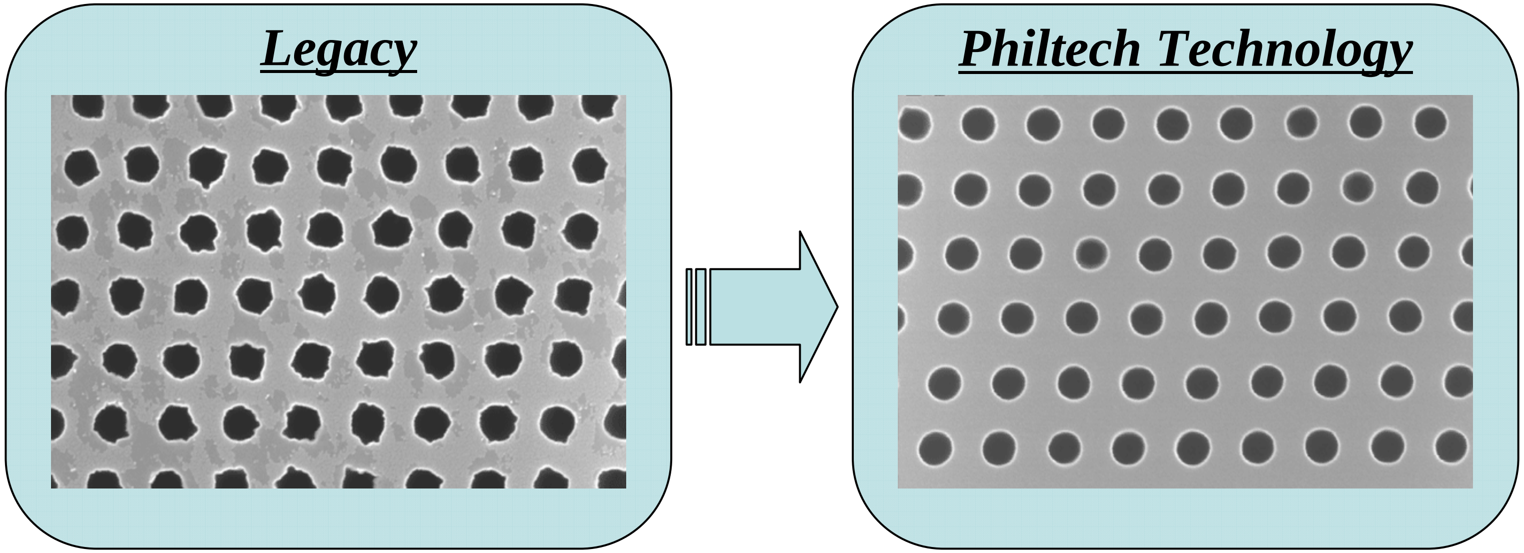
Striation Free Etch Technology



***P*hiltech *I*nc.**
mura@philtech.co.jp

July 26th, 2007

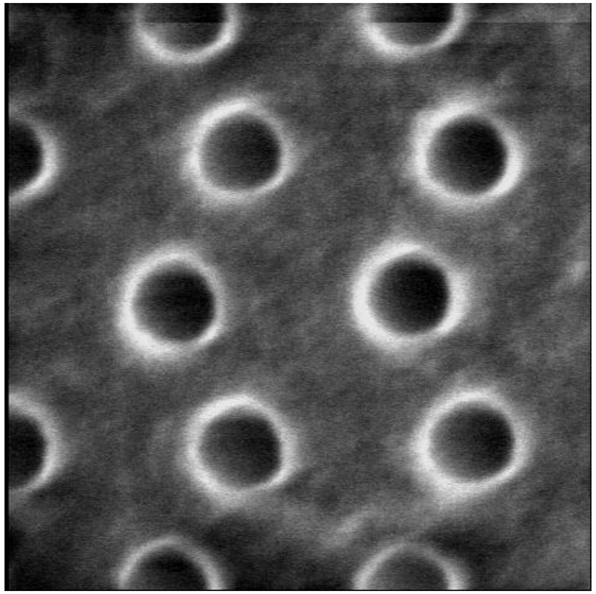
Outline

1. **Corporate Overview**
   …Why we promote CF_3I gas for Dielectric etch ?
2. **Initial Experiment… *"Working Pressure and Striation"***
3. **2^{nd} Experiment… *"Iodine Effect"***
4. **Proposed Solution Model**
5. **3^{rd} Experiment… *"SiCOH etch with CF_3I chemistry"***
6. **4^{th} Experiment… *"Residue originated in Iodine"***
7. **Historical CF_3I etching property**
8. **Summary**

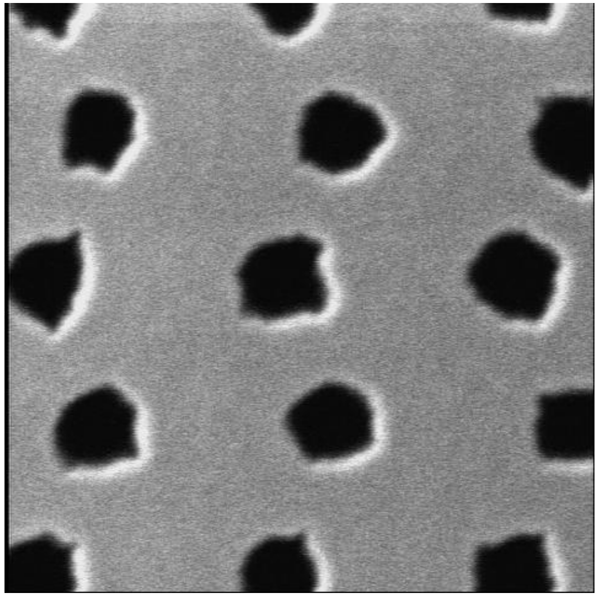
Corporate Overview

Founded	**May, 2001**
Funding	**727M Yen to date**
Business	**Design and Manufacture (fabless) Test Wafers with consulting.** **Develop Unique Manufacturing Processes.**
Customers	**Semiconductor Equipment & Materials Manufacturers, Chip Manufacturers**
Mission	**Contribute to industry progress by turning basic Process Development into horizontal Industry Segment** ***Placing an emphasis on manufacturing with X-ray lithography that has a projection capability for 22nm technology node with 300mm wafers***

Why we promote CF_3I gas for Dielectric etch ?



100nm hole patterned photoresist film on TEOS layer by X-ray lithography



After TEOS etch process

Severe striations were observed and had to find out a solution.

