#### ABATEMENT IN INDUCTIVELY COUPLED PLASMA REACTORS USING Q, H<sub>2</sub> AND H<sub>2</sub>O AS ADDITIVE GASES

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- Geometries of Etching Reactor and Burn Box
- Plasma Chemistry in Burn Box
- Validation
- Plasma Remediation of PFCs in Burn Box
- Concluding Remarks

#### INTRODUCTION

- Perfluorocompounds (PFCs), important process gases, are absorbers of infrared radiation having long atmospheric lifetimes and thus have high global warming potential.
- Since finding suitable substitutes for PFCs is unlikely, remediation of the effluent of plasma etching reactors must be done. Plasma remediation of gas emissions from plasma reactors is an attractive alternative abatement strategy.
- Efficient destruction of C<sub>2</sub>F<sub>6</sub> as found in reactor effluent by plasmas has been experimentally demonstrated in low pressure devices.
- Computer modeling is a useful tool for investigating the physical processes occurring in plasma remediation of PFCs. It supplements the experiments and will be used to optimize the development of plasma unit designs.
- 2-D simulations of low pressure plasma remediation of PFCs have been performed.

### PLASMA REMEDIATION FOR PFCS

 The effluent from the etching reactor having Ar/C<sub>2</sub>F<sub>6</sub> = 40/60, 200 sccm and 350 W power deposition is used as input for the burn box.

Ar	0.306	C <sub>2</sub> F <sub>6</sub>	0.289
CF3	0.173	CF <sub>2</sub>	0.057
C <sub>2</sub> F <sub>4</sub>	0.011	$C_2F_5$	0.020
SiF <sub>2</sub>	0.038	F	0.038
$F_2$	0.009		

Total flowrate is 227.7 sccm larger than the input flowrate due to dissociation.



- $\bullet$  Using H2 or H2O as an additive for PFC abatement, H and OH generated by electron impact dissociation become the primary species for abating CF\_X radicals.
- H<sub>2</sub> and H<sub>2</sub>O can also directly react with F, which thereby acts as a sink to remove free fluorine atoms which might otherwise recombine to form CF<sub>4</sub>.

$H + CF_3$	$CF_2 + HF$	$H + CF_2$	CF + HF
H+CF (	C + HF	H <sub>2</sub> + F	H + HF
OH + CF3	COF <sub>2</sub> + F	OH + CF <sub>2</sub>	COF + HF
OH + CF	CO + HF	OH + CO	CO <sub>2</sub> + HF
F + H <sub>2</sub> O	OH + HF		

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$H + CF_3$	$CF_2 + HF$	$H + CF_2$	CF + HF
H+CF (	C + HF	H <sub>2</sub> + F	H + HF
OH + CF3	COF <sub>2</sub> + F	OH + CF <sub>2</sub>	COF + HF
OH + CF	CO + HF	OH + CO	CO <sub>2</sub> + HF
F + H <sub>2</sub> O	OH + HF		

#### VALIDATION

- The model results were compared with the experimental results of Sawin and Vatile.
- The branching ratio for  $C_2F_6 + e$  negative ions significantly changes the formation of CF4.



#### PLASMA PARAMETERS IN BURN BOX

• A "standard" ICP burn box having a 2-turn coil with radius 4.25 cm and height 26.5 cm is used as a baseline.







#### CxFy ABATEMENT IN PLASMA BURN BOX

• CF<sub>2</sub>, CF<sub>3</sub>, C<sub>2</sub>F<sub>4</sub> and C<sub>2</sub>F<sub>5</sub> from the etching reactor effluent are almost completely removed in the burn box.



- Power: 500 W
- O<sub>2</sub> injection: 150 sccm Pressure: 150 mTorr
- Effluent: 227.7 sccm

# C<sub>2</sub>F<sub>6</sub> ABATEMENT AND CF<sub>4</sub> GENERATION

• C<sub>2</sub>F<sub>6</sub> in the etching reactor effluent is abated by 53%, but a significant amount of CF<sub>4</sub> can be generated (increased by a factor of 2.4).



• Power: 500 W

- Effluent: 227.7 sccm
- O<sub>2</sub> injection: 150 sccm
- Pressure: 150 mTorr

## OXIDATION PRODUCTS IN PLASMA BURN BOX

• The major oxidation products are CO, CO<sub>2</sub>, and COF<sub>2</sub> which can be removed by conventional methods.



