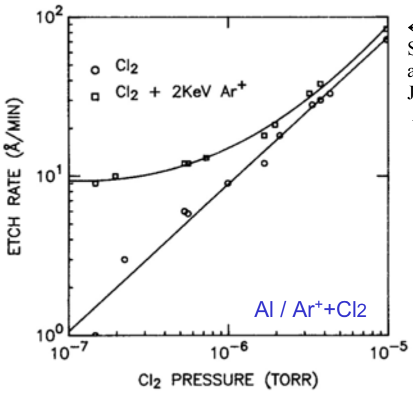
Charging (2): Dielectric feature surfaces

Al etch

Reactive species in Al etching with BCl3/Cl2 and BCl3/Cl2/O2 plasmas [a)]

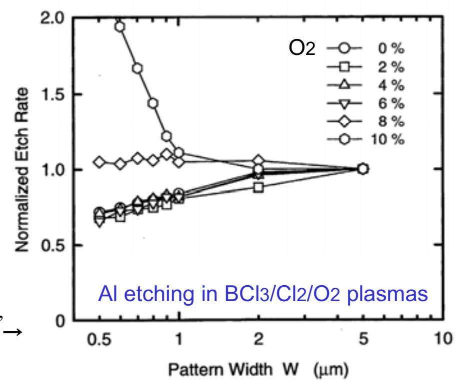
Role in Surface Reactions \ Source		Feed Gas	Reaction Product	Impurity from Walls and Windows	Mask Material
Neutral Reactant		Cl_2, Cl			
Ion		Cl_2^+, Cl^+, BCl^+		O_2^+, O^+	
Surface Inhibitors	Depositing	B_xCl_y, B_xO_y [b)]	$AlCl_x$, AlO_xCl_y [c)]		C_xH_y [c)]
	Reactive			O_2, O	

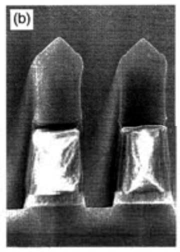
[a)] Al is etched pure-chemically in Cl_2, showing no ion-assisted reaction characteristics. Thus, surface inhibitor deposition is indispensable on sidewalls to obtain anisotropic profiles of Al. Selectivity is required over photoresist mask. [b)] $(BOCl)_x$ is volatile.
[c)] Compounds of $AlCl_x$ and C_xH_y are usually primary surface inhibitors during Al etching.



← S. Park, L.C. Rathbun, and T.N. Rhodin, J. Vac. Sci. Technol., A **3**, 791 (1985).

T. Banjo *et al*., Jpn. J. Appl. Phys., **36**, 4824 (1997). →





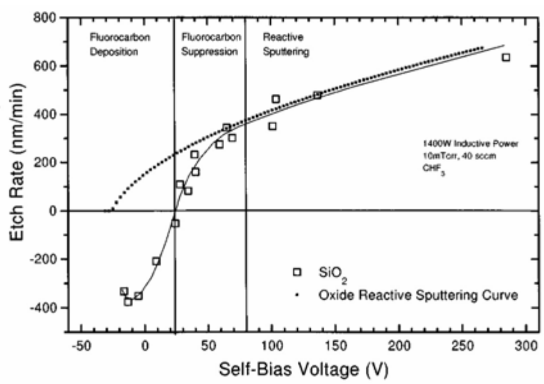
SiO2 etch

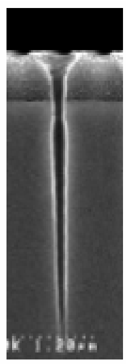
Reactive species in SiO2 etching with fluorocarbon plasmas [a)]

Role in Surface Reactions \ Source		Feed Gas	Reaction Product	Impurity from Walls and Windows	Mask Material
Neutral Reactant		F_2, F			
Ion		F_2^+, F^+, CF_x^+		O_2^+, O^+	
Surface Inhibitors	Depositing	C_xF_y [b)], (CF_x^+)	SiF_x, SiO_xF_y [c)]		C_xH_y [d)]
	Reactive			O_2, O	

[a)] SiO_2 is etched in fluorocarbon (CF_4, C_4F_8, etc.) plasmas with relatively high rf bias voltage; thus the etched profiles are usually anisotropic. C is indispensable in SiO_2 etching through breaking strong Si–O bonds and/or oxygen removal in the form of volatile compounds such as CO. In addition, F is also indispensable for Si removal through the formation of volatile SiF_4 [e.g., $SiO_2 + 2CF + 2F \rightarrow SiCl_4 + 2CO$].
[b)] Selectivity is required over Si, where fluorocarbon radicals C_xF_y play an important role; in some cases, H_2 is added to scavenge F and thus to release or increase surface inhibitors C_xF_y.
[c)] Surface reaction layer contains $SiC_xF_yO_z$.
[d)] Hard mask (e.g., poly-Si) is also often employed.