Initial Experiment

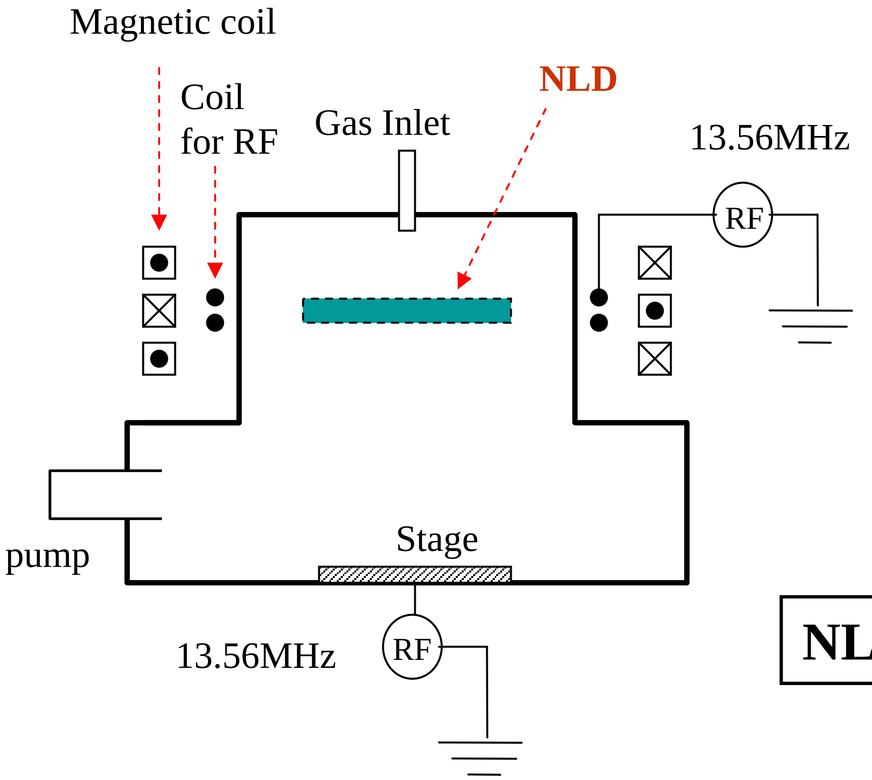
1. Equipment Set-up

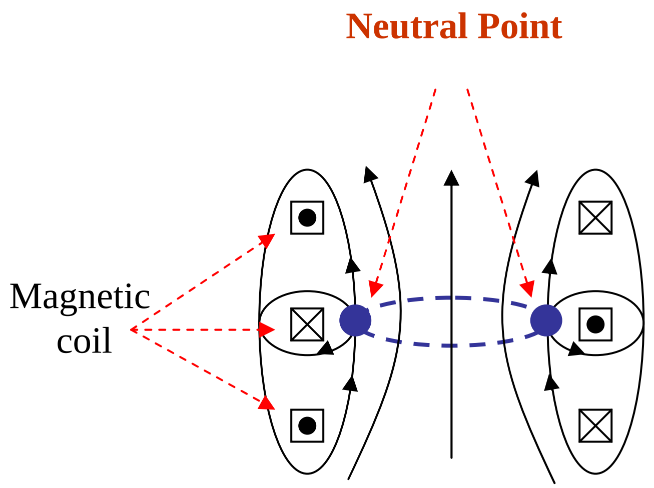
Neutral Loop Discharge : NLD plasma

Features of NLD

→ **High Density Plasma**（**for Ar, > 10^{11}cm^{-3}@ 10-1Pa order**）

→ **Good Uniformity**

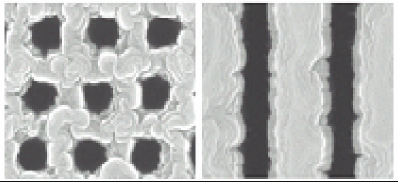
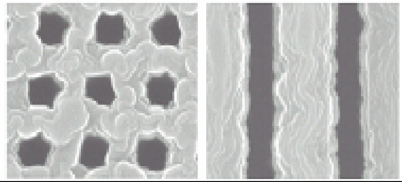
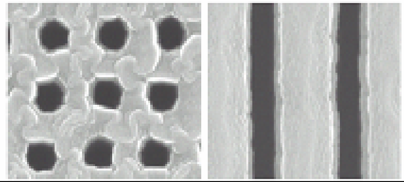
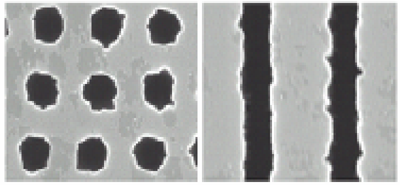
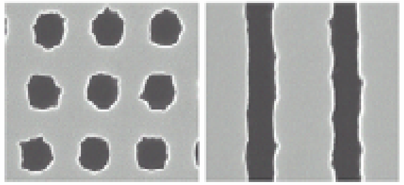
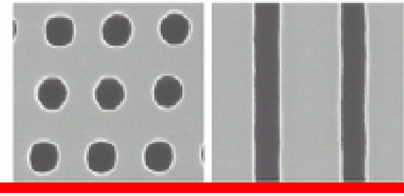




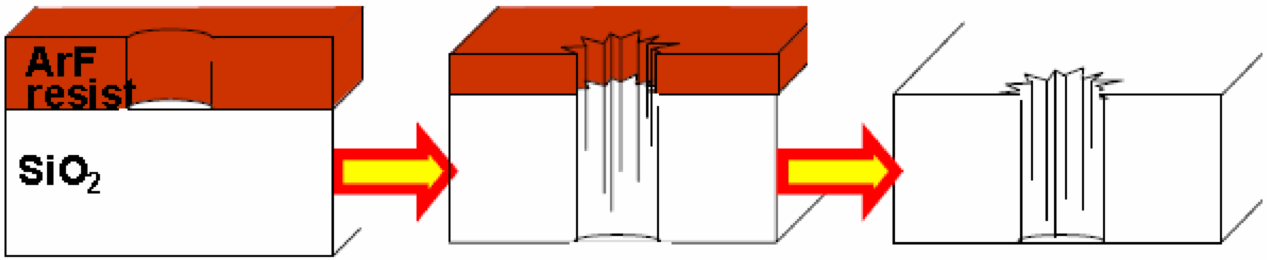
NLD Plasma Etcher

Initial Experiment

2. Results: Working Pressure and Striation

	1.3 Pa	0.67 Pa	0.4 Pa
After etching			
After resist removal			

Striation FREE



Initial   After etch   Resist removal

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Origin of the Striation (LER)

- In the high density plasma at lower pressure ⇒ No Striation
- Increasing the pressure ⇒ Striation (LER)

⇓

- Ion damage + Radical reaction

Therefore, the reduction of F radicals (atoms) is very important.
Iodine atom may react with other halogen atoms and give stable Inter-halogen compounds.