## SPECIES DENSITY USING H<sub>2</sub> AS AN ADDITIVE

- Compared to the O<sub>2</sub> case, the electron density is increased by a factor of 2.4 due to the lower rate of attachment to H<sub>2</sub>.
- C<sub>2</sub>F<sub>6</sub>, CF<sub>3</sub>, and CF<sub>4</sub> are abated in the burn box.



## PRODUCTS USING $H_2$ AS AN ADDITIVE

- HF is the major product (0.49) leaving the burn box with lesser amounts of CF (0.094), C (0.074) and CF<sub>2</sub> (0.041).
- The higher mole fraction of CF and CF<sub>2</sub> compared to O<sub>2</sub> are due to there being insufficient H to reduce them to C.



- Power: 500 W
- H<sub>2</sub> injection: 150 sccm
- Effluent: 227.7 sccm

Pressure: 150 mTorr

## SPECIES DENSITY USING H<sub>2</sub>O AS AN ADDITIVE

• The electron density is higher than the base case with O<sub>2</sub> as an additive, but lower than for H<sub>2</sub>, due largely to the rate of attachment of H<sub>2</sub>O being between  $O_2$  and  $H_2$ .



500 W • Power: • H<sub>2</sub>O injection: 150 sccm • Pressure: 150 mTorr xxu\_avs99\_13

• Effluent: 227.7 sccm

## PRODUCTS USING H<sub>2</sub>O AS AN ADDITIVE

- Using H<sub>2</sub>O as an additive, the major products are HF, COF<sub>2</sub>, CO and C.
- The F atoms which were initially bound in all C<sub>x</sub>F<sub>y</sub> were converted to products in the proportions: HF, 59.8, and COF<sub>2</sub>, 40%. The carbon atoms initially bound in C<sub>x</sub>F<sub>y</sub> were converted to products in COF<sub>2</sub>, 63.3%; CO, 3.4%; C, 3.9%; and CO<sub>2</sub> 1.4%.



## ABATEMENT USING O<sub>2</sub>, H<sub>2</sub>, OR H<sub>2</sub>O AS AN ADDITIVE

 Abatement of each C<sub>x</sub>F<sub>y</sub> species and total PFC species, primary products, W value of all C<sub>x</sub>F<sub>y</sub> using 150 sccm O<sub>2</sub>, H<sub>2</sub>, or H<sub>2</sub>O as additives at 500 W

Species	Fractional Abatement for Additives		al - Final Initial
	O <sub>2</sub> Additive	H <sub>2</sub> Additive	H <sub>2</sub> O Additive
C <sub>2</sub> F <sub>6</sub>	0.53	0.54	0.73
C <sub>2</sub> F <sub>5</sub>	>0.99	-0.47	0.37
C <sub>2</sub> F <sub>4</sub>	>0.99	-2.71	-0.31
C <sub>2</sub> F <sub>3</sub>	>0.99	0.22	0.35
CF4	-1.4	0.23	0.04
CF3	>0.99	0.96	0.98
CF <sub>2</sub>	>0.99	-0.4	0.05
Products	COF <sub>2</sub> , CO <sub>2</sub> , CO, F, F <sub>2</sub>	HF, , C, CF	HF, COF <sub>2</sub> , CO <sub>2</sub> , CO, C, CF
of C <sub>X</sub> Fy	0.54	0.42	0.65
W Value (ev)	124.9	159.8	119.3

# FRACTION OF C<sub>X</sub>F<sub>y</sub> ABATEMENT

• The fraction of C<sub>x</sub>F<sub>y</sub> abatement increases with increasing power deposition and the amount of addictive gases.



• The W-value increases (lower power efficiency) with increasing power deposition decreasing the amount of addictive gases.



- The model was validated by comparison to experiments using O<sub>2</sub>/C<sub>2</sub>F<sub>6</sub>.
- PFCs from plasma etching effluent can be efficiently destroyed in ICP burn box.
- In general, CF<sub>4</sub> generation occurs during abatement of C<sub>2</sub>F<sub>6</sub> using O<sub>2</sub> as an additive. The major oxidation products are COF<sub>2</sub>, CO and CO<sub>2</sub>.
- H<sub>2</sub> can be used as an alternative to O<sub>2</sub> without producing CF<sub>4</sub> since hydrogen reacts rapidly with free fluorine which otherwise reassociates with CF<sub>x</sub>to form CF<sub>4</sub>. F and C atoms initially contained in C<sub>x</sub>F<sub>y</sub> were converted to HF and C.
- H<sub>2</sub>O is a promising and efficient abatement additive gas since it has a source of both oxygen and hydrogen. The primary products are HF, CO, COF<sub>2</sub> with a small amount of C and CO<sub>2</sub>.