Processing of Model Dielectric Polymers: Parylenes

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Vision

- Develop environmentally-friendly, vapor-deposited photoimageable dielectric polymers for microelectronic, biomaterial applications
  - Packaging
  - MEMS, BioMEMS
  - Interconnect processing
- Perform proof-of-concept experiments
- Develop fundamental process models for industry use in optimizing polymer applications

Significance of Research

- Environmentally acceptable patterning, deposition
  - CO_2, H_2O, (HCl) are by-products of oxygen plasma etch
  - Vapor deposition eliminates solvent waste
- Characteristics
  - Parylene-N dielectric constant ~2.7
  - Well suited for packaging, MEMS, interconnect
    - ⇒ patternable
    - ⇒ thermally stable
- Biocompatible
  - Parylenes well-tolerated *in vivo*
    - ⇒ parylene-C leading biomaterial
  - BioMEMS

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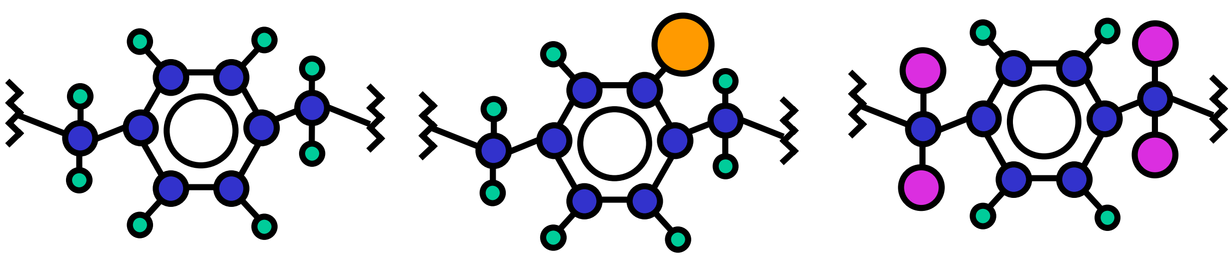
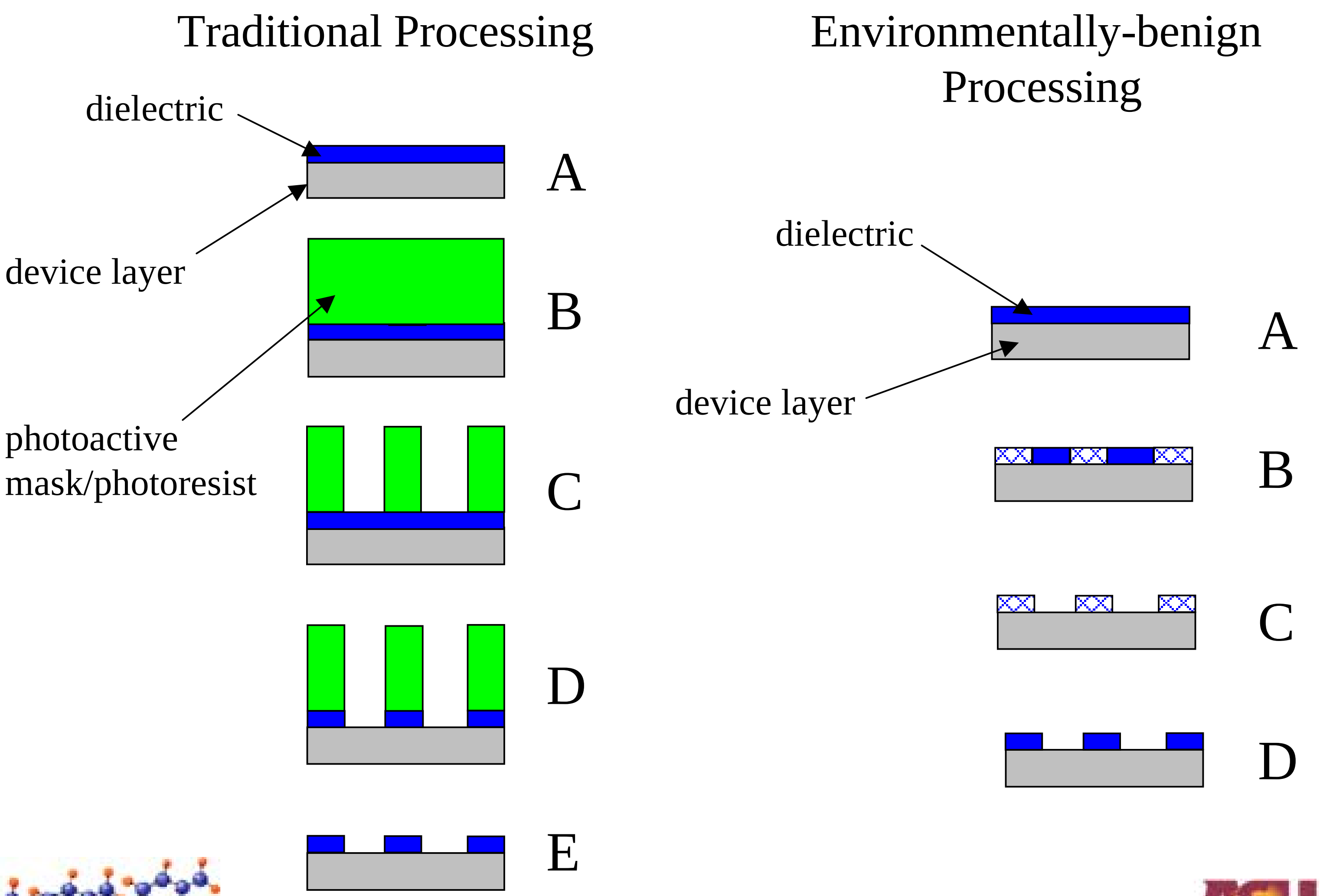
Parylene Comparison

Property	Parylene-N	Parylene-C	Parylene AF-4
Dielectric constant	2.65	2.95	2.28
Water vapor transmission *	1.50	0.14	N/A
Melting point [°C]	410	290	510