2^{nd} Experiment

1. Recipe Comparison

(1) Conventional

		Value	Unit
Pressure		2.67	Pa
Flow	Ar	230	sccm
	C_3F_8	50	sccm
	O_2	20	sccm
RF Power(Upper)		1.0	kw
	(Lower)	0.3	kw
Stage Temp.		10	C

(2) Philtech Technology

		Value	Unit
Pressure		2.67	Pa
Flow	Ar	230	sccm
	C_3F_7I	50	sccm
	O_2	20	sccm
RF Power(Upper)		1.0	kw
	(Lower)	0.3	kw
Stage Temp.		10	C

200mm Φ equipment

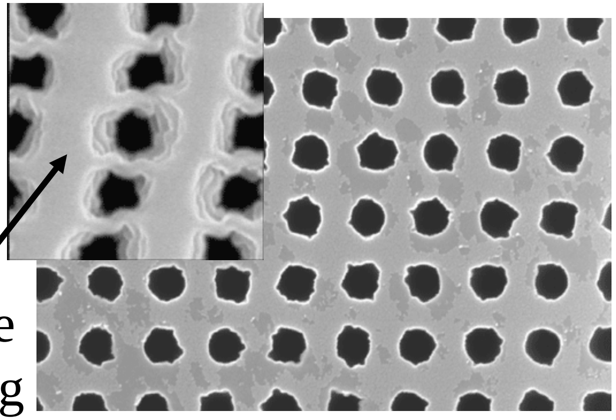
Low Pressure is not a requirement for Philtech Technology to effectively reduce striation ➔ Special Equipment is not required

2nd Experiment

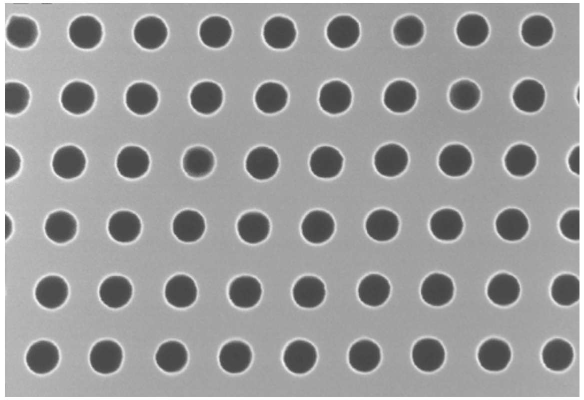
2. Results

	(1) Legacy	(2) Philtech technology

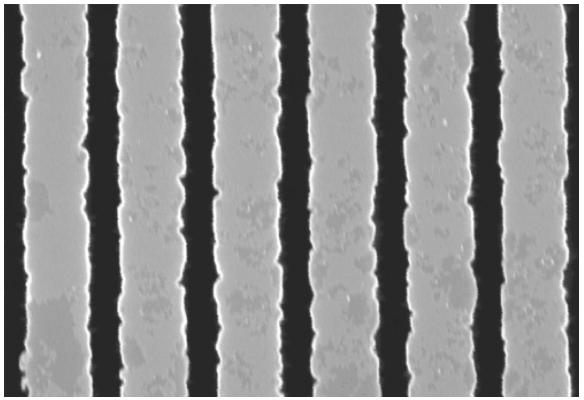
Hole area

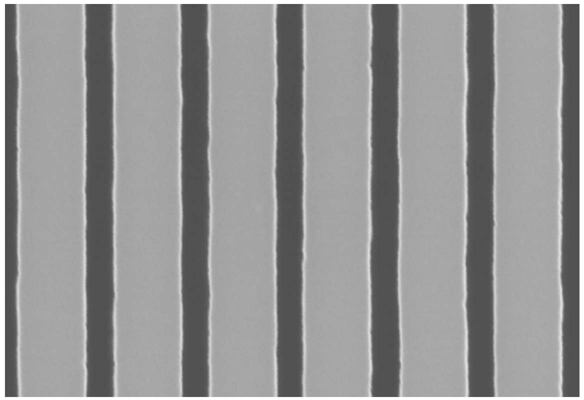


Before Ashing



Trench area



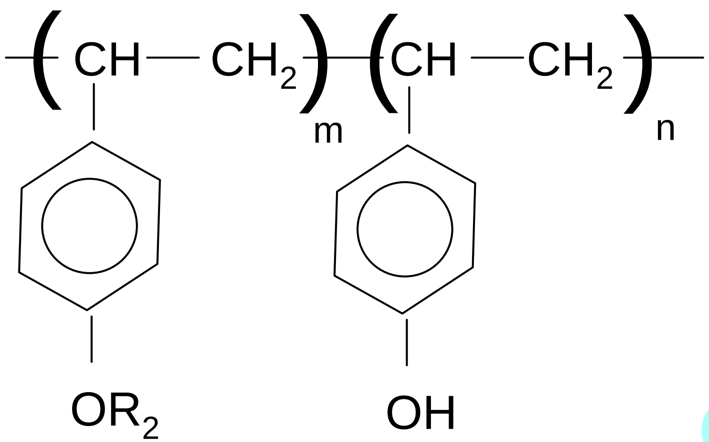


SEM （Top View）

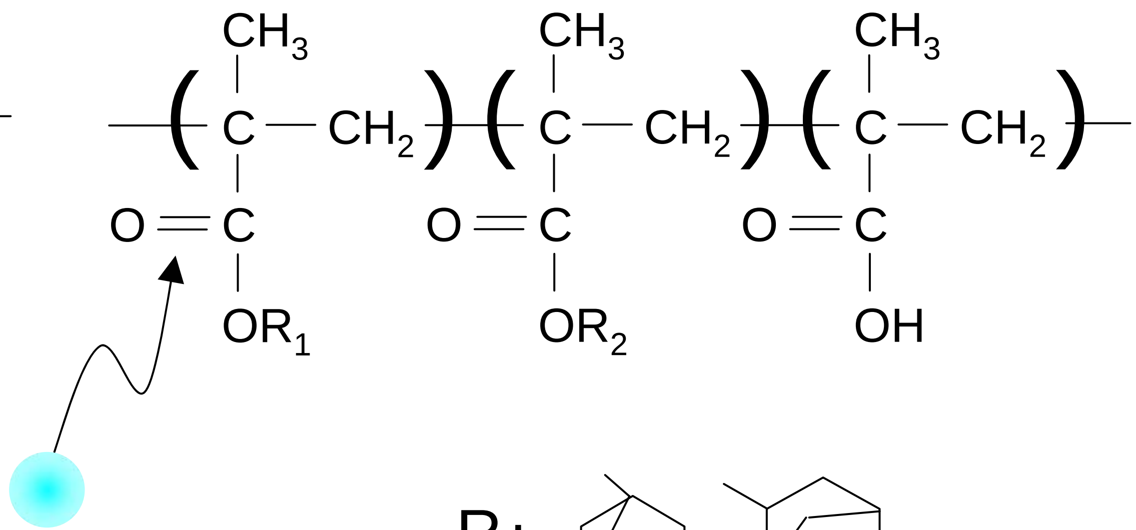
Proposed Solution Model

Photo-resist Molecular Structures

KrF (248nm)

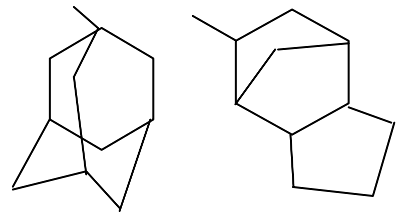


ArF (193nm)