N.R. Rueger *et al*., J. Vac. Sci. Technol. A **15**, 1881 (1997). –
SiO2 etching in CHF3 plasmas





5. Current Issues of Plasma Etching Technology

– Current issues
– Poly-Si gate etch
– High-*k* gate etch
  (HfO_2, Dual metal gate)
– Metal etch (Pt, Ru)
– Deep RIE of Si

Current Issues

- **Etching of Conventional Materials :**
  – Etch anisotropy and selectivity
    *Profile and CD control on atomic scale
    *Selectivity over underlying ultra thin films
    *Surface roughness on atomic scale (LER+, etc.)
  – Microscopic uniformity
  – Plasma damage

+ LER: line edge roughness

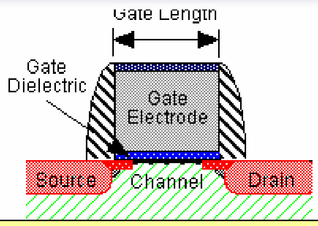
These issues are also to be resolved in etching of new materials

- **Etching of New Materials :**
  – Substrate : SiGe, Ge
  – Gate : High-*k** dielectrics (HfO_2, ZrO_2, etc.)
    / Metal electrodes (TaN, Mo, Ru, W, etc.)
  – Capacitor : High-*k** dielectrics (Ta_2O_5, BST)
    / Metal electrodes (Pt, Ir, Ru)
  – Inter layer dielectrics (ILD) :
    Low-*k* dielectrics (SiOC, MSQ**, Organic)

* *k*: dielectric constant

** MSQ: mechylsilsesquioxane

Gate Etch



Gate Length : L< 0.1 μm, Spacing < 0.1 μm
Gate Electrode : Poly-Si (thickness ~ 300 nm)
metal (W, TiN, TaN, Pt, Ir, Ru, etc.
thickness~ 50~60 nm)
Gate Dielectric: SiO_2, SiON
High-*k* dielectric (Al_2O_3, HfO_2, ZrO_2)
thickness ~ 1 ~ 2 nm
Buffer layer : Mask / Gate Electrode
Gate Electrode / Gate Dielectrics

(1) Profile (Mainly gate electrode)

- Feature: feature size、critical dimension
  Minimum feature size L< 0.1 μm
  CD loss/gain ΔL< 0.01 μm (=10 nm)
- Profile irregularities: notch, microtrench, (owing to bending of ion trajectory)

*In case of hard etching materials
More sidewall deposition → CD gain,
Needs for removing of residues on sidewalls

(2) Selectivity

- Gate Electrode (poly-Si, metal)
  Mask ----- Hard mask (SiO_2)
  Underlying Layer ------- Gate Dielectrics
- Gate Dielectric (SiO_2, SiON, High-*k* dielectric)
  Mask ----- Gate Electrode (+ Mask)
  Underlying Layer------- Si

(3) Plasma Damage

- Charging Damage
  Gate Dielectrics (Dielectric Breakdown)
  Transistor (deterioration)
- Gate Dielectrics : deterioration of dielectric
- Gate Dielectrics : penetrate

(4) Microscopic Uniformity

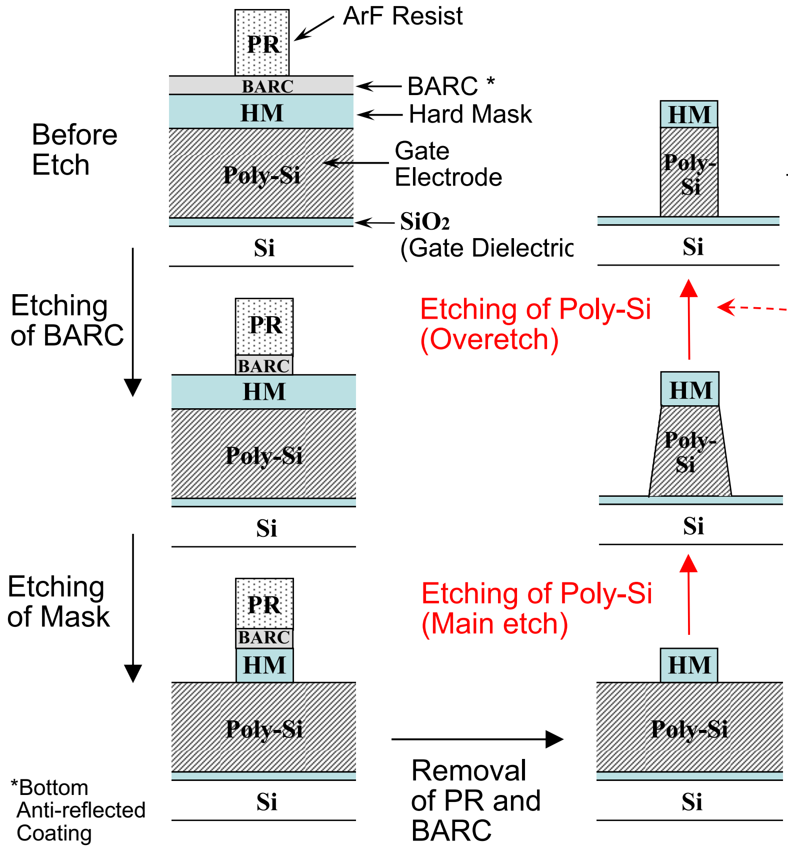
- Pattern sensitivity* of feature or profile irregularities
- Pattern sensitivity of etch rate or selectivity
  RIE lag, inverse RIE lag
- Pattern sensitivity of damage