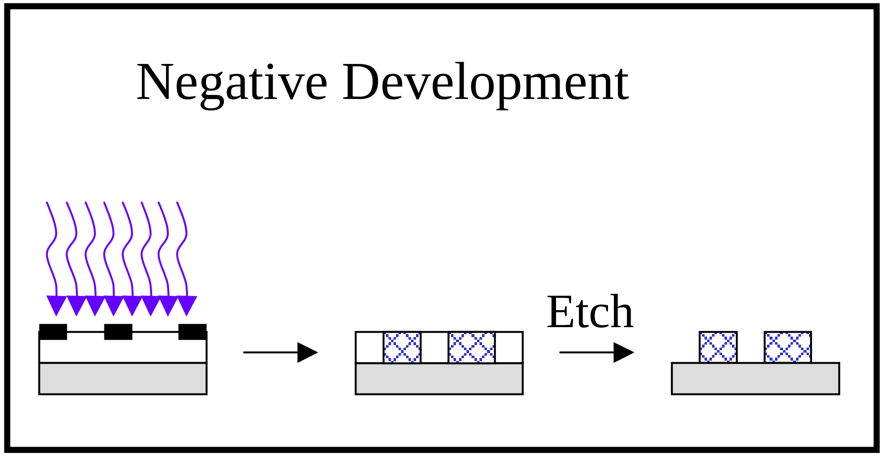
* [mol/100 in^2 in 24hr, 37ºC, 90% RH]

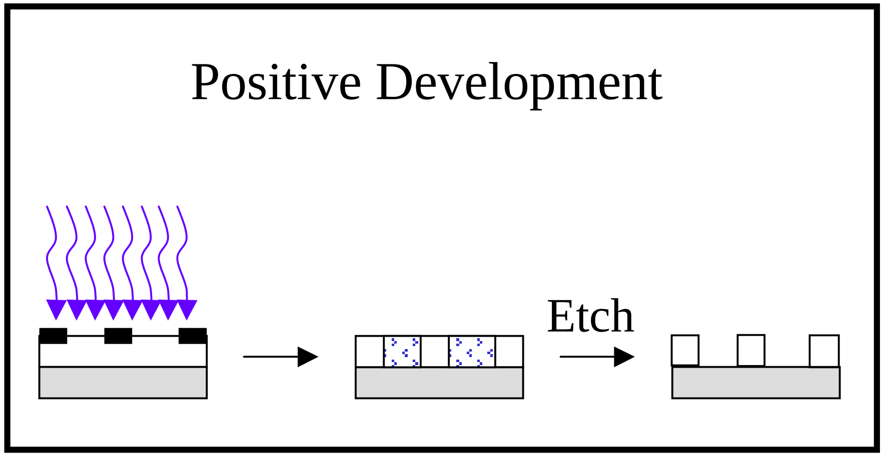


Example: Microelectronic Processing With Directly Photoimageable Dielectric



Patterning of Parylene





- Crosslinking
  - UV light, absence of oxygen → crosslinking
- Chain scission
  - UV light, oxygen ambient → chain scission

Scope of Work

- Experimental
  - measure chain scission
  - evaluate oxygen incorporation as a function of dose
  - determine how oxygen is incorporated into film
- Modeling
  - propose chain scission mechanism
  - evaluate rates of chain scission
  - model chain scission from a first-principles perspective

Experimental Methods

- Exposure
  - UV germicidal lamp (peak output 253.7 nm)
    - ⇒ located ~ 5 inches above sample
  - environment
    - ⇒ air for chain scission
    - ⇒ N_2 for crosslinking
  - samples
    - ⇒ parylene-N and parylene-C coated Si wafer coupons
- Measurement of oxygen incorporation
  - RBS (surface)
  - SIMS (depth profiles)
- Determination of oxygenated structures
  - FTIR
- Concentration of available active sites
  - RBS
  - XRD

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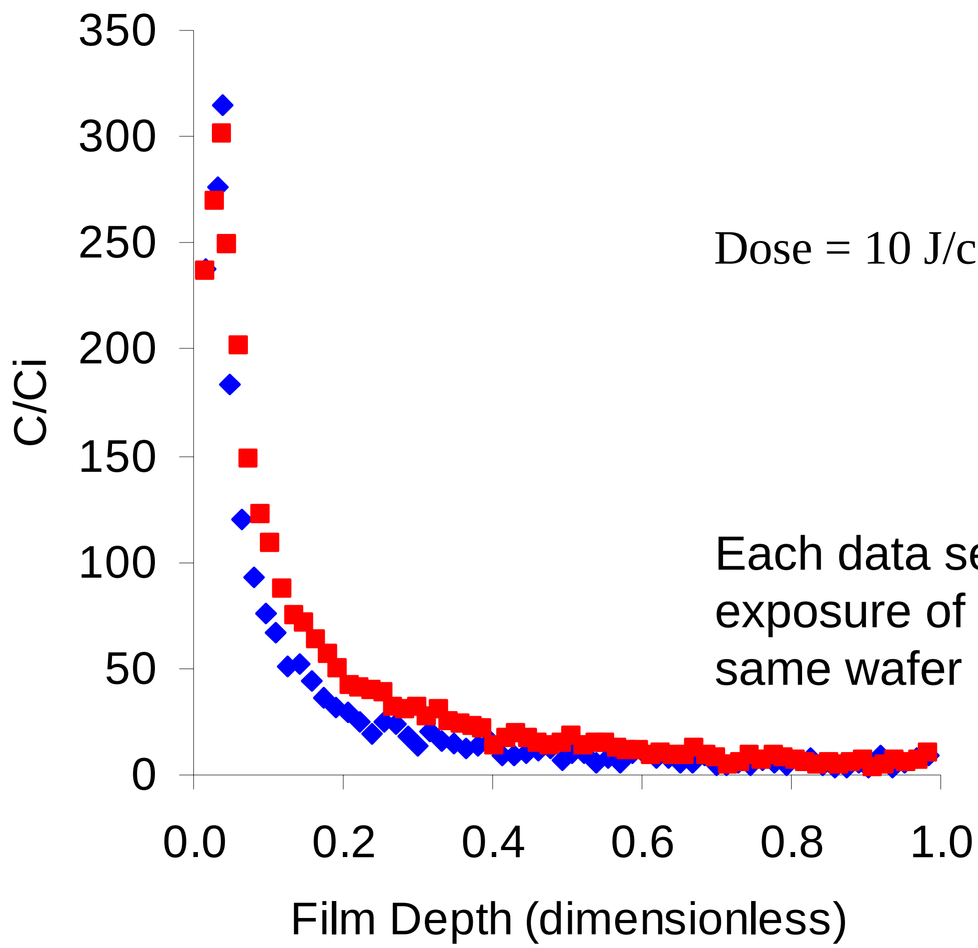
Depth Profile: Atomic Oxygen Incorporation into Film

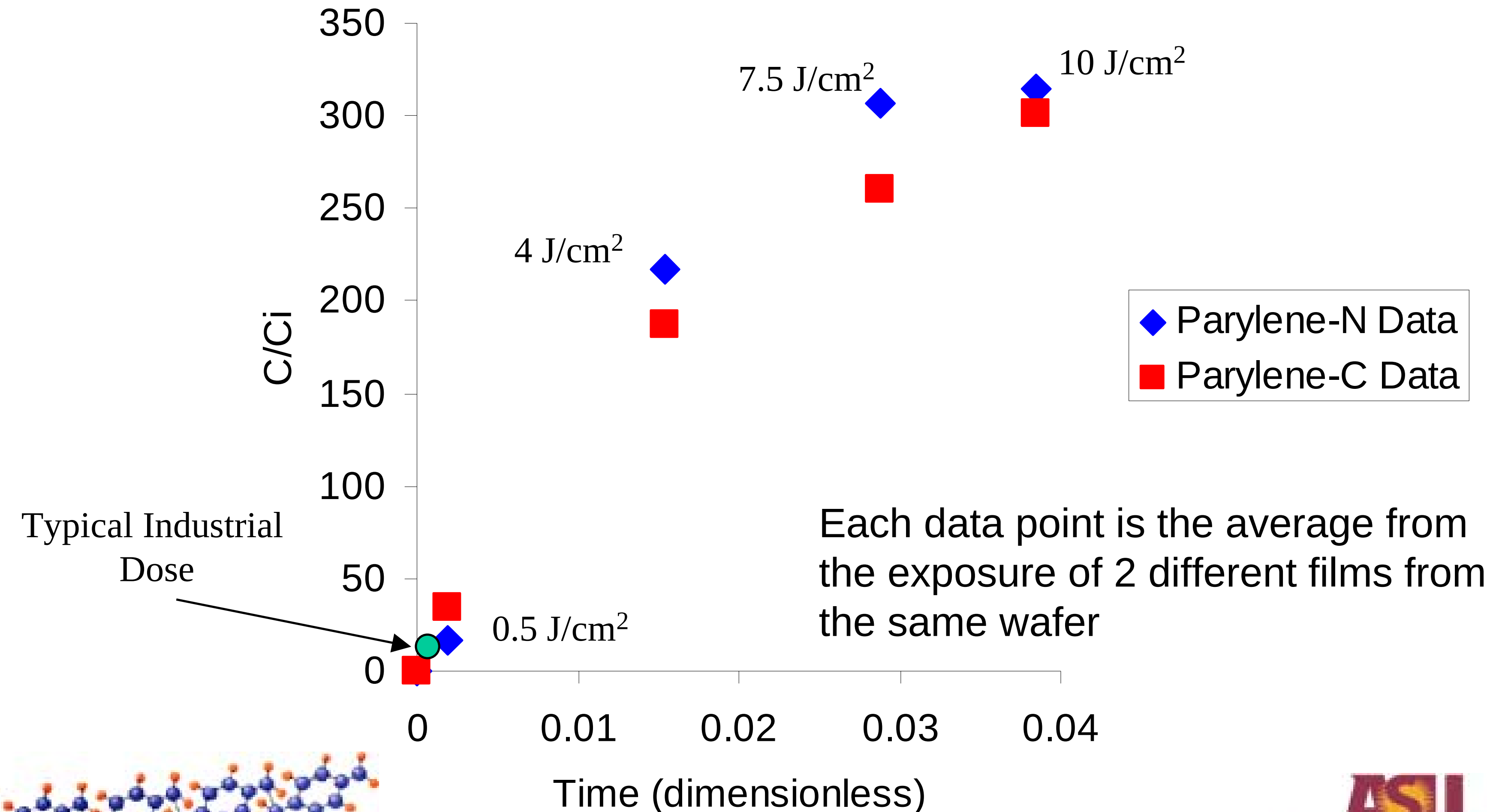


Each data set is the average from the exposure of 2 different films from the same wafer

Error = ~$\underline{+}$50 dimensionless concentration units calculated from error in RBS

Atomic Oxygen Incorporation at Film Surface

Film surface is top 10% of film



1st Generation Model: Chain Scission

Initiation

$PH \rightarrow P\cdot + H\cdot$

Propagation

$P\cdot + O_2 \rightarrow PO_2\cdot$ (rate limiting)

$PO_2\cdot + PH \rightarrow PO_2H + P\cdot$

$PO_2H \rightarrow PO\cdot + \cdot OH$

$PO\cdot \rightarrow A + P\cdot$

$A + P\cdot \rightarrow A\cdot + PH$

$A + \cdot OH \rightarrow A\cdot + H_2O$

$A + PO_2\cdot \rightarrow A\cdot + PO_2H$

$A\cdot + \cdot OH \rightarrow CA$

Termination

$2P\cdot \rightarrow PP$ (Low O_2)

$2PO_2\cdot \rightarrow PO_2PO_2$ (High O_2)

- Our system
  - Propagation is rate limiting
  - Rate of initiation depends on light absorbance which is governed by Beer's Law
  - Only chain PH bonds participate in reaction
  - Termination mechanism depends on oxygen concentration
    - ⇒ low concentration → subatmospheric
  - IR showed aldehyde groups produced instead of carboxylic acids

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Model Equations

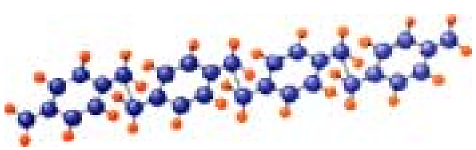
$$\frac{\partial \Omega}{\partial \tau} = \frac{-L^2 k_1 I_o (1 - e^{-aY\psi})\Omega}{D} - \frac{D_a C_i \xi \Omega^{1/2} (1 - e^{-aY\psi})^{1/2}}{[PH_o]}$$

$$\frac{\partial \xi}{\partial \tau} = \frac{L^2}{Y^2}\frac{\partial^2 \xi}{\partial \psi^2} + \frac{\partial^2 \xi}{\partial \alpha^2} - D_a \xi \Omega^{1/2} (1 - e^{-aY\psi})^{1/2}$$

$$\frac{\partial \lambda}{\partial \tau} = D_a \xi \Omega^{1/2} (1 - e^{-aY\psi})^{1/2}$$

$$D_a = \frac{L^2 k I_o^{1/2} [PH_o]^{1/2}}{D}$$

ξ = molecular oxygen concentration
λ = atomic oxygen concentration
Ω = available reaction site concentration
τ = time
Ψ = film depth
α = film width
C_i = initial molecular oxygen concentration
Y = maximum film thickness
L = maximum film width
k = combined reaction rate constant
k_1= initiation reaction rate constant
I_o = incident dose
a = light absorbance
$[PH_o]$ = initial reaction site concentration



Model Parameters

Initial Oxygen Concentration (mol/cm^3)	**$7x10^{-5}$**
Combined Rate Constant ($cm^{5/2}/mW^{1/2}mol^{1/2}$-s)	**$1.43x10^{5}$**
Combined Initiation Rate Constant (cm^2/mW-s)	**$1x10^{-3}$**
Initial Reaction Site Concentration (mol/cm^3)	**$2.4x10^{-2}$**
Diffusion Coefficient (cm^2/s)	**$1x10^{-7}$**
Damköhler Number	**$7x10^{9}$**

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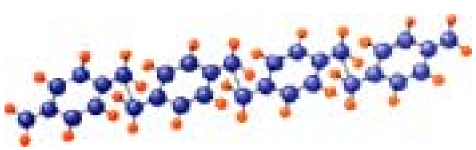
Diffusion and Reaction in Parylene

- Diffusion mechanisms
  - thick films
    - ⇒solution-diffusion
    - ⇒predict diffusion constant based on time lag method
  - thin films (< 8μm)
    - ⇒pore flow + solution-diffusion
    - ⇒predicted diffusion coefficients do not apply
    - ⇒permeability can change up to several orders of magnitude as film thickness decreases
- Available reactive sites
  - crystallinity
    - ⇒only amorphous sections can be penetrated by diffusing oxygen
    - ⇒parylene-N is typically crystalline
    - ⇒our films were 32% crystalline
      - validated at ASU with XRD
  - chain length distribution
    - ⇒no evidence that C/H ratio was non-ideal
    - ⇒polymer consists of long chains



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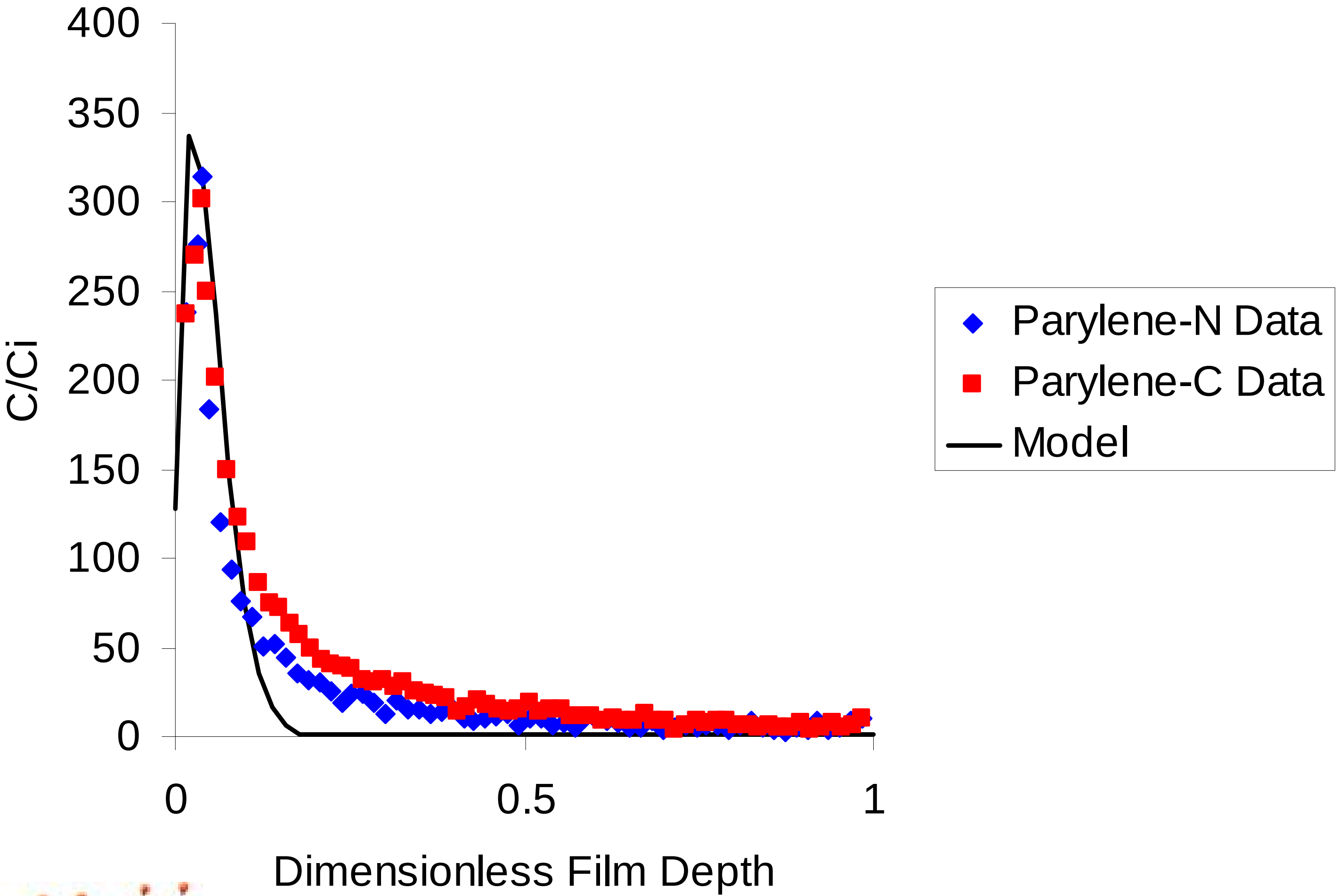
Model Validation: Atomic Oxygen Incorporation into Film



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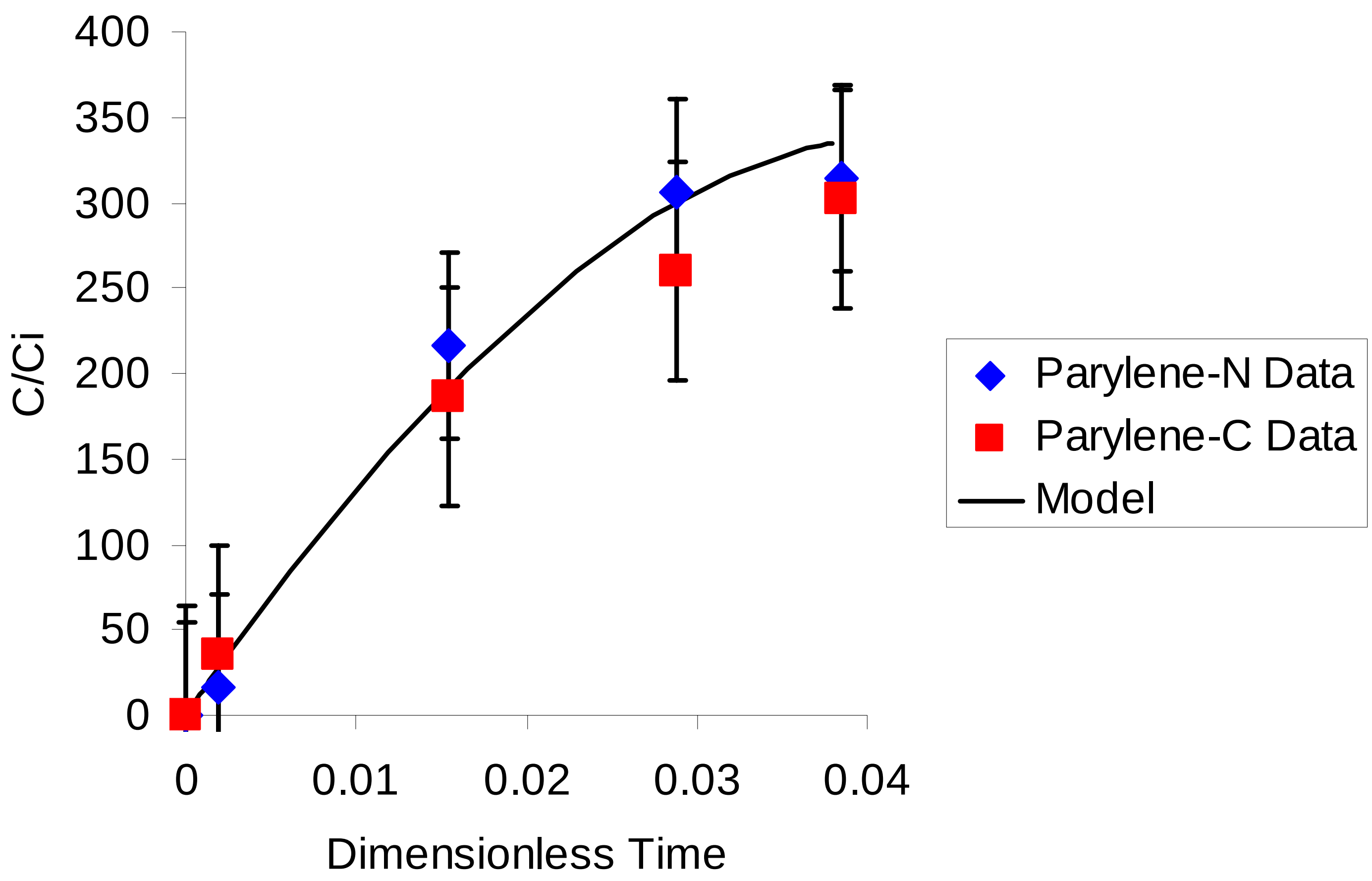
Model Validation: Atomic Oxygen Incorporation at Film Surface



Conclusions

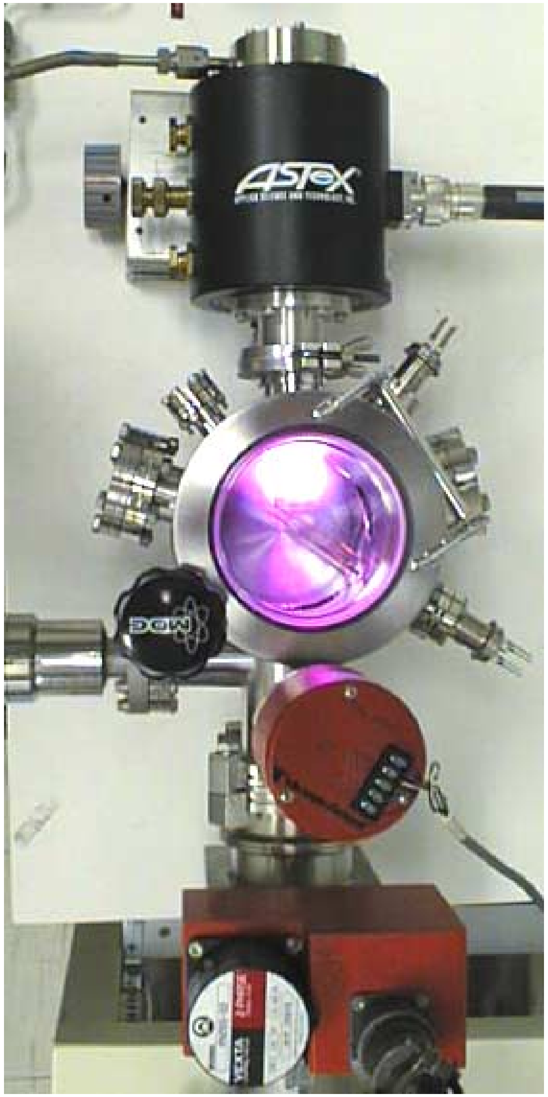
- Observed that parylene-C undergoes chain scission at the same rate as parylene-N
  - suggests oxygen incorporation/chain scission through chain carbons
- Model correctly predicts experimental observations
  - depth profile and saturation behavior
- Future work
  - examine dependence of chain scission rate on initial oxygen concentration and temperature

Research Goals: Parylene Etching

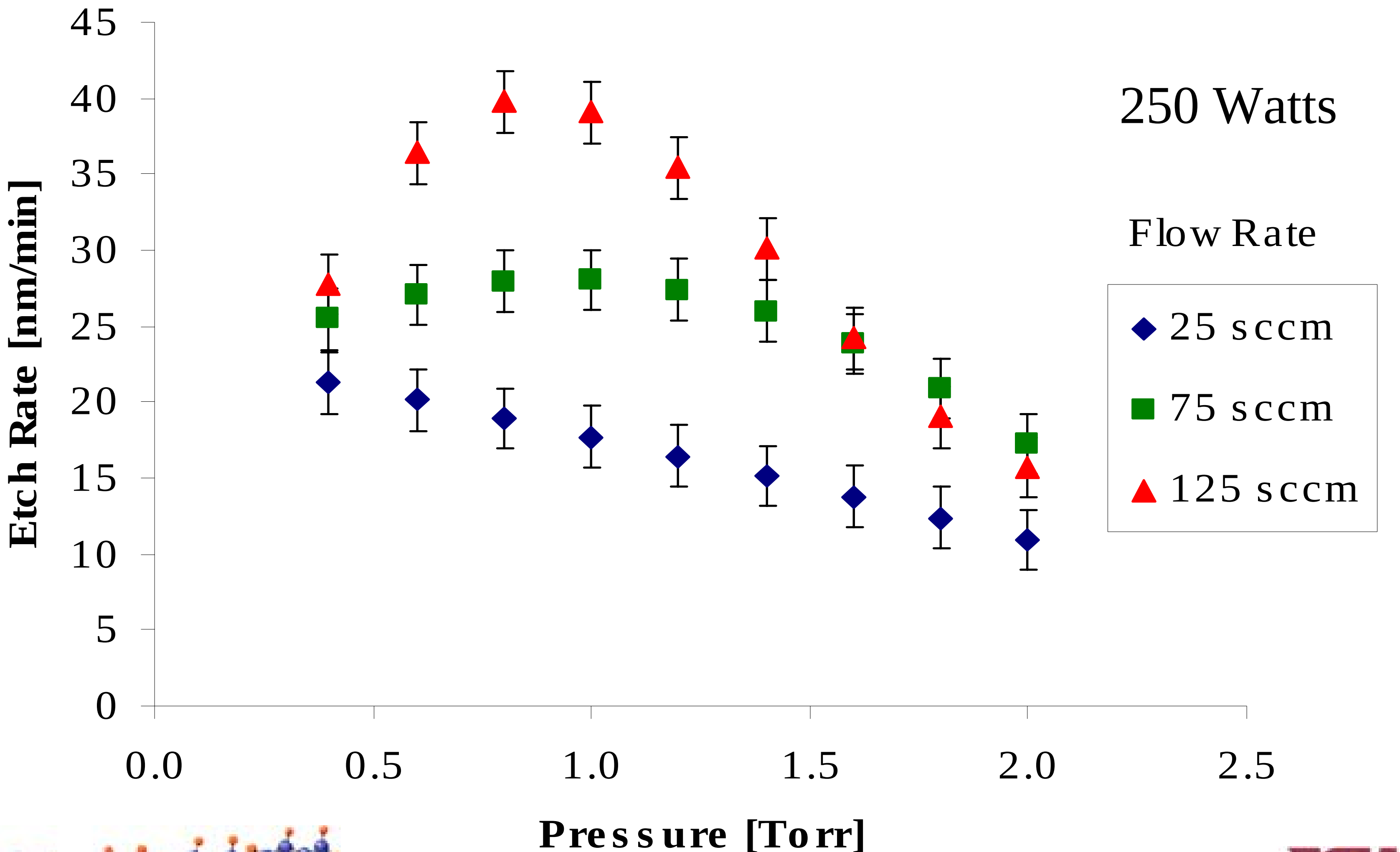
- Investigate effects of process variables on etch performance
  - Temperature
  - Pressure
  - Total gas flow
- Develop experimentally-validated transport and reaction models
- Develop mechanistic description of etching
- Used to develop processing and integration protocols for parylene use

Downstream Etching Apparatus

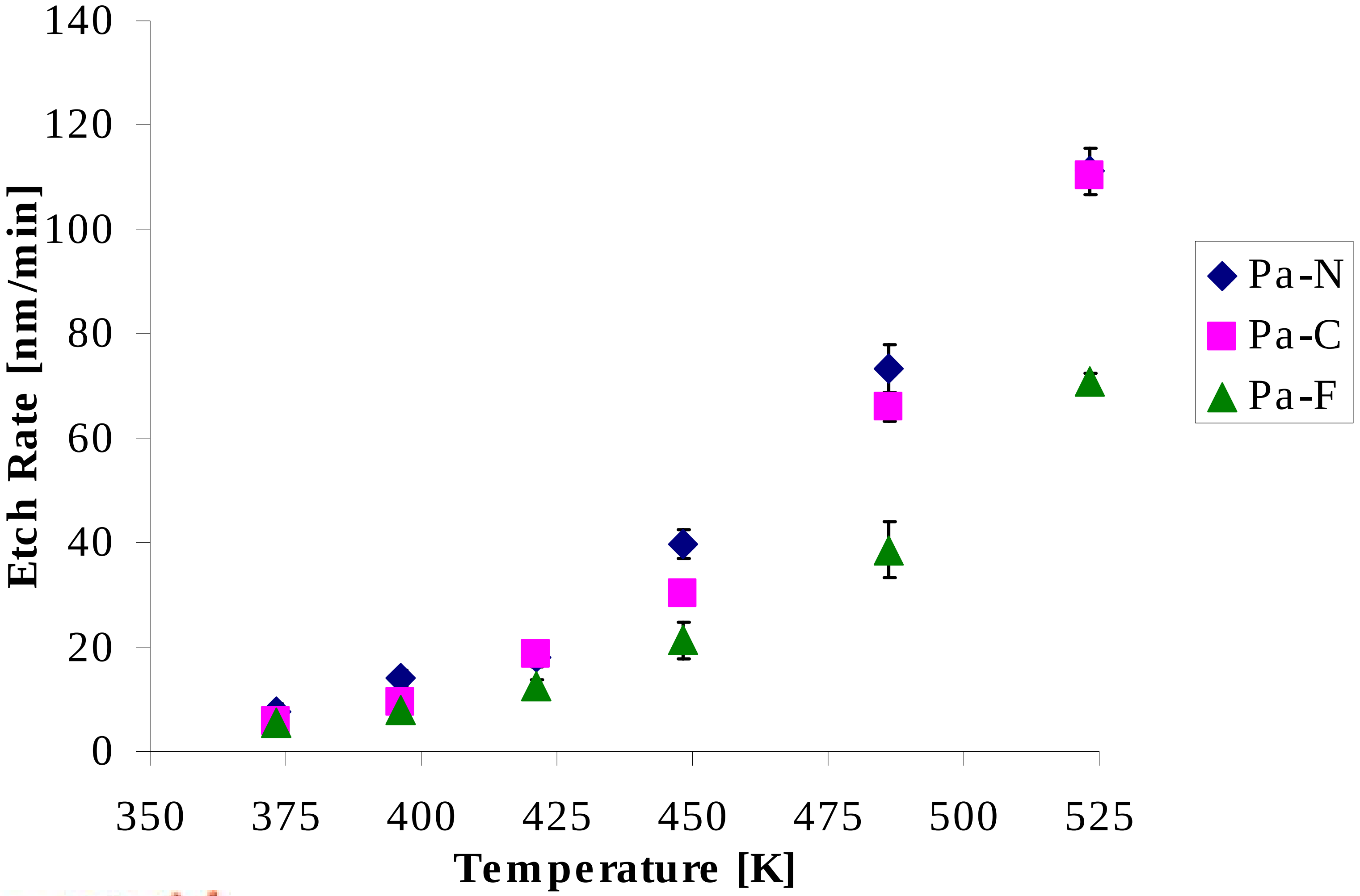
- 250 W Astex microwave generator to create downstream oxygen plasma
- Base pressure = 4×10^{-7} Torr
- Temperature controlled substrate holder



Experimental Results: Etch Rate as a Function of Pressure and Flow Rate



Comparison of Parylene Etch Data



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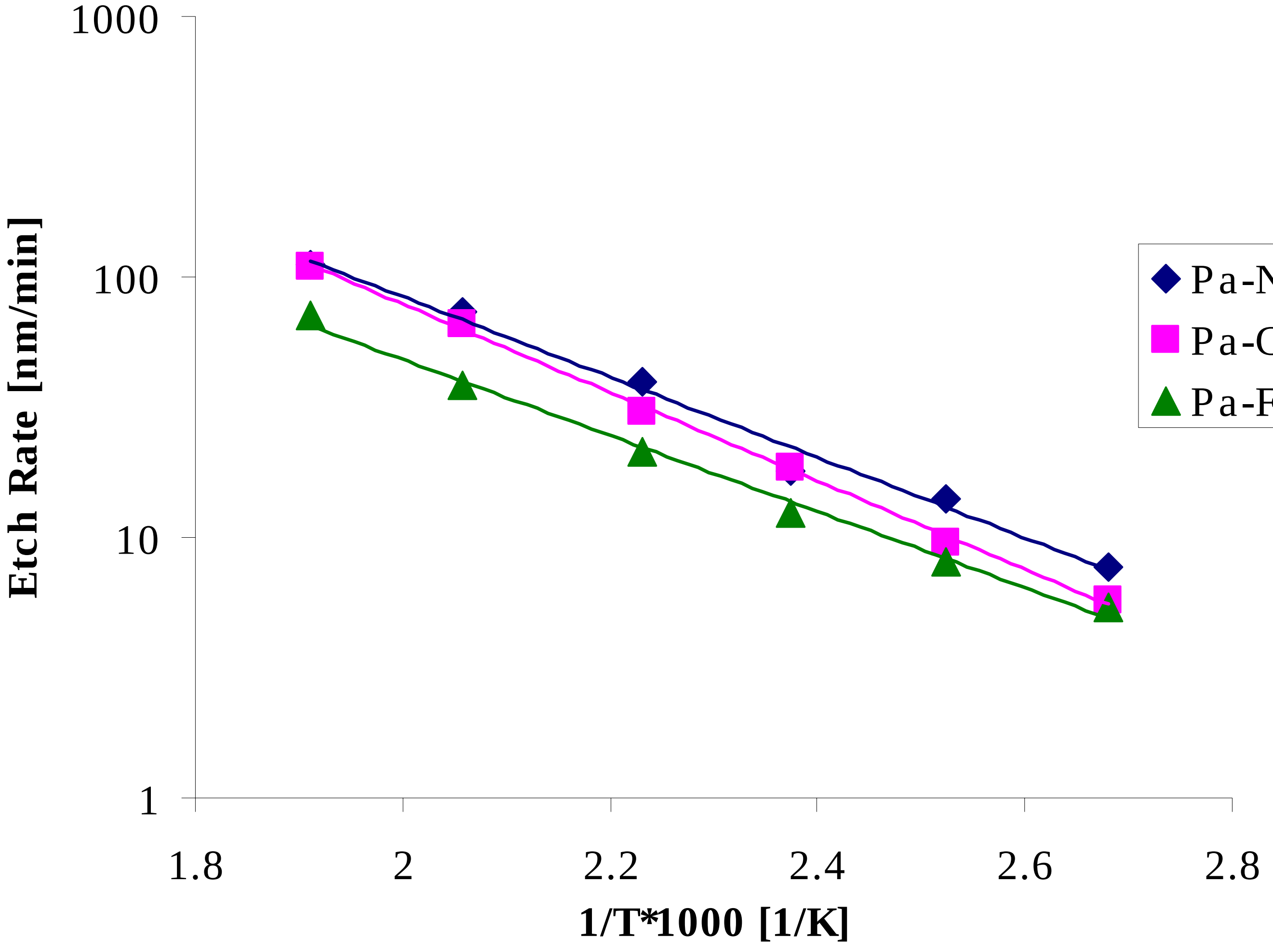
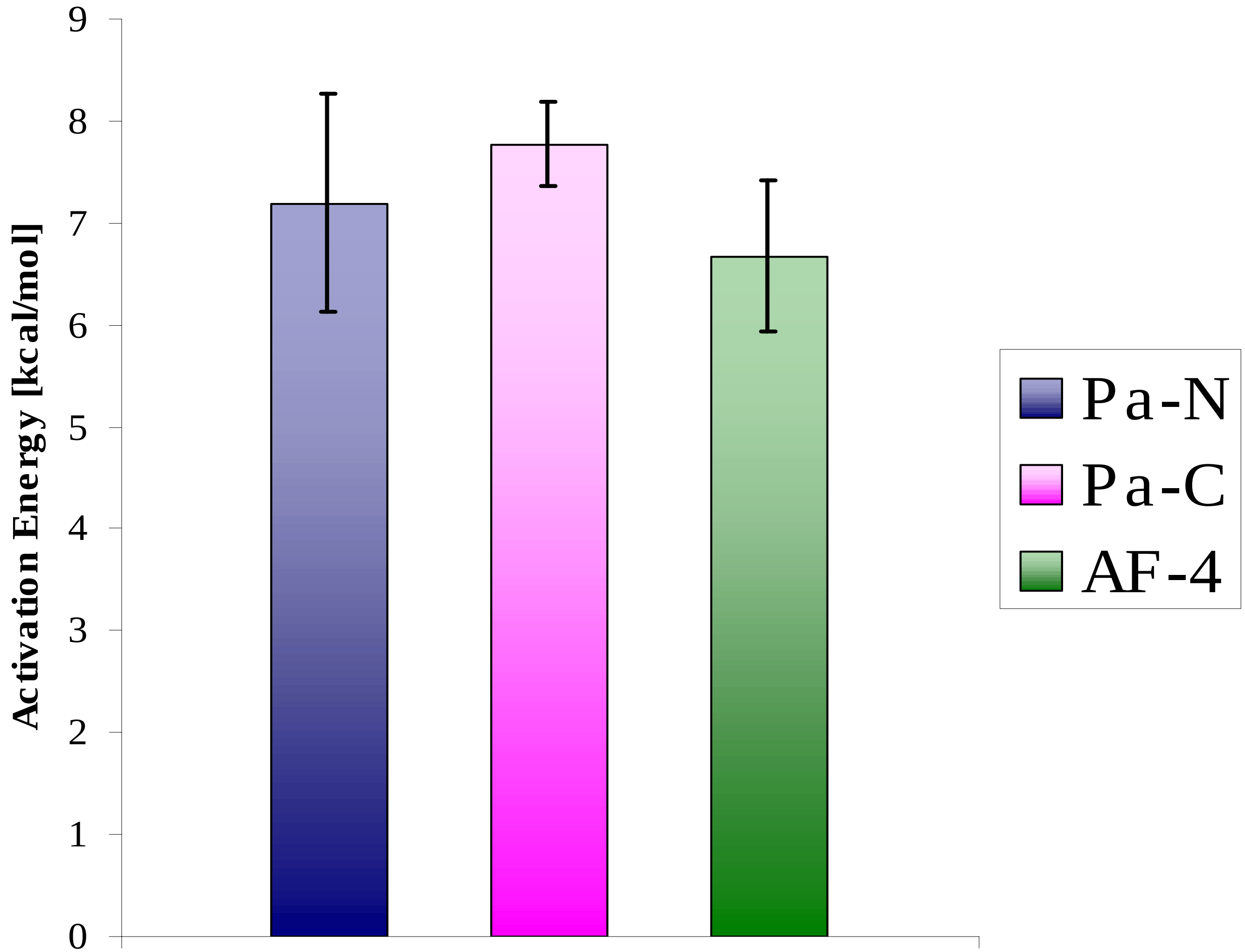
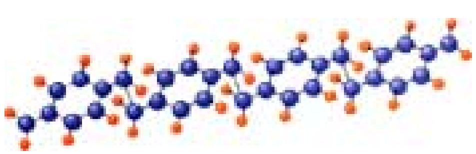