F radical

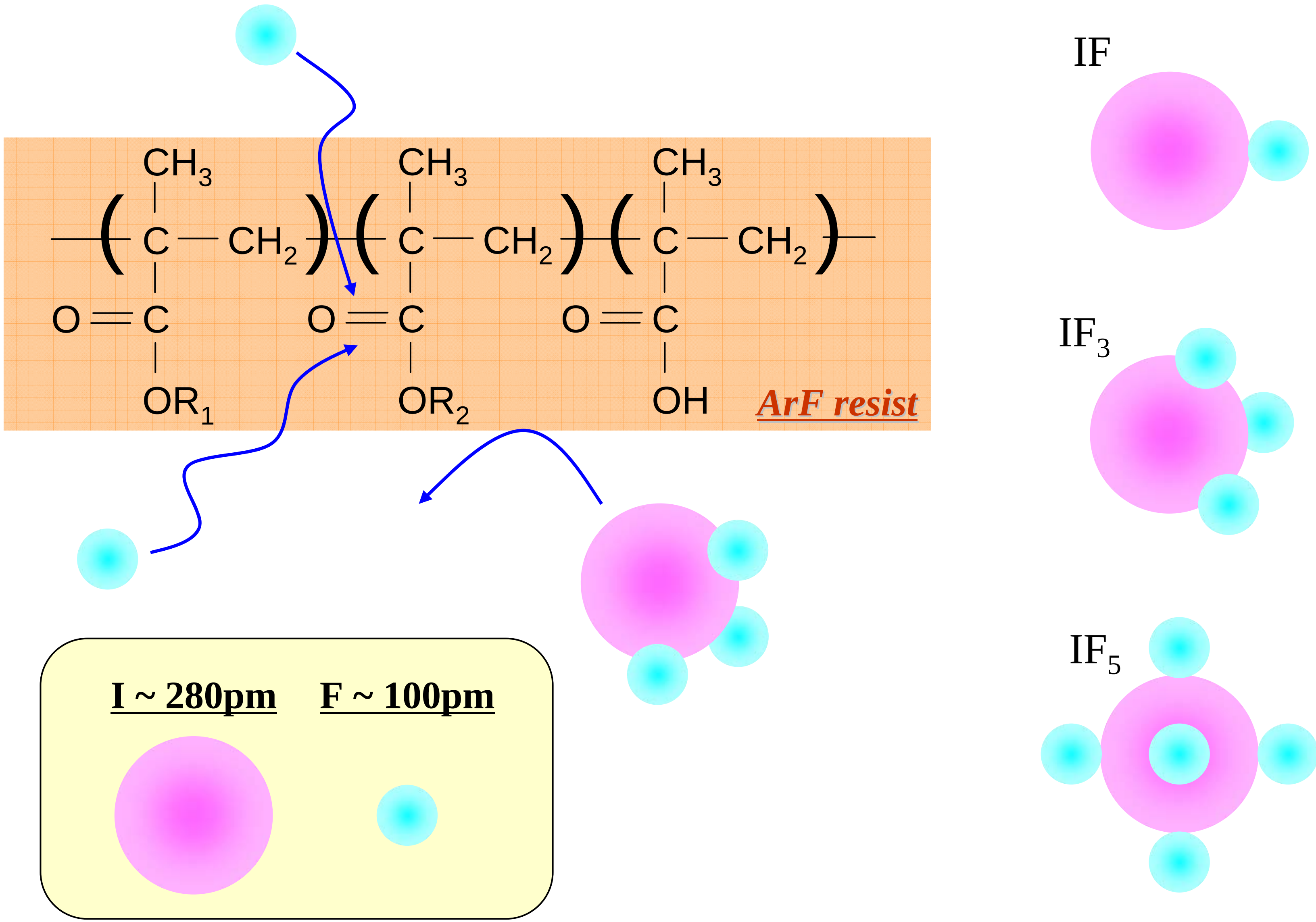
R :



Active F radicals attack C=O double bonds and degrade ArF photoresist.

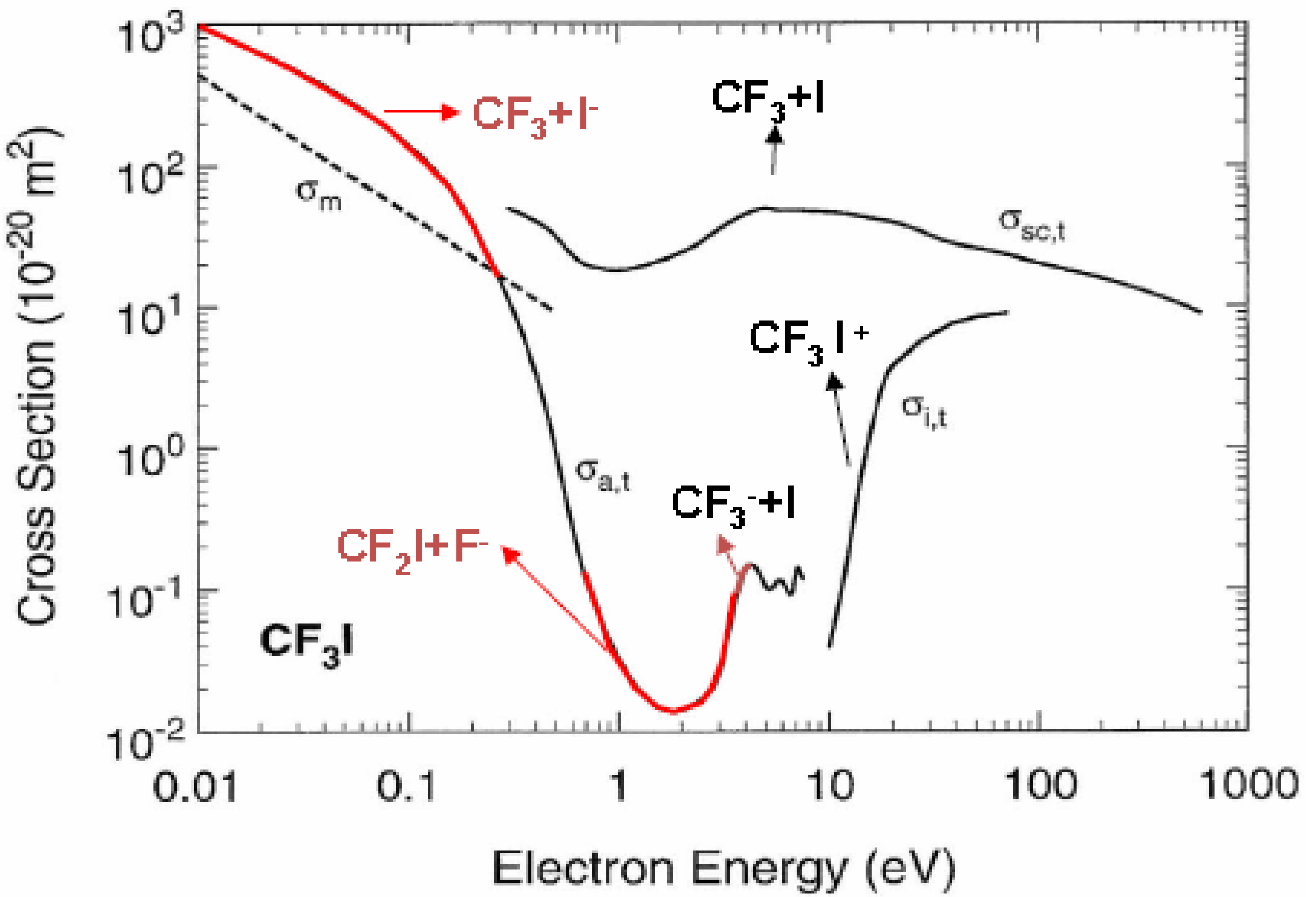
Striation

Proposed Solution Model



Proposed Solution Model

Interactions with Energetic Electron



L.G. Christphorou and J.K. Olthoff (2000)

Proposed Solution Model

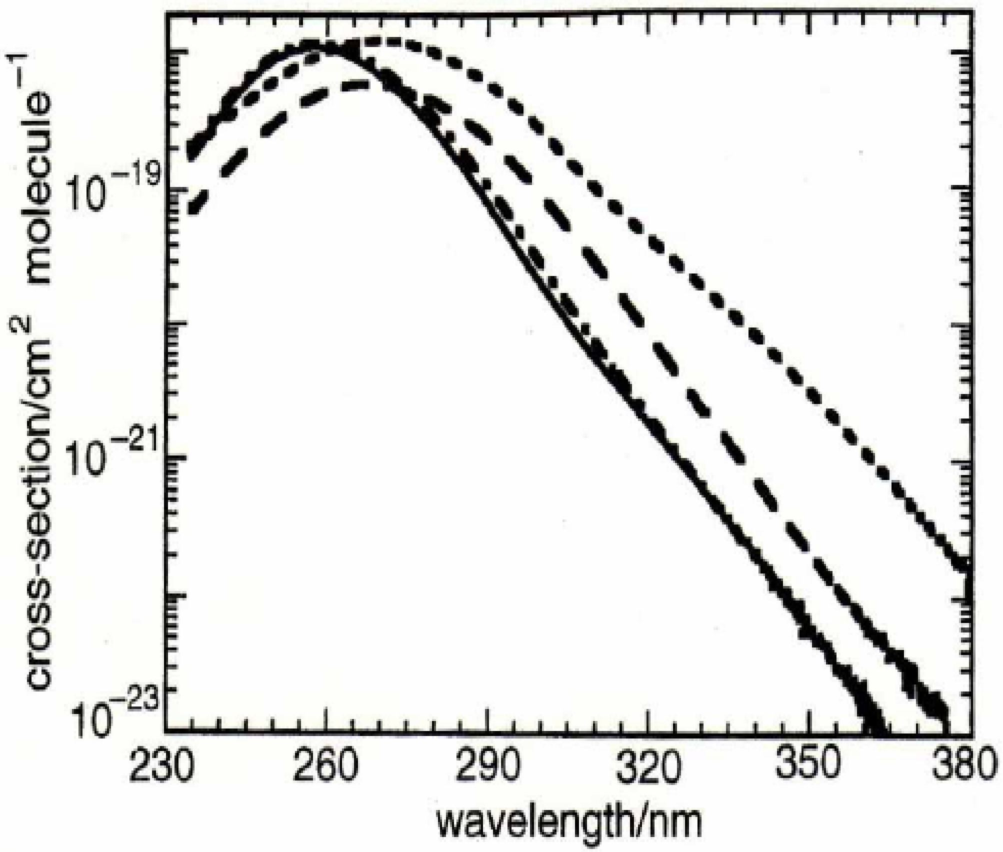
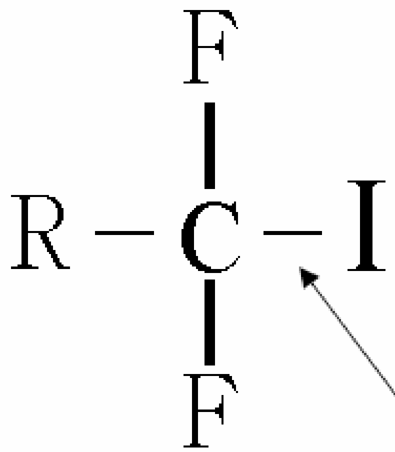


Fig. 1 UV absorption cross-sections (cm^2 molecule^{-1}) of CF_3I (– – –), CH_3I (——), C_2H_5I (– · –) and CH_2ICl (- - - -) over the wavelength range 235–400 nm with a spectral resolution of 0.6 nm (FWHM) at 298 K

O.V.Rattigan et al., (1997)

Proposed Solution Model



Broad UV absorption maximum at 270nm

$$CF_3I + h\nu \rightarrow CF_3 + I(^2P_{3/2})$$

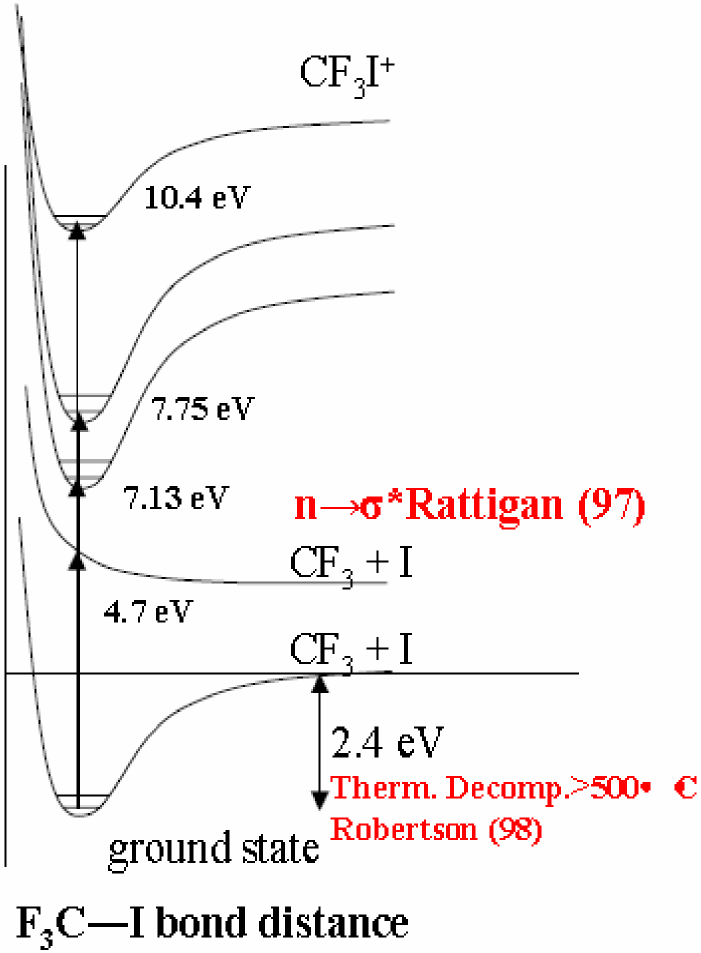
$$CF_3I + h\nu \rightarrow CF_3 + I^*(^2P_{1/2})$$

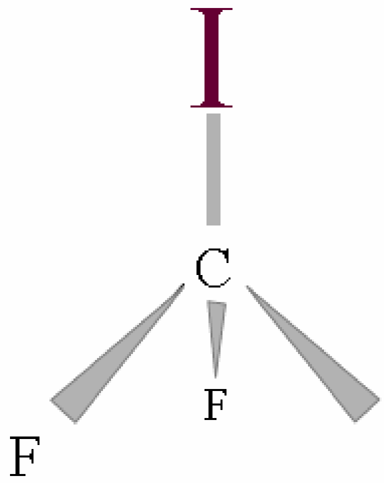
$$\left.\begin{array}{l} CF_3I \\ C_2F_5I \\ n\text{-}C_3F_7I \end{array}\right\}$$ have similarly broad absorption maximum at around 270nm.

O.V.Rattigan et al., (1997)

Proposed Solution Model

Electronic properties of CF_3I





Electron affinity ; ~1.5 eV
Proton affinity ; ~6.5 eV
Appearance energy
$CF_3I \rightarrow CF_3^+$ 10.9~11.36 eV
$CF_3I \rightarrow CF_2I^+$ 13.4~15.3 eV
$CF_3I \rightarrow I^+$ 13.4 eV

Herzberg; "Electronic spectra and structure of polyatomic molecules"

Proposed Solution Model

Reaction between I and F species

Reaction scheme	Temp. K	rate coefficient (cm^3/molecules· s)
$CF_3I + \cdot I \rightarrow \cdot CF_3 + I_2$	628 – 795	$1.26 \times 10^{-11}\ e^{-18.88/RT}$
$\cdot CF_3 + \cdot I \rightarrow CF_3I$	298	2.51×10^{-11}
$I_2 + \cdot F \rightarrow IF + \cdot I$	298	4.3×10^{-10}
$CF_3I + \cdot F \rightarrow \cdot CF_3 + IF$	283	1.62×10^{-10}
$Xe + \cdot F \rightarrow XeF$	298	1.1×10^{-32}

From NIST database

Proposed Solution Model

Electron collisions and Chemical reactions in the plasma

Electron collision process

CF_3I + e(<1 eV) → $CF_3 + I^-$
→ $CF_2I + F^-$

CF_3I + e(1>, <4 eV) → $CF_3^- + I$

CF_3I + e(~4 eV) → $CF_3 + I$

CF3I + e(>9 eV) → CF_3I^+
→ $CF_3^+ + I$
→ $CF_2I^+ + F$
.
.

CF_3 + e(>9.3 eV) → CF_3^+

Chemical reaction process

$CF_3I + F \rightarrow CF_3 + IF$

$I_2 + F \rightarrow IF + I$

$I + F \rightarrow IF$

$IF + I^- \rightarrow I_2F^-$

$I^- + F_2 \rightarrow IF_2^-$

$IF_2^- + F_2 \rightarrow IF_4^-$

$IF_2^- + F^+ \rightarrow IF_3$

$IF_4^- + F^+ \rightarrow IF_5$

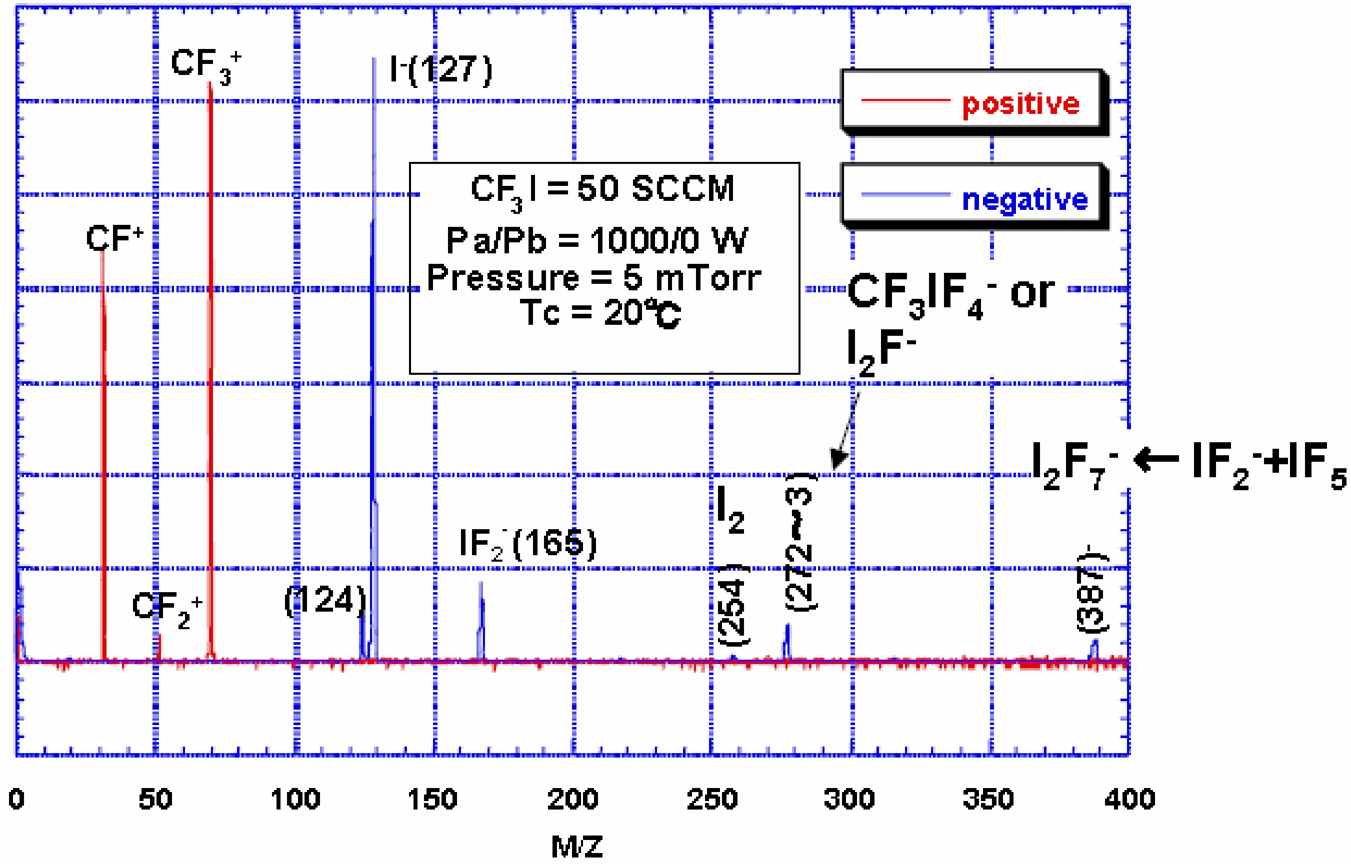
$I_2F^- + IF_5 \rightarrow I_2F_7^-$

(Red species denote observed or plausible ones in the plasma)

3rd Experiment

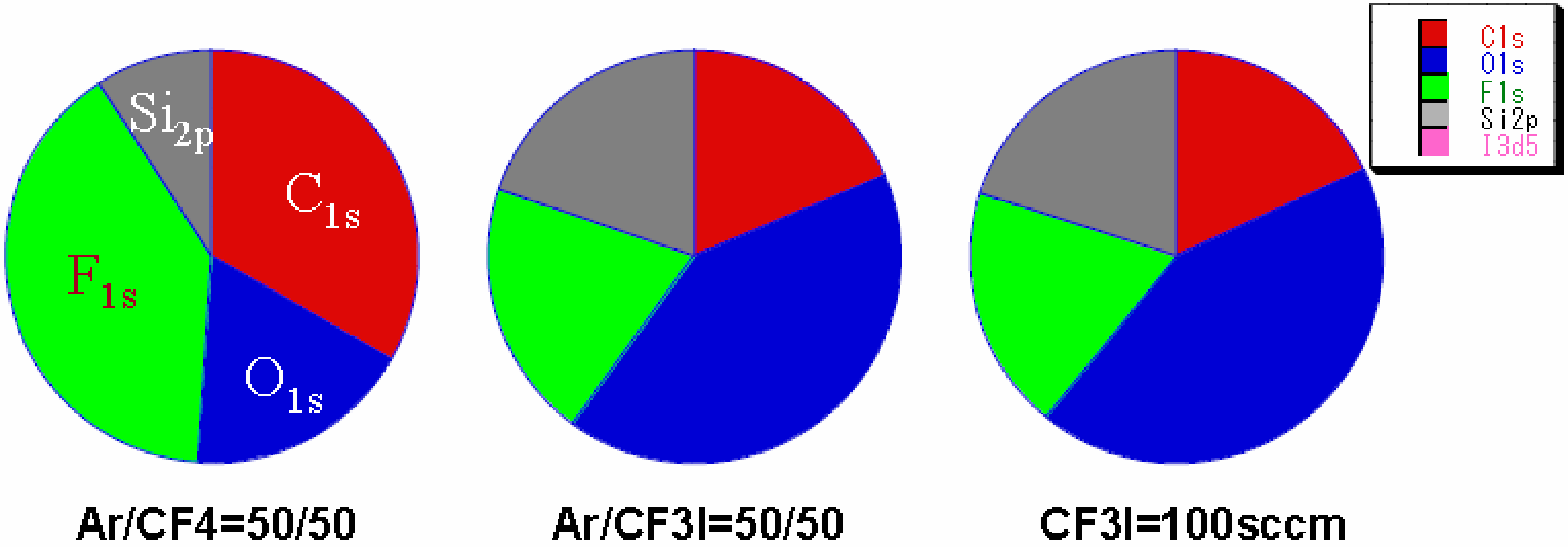
Observed positive and negative ions in the plasma

CF_3I



3rd Experiment

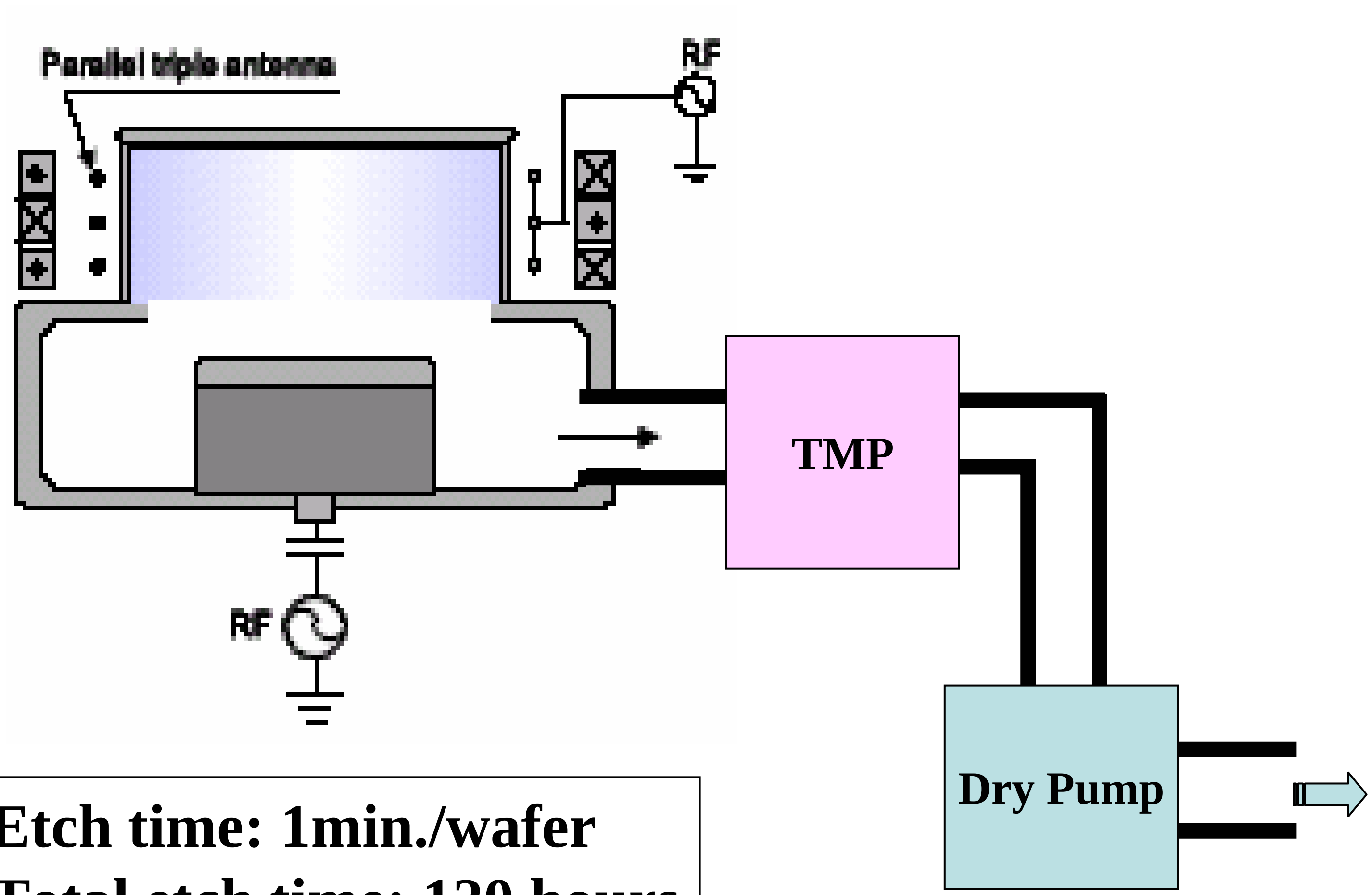
Residual species on an etched surface of porous SiCOH observed by XPS



	Ar/CF4=50/50	Ar/CF3I=50/50	CF3I=100sccm
C1s	33.3	18.7	18.0
O1s	17.8	41.4	43.0
F1s	39.7	20.1	19.0
Si2p	9.2	19.7	19.9
I3d5	0.02	0.07	0.09

4th Experiment

1. Equipment Set-up

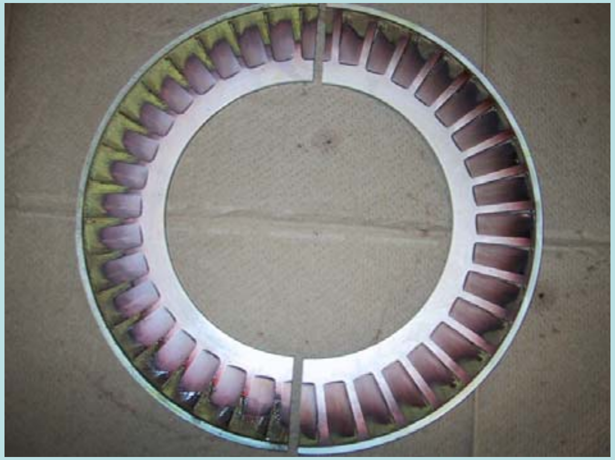


Etch time: 1min./wafer
Total etch time: 120 hours

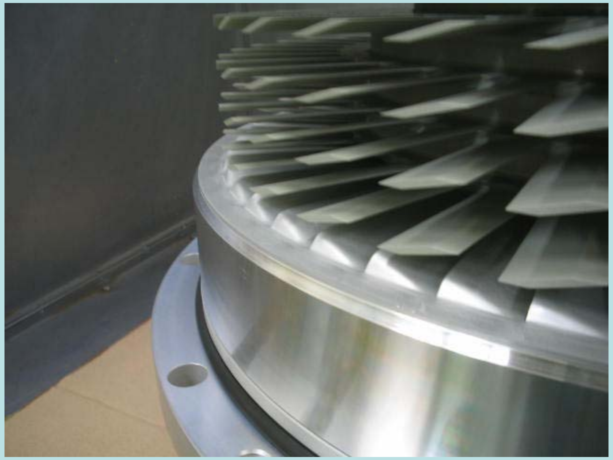
4th Experiment

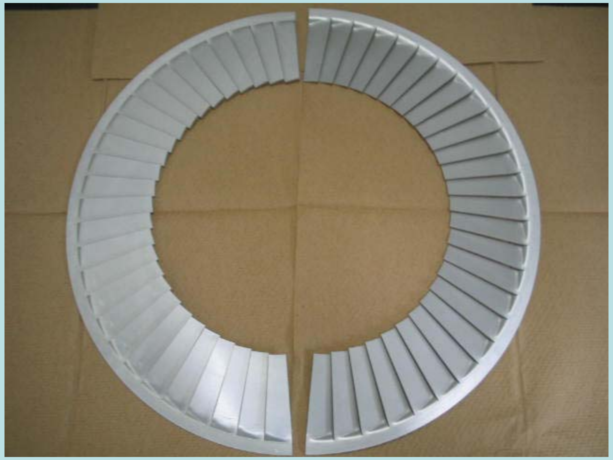
2. Results

After ITO etch by HI plasma



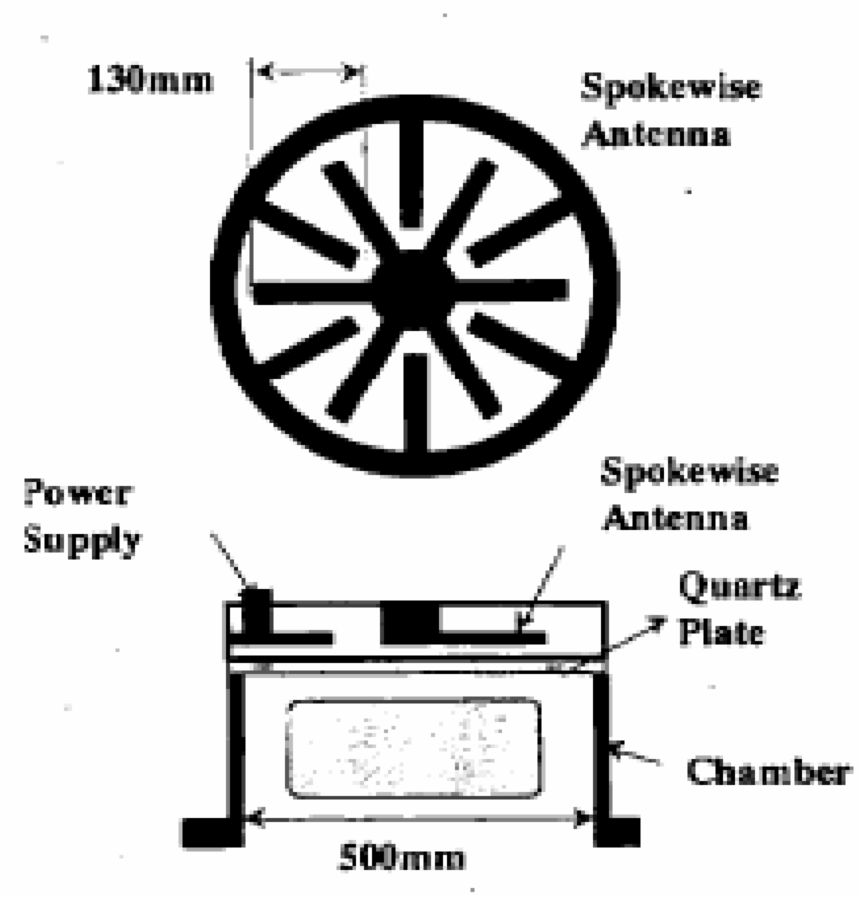
After SiO_2 etch by CF_3I plasma

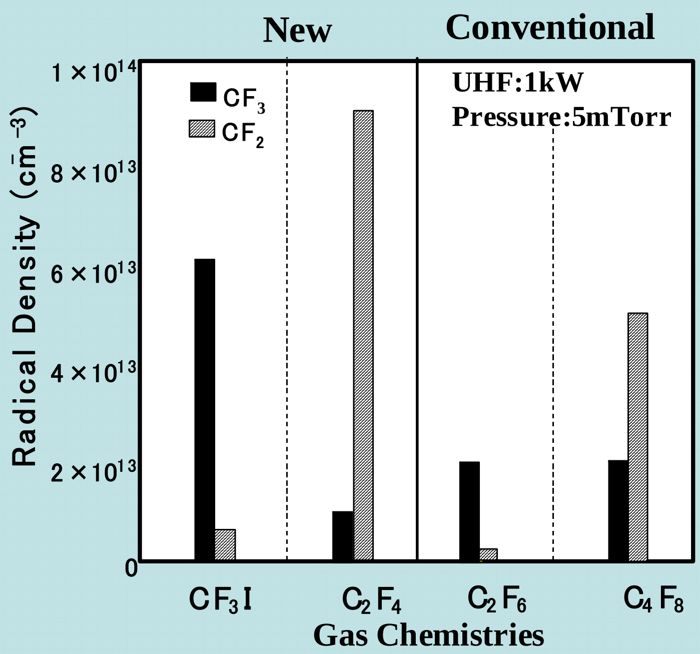




Historical CF_3I Etching Property

UHF Plasma Etcher





CF_3 and CF_2 radical density in CF_3I, C_2F_4, C_2F_6 and C_4F_8 UHF plasmas at the same discharge condition. CF_3I and C_2F_4 were good sources of CF_3 and CF_2 radicals, respectively.

GWP(CF_3I) < 1 , Biologically friendly

Seiji Samukawa and Tomonori Mukai (1999)

Philtech Inc.

Summary

1. CF_3I molecule is a very fragile compound and decomposed by electron attachment, electron excitation and UV excitation, and accordingly produces CF_3 radical and negative ions.

2. When CF_3I was used, ArF resist surface was not damaged. Also the etching tended to strongly ionic due to effective production of CF_3^+ ions.

3. Residual Iodine on the etched surface was not apparently observed by XPS spectra. This suggests that iodine is exhausted as iodine fluorides, not staying on the surface.

4. Iodine containing perfluoro carbon gas showed good gas evacuation & corrosive properties.

5. Therefore, iodine containing perfluoro carbon gas is the most promising candidate to etch ArF resist patterned wafers, combined with proper polymerizing additive gas.

6. Known Environmental & Biological Safety