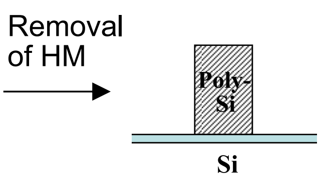
*feature size, aspect ratio, pattern density

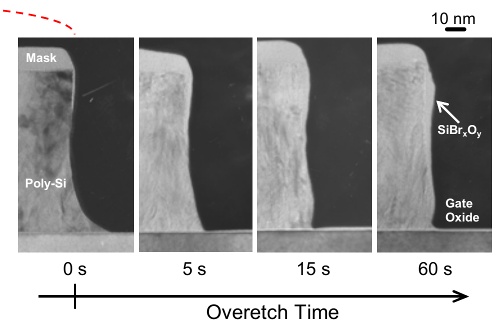
(5) Macroscopic Uniformity

- Wafer Uniformity

Poly-Si Gate Etch

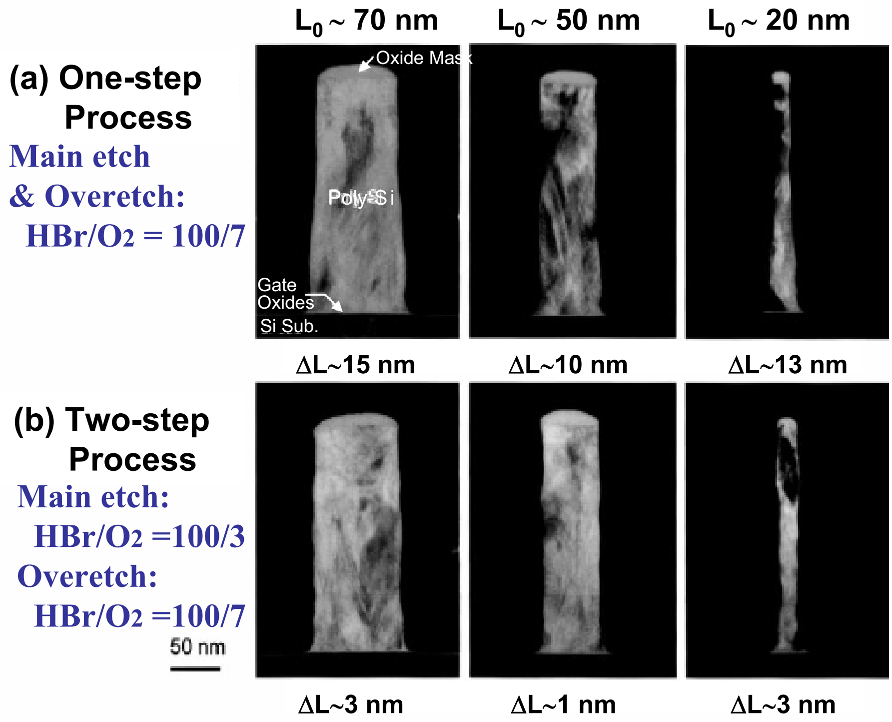






- A thin passivation layer of feature sidewalls plays a key role in achieving the nanometer-scale control of the profile and CD during main etch and overetch processes.

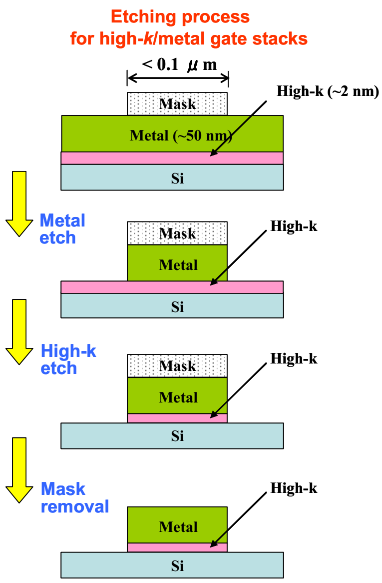
Poly-Si Gate Etch *(continued)*



In the plasma etching of 10-nm-scale microstructures, the ion-enhanced etching at the bottom of the feature and the passivation layer formation on feature sidewalls are still key mechanisms to be precisely controlled.

High-*k* Gate Etch

- **As integrated circuit device dimensions continue to be scaled down, recent efforts have been made to replace gate silicon-oxides with silicon-oxynitrides of slightly higher dielectric constant (*k*), and nowadays, new high-*k* (>20) dielectrics or metal oxides such as Al_2O_3, HfO_2, and ZrO_2 are being developed to replace SiO_2.**
- **In integrating these high-*k* dielectric materials into device fabrication, selective etching over the underlying Si is required for their removal prior to forming the source and drain contacts.**
- **Moreover, the etching of high-*k* dielectrics at higher etch rates with low ion energies and/or less ions is indispensable in mass production, for chamber cleaning of the chemical vapor deposition (CVD) and atomic layer deposition (ALD) apparatuses to prepare high-*k* thin films.**
- **The etching of HfO_2 films in BCl_3-containing plasmas without rf biasing or under low ion-energy conditions, together with a wafer temperature control, would be promising candidate for the process concerned.**



Etching of High-*k* Materials

High-*k* dielectrics are generally difficult materials for etching, owing to strong metal-oxygen bonds and non-volatile etch products or halogen compounds.

Physical properties of potential etch 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

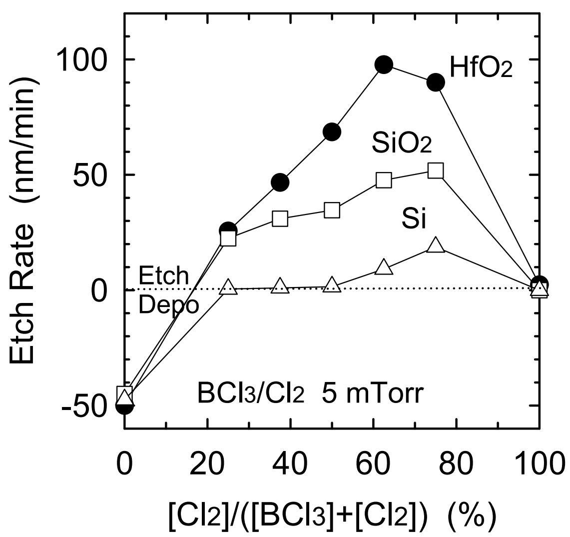
Bond	Bond Strength (eV)	Bond	Bond Strength (eV)
B-O B-F B-Cl B-Br	8.38 7.85 5.30 4.11	Si-O Si-F Si-Cl Si-Br Si-Si	8.29 5.73 4.21 3.81 3.39
C-O C-F C-Cl C-Br	11.15 5.72 4.11 2.90	Zr-O Zr-F Zr-Cl Zr-Br	8.03 6.38 5.11 –
Al-O Al-F Al-Cl Al-Br	5.30 6.88 5.30 4.45	Hf-O Hf-F Hf-Cl Hf-Br	8.30 6.73 5.16 –

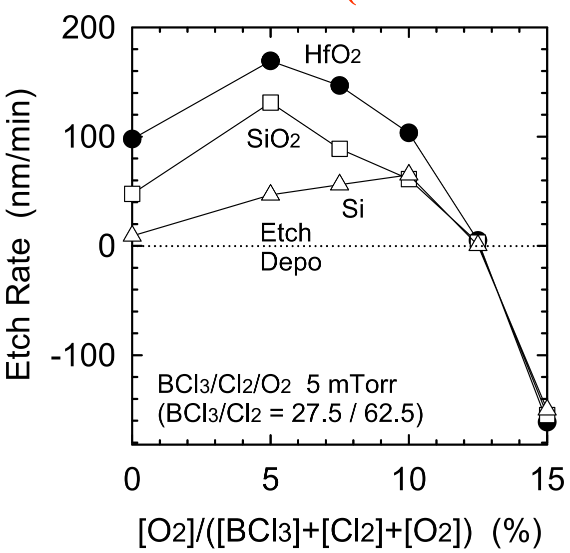
(from CRC Handbook of Physics and Chemistry, 1998)

- **Hafnium chlorides are relatively volatile, and thus Cl is expected to be useful for removal of Hf.**
- **Boron-oxygen bonds are relatively strong, and thus B and/or BCl species are expected to be useful for breaking strong metal-oxygen (Hf-O) bonds.**

Etching of High-*k* *(continued)*

HfO_2 etch in BCl_3 **MW: 600 W** **(without rf biasing)**



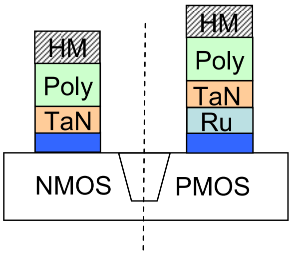


- **The etching of HfO_2 occurred at >20% Cl_2 addition. The HfO_2 etch rate was maximum at ~ 60% Cl_2, being ~ 100 nm/min with a selectivity of ~ 10 over Si and of ~ 2 over SiO_2.**
- **Note that a high etch selectivity of >50 for HfO_2/Si was obtained at 40-50% Cl_2 addition, with a HfO_2 etch rate of ~50 nm/min and HfO_2/SiO_2 selectivity of 1.5~2, where the deposition was still dominant over the etching on Si.**
- **In BCl_3/Cl_2/O_2 plasmas, the HfO_2 etch rate was enhanced with O_2 addition, being ~150 nm/min at ~5% O_2 with a selectivity of ~4 over Si and of ~1.2 over SiO_2.**
- **At high O_2 addition > 10%, the heavy deposition occurred to inhibit etching on all sample surfaces.**

Etching of Metals

Metals for high-*k* gate stack

FET	Metals	Nitrides, Carbides
N-MOSFET	Ti, Ta	TaN, TaC
P-MOSFET	Pt, Ir, Mo, Ru	
Midgap	W	TiN



- Regarding high-*k*/metal gate stack, one approach is to employ a single metal gate material with a midgap work function for both *n*- and *p*-MOSFETs.
- However, a dual-work-function metal gate technology would be preferred, because of several drawbacks such as high threshold voltage of the single metal gate material.

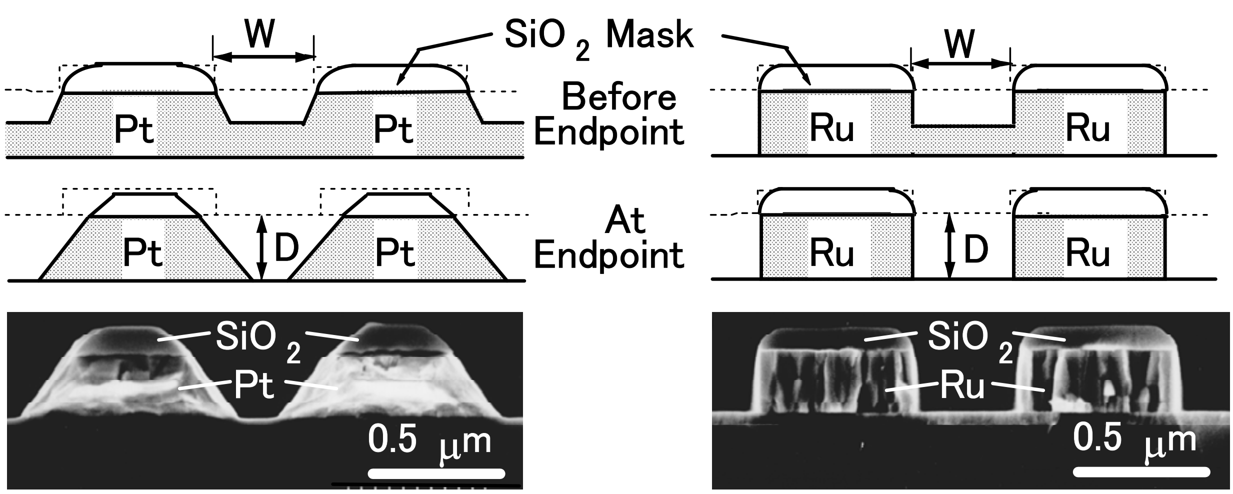
Physical properties of potential etch product species

Element	Halogen compound	Melting point (°C)	Boiling point (°C)
Ti (Z=22)	TiF_4 $TiCl_4$ $TiBr_4$	284 –25 39	— 136.45 230
Ru (Z=44)	RuO_4 RuO_2 RuF_5 RuF_3 $RuCl_3$ $RuBr_3$	25.4 — 86.5 > 600 *dec > 500 *dec > 400 *dec	40 — 227 — — —
Ta (Z=73)	TaF_5 $TaCl_5$ $TaBr_5$	95.1 216 265	229.2 239.35 349
Ir (Z=77)	IrF_6 IrF_3 $IrCl_3$ $IrBr_3$	44 250 763 —	53 — — —
Pt (Z=78)	PtF_6 PtF_4 $PtCl_4$ $PtBr_4$	61.3 600 327 180	69.1 — — —

*dec: decomposes *(from CRC Handbook of Physics and Chemistry, 1998)*

Metal Etch *(continued)*

Pt Electrode *Ru Electrode*



Etched in Ar/O_2 Plasma
Selectivity (Pt/SiO_2) ~ 6

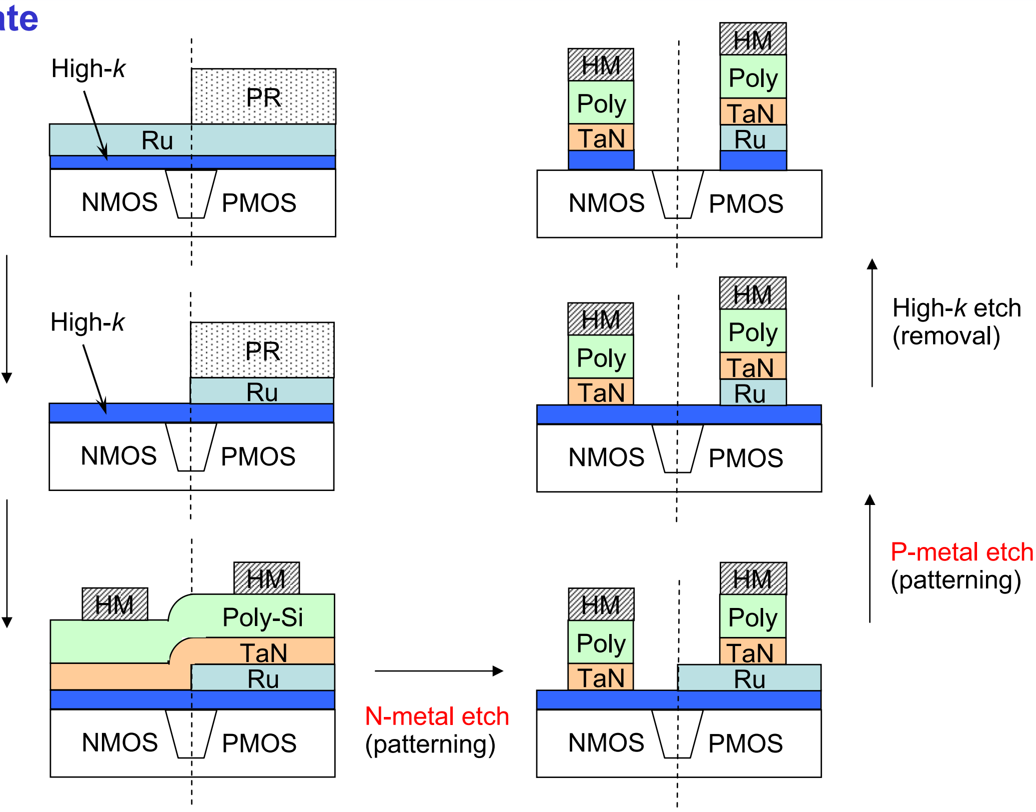
Etched in O_2/Cl_2 Plasma
Selectivity (Ru/SiO_2) ~20

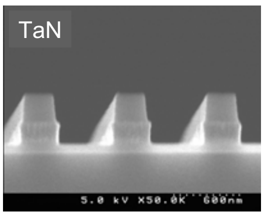
- Etching of Pt relies intrinsically on physical sputtering, because halogen and other compounds of Pt are not volatile; thus, the Pt sidewalls are largely tapered owing to redeposition of Pt sputtered on feature sidewalls during etching.
- Etching of Ru is caused by ion-assisted reaction in O_2-containing plasmas, because RuO_4 is volatile to be relatively easily desorbed from surfaces; thus, vertical sidewalls are obtained for Ru.

Metal Etch

(continued)

Dual metal gate





Deep RIE

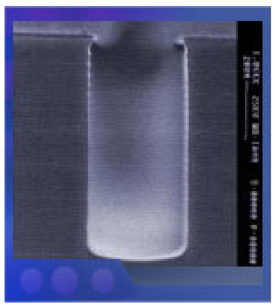
– Bosch process (for MEMS) –

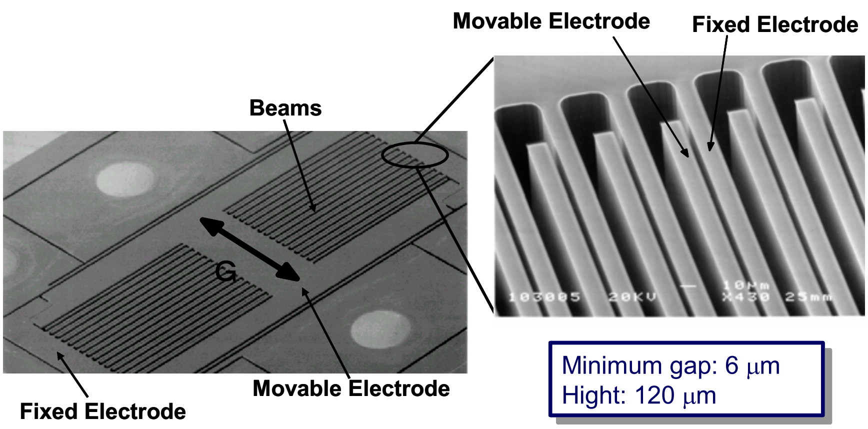
To fabricate 3D, deep structures with higher throughputs and lower costs

Deep RIE* (Bosch process)

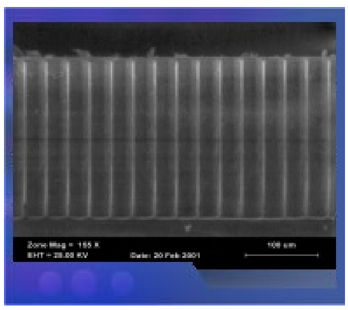
*RIE: reactive ion etching

Cyclic process consisting of
isotropic etching with SF_6 plasmas
→ sidewall passivation with C_xF_y plasmas
→ anisotropic etching with SF_6 plasmas
→ isotropic etching with SF_6 plasmas
achieves an etch rate of > 10 μm/min for Si.

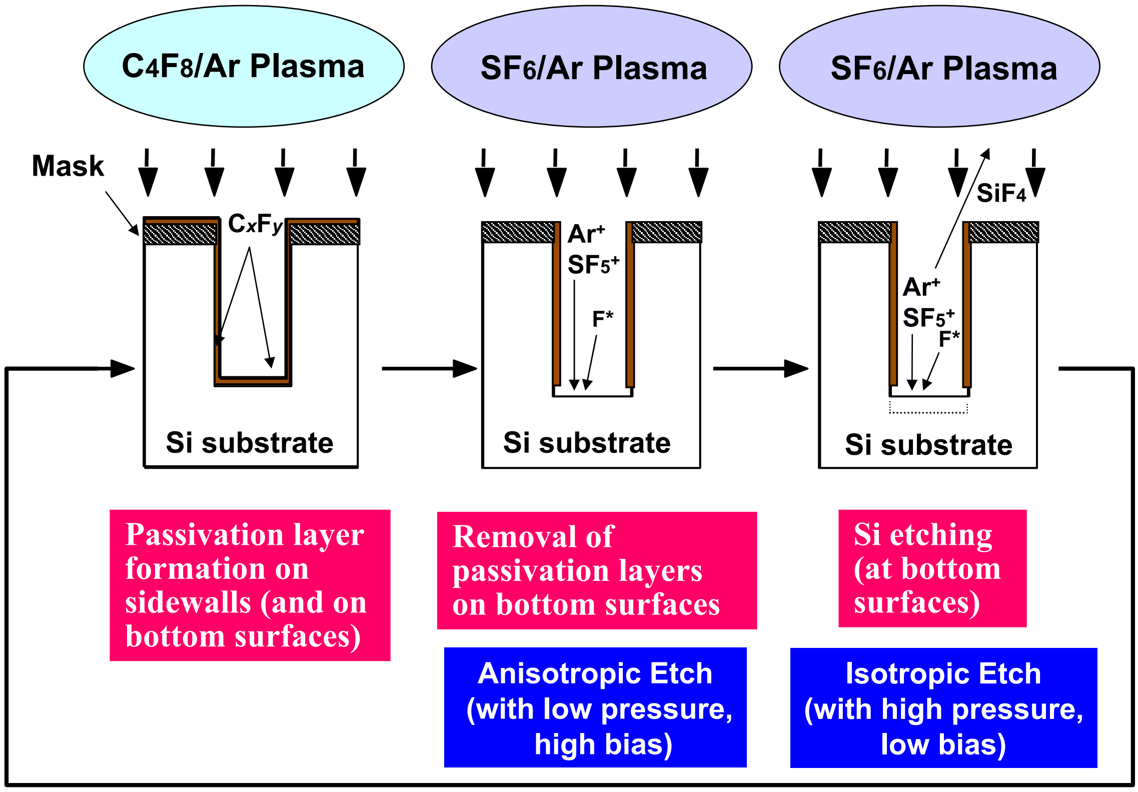




Minimum gap: 6 μm
Hight: 120 μm



Deep RIE *(continued)*



*Higher etch rates and the suppress of scallops on sidewalls are issues to be further improved.

6. Summary

– Future Prospects

Nanofabrication Technology

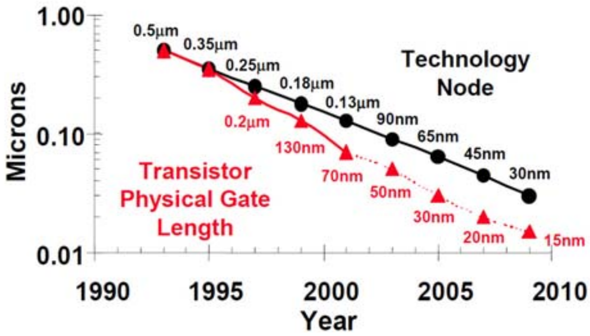
—Top-down approach, Bottom-up approach—

1000 nm (1 μm) | 100 nm | 10 nm | 1 nm | 0.1 nm (1 A)

Top-down approach
—fabrication from bulk materials and/or thin films of the material to obtain microstructures (devices)

Bottom-up approach
—manipulation/rearrangement of atoms
—self-assembly/re-organization of atoms to obtain nanostructures (materials, devices,)

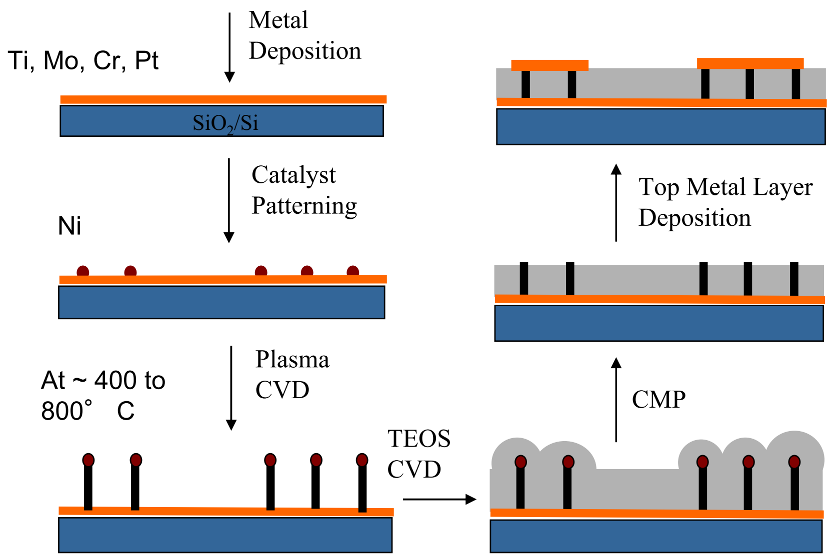
VLSI ULSI Nanoelectronics

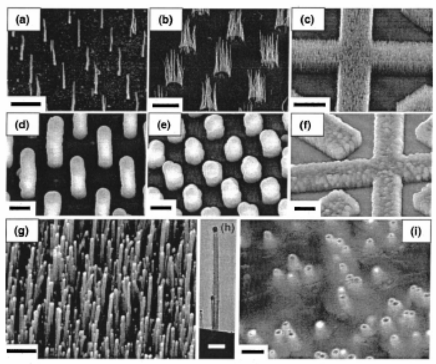


A combination of top-down and bottom-up approaches will be important in nanofabrication technologies for mass production, because the bottom-up approach is not available for mass production owing to its slow rate of fabrication.

Fabrication of Nanoelectrode Arrays

—Bottom-up approach— (CNT Nanoelectrode Array / CNT Interconnects)





The scale bars are (a) 5, (b) 3, (c) 10, (d) 2, (e) 5, (f) 10, (g) 1, (h) 0.2, and (i) 0.2 μm.

J. Li, Q. Ye, A. Cassell, H. T. Ng, R. Stevens, J. Han, M. Meyyappan, *Appl. Phys. Lett.*, **82**(15), 2491 (2003).

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Summary

- Plasma etching is now an indispensable technology for micro- and nano-fabrication of ULSI and MEMS devices.
- To meet the requirements for near-future and future devices, the precise control of etching characteristics is further required, based on the precise control of the etching mechanisms concerned.
  - *Current issues / requirements for plasma etching technology have been summarized in this lecture.
- In turn, a better understanding of the physical and chemical mechanisms underlying the processing continues to be required in the gas-phase and on the surfaces,
  - *Ion-assisted reaction and passivation layer formation continue to be key mechanisms to be precisely controlled on surfaces.
- A combination of top-down (plasma etching) and bottom-up approaches would be important for nanofabrication technology of <10 nm scale.

For further reading

- **Books**

*VLSI Technology, edited by S.M/ Sze (McGraw-Hill, New York, 1988).
*ULSI Technology, edited by C.Y. Chang and S.M. Sze (McGraw-Hill, New York,1996).
*J.D. Plummer, M.D. Deal and P.B. Griffin, Silicon VLSI Technology: Fundamentals, Practice and Modeling (Prentice Hall, New Jersey, 2000).
*K.P. Cheung, Plasma Charging Damage (Springer, Berlin, 2001).
*Handbook of Advanced Plasma Processing Techniques, edited by R.J. Shul and J. Pearton (Springer, Berlin, 2000).
*M.A. Lieberman and A.J. Lichtenberg, Principles of Plasma Discharges and Materials Processing , 2nd ed. (Wiley, New York, 2005).
*M. Elwenspoek and H.V. Jansen, Silicon Micromachining, (Cambridge Univ. Press, Cambridge, 1998). <for MEMS>
*M.J. Mandou, Fundamentals of Microfabrication: The Science of Minituarization, 2nd ed.(CRC Press, New York, 2002). <for MMS>

- **Journals :**

*Journal of Vacuum Science and Technology A, B (AVS/AIP)
*Applied Physics Letters (AIP)
*Journal of Applied Physics (AIP)
*Journal of Physics D : Applied Physics (IOP)
*Plasma Sources Science and Technology (IOP)
*Japanese Journal of Applied Physics (JSAP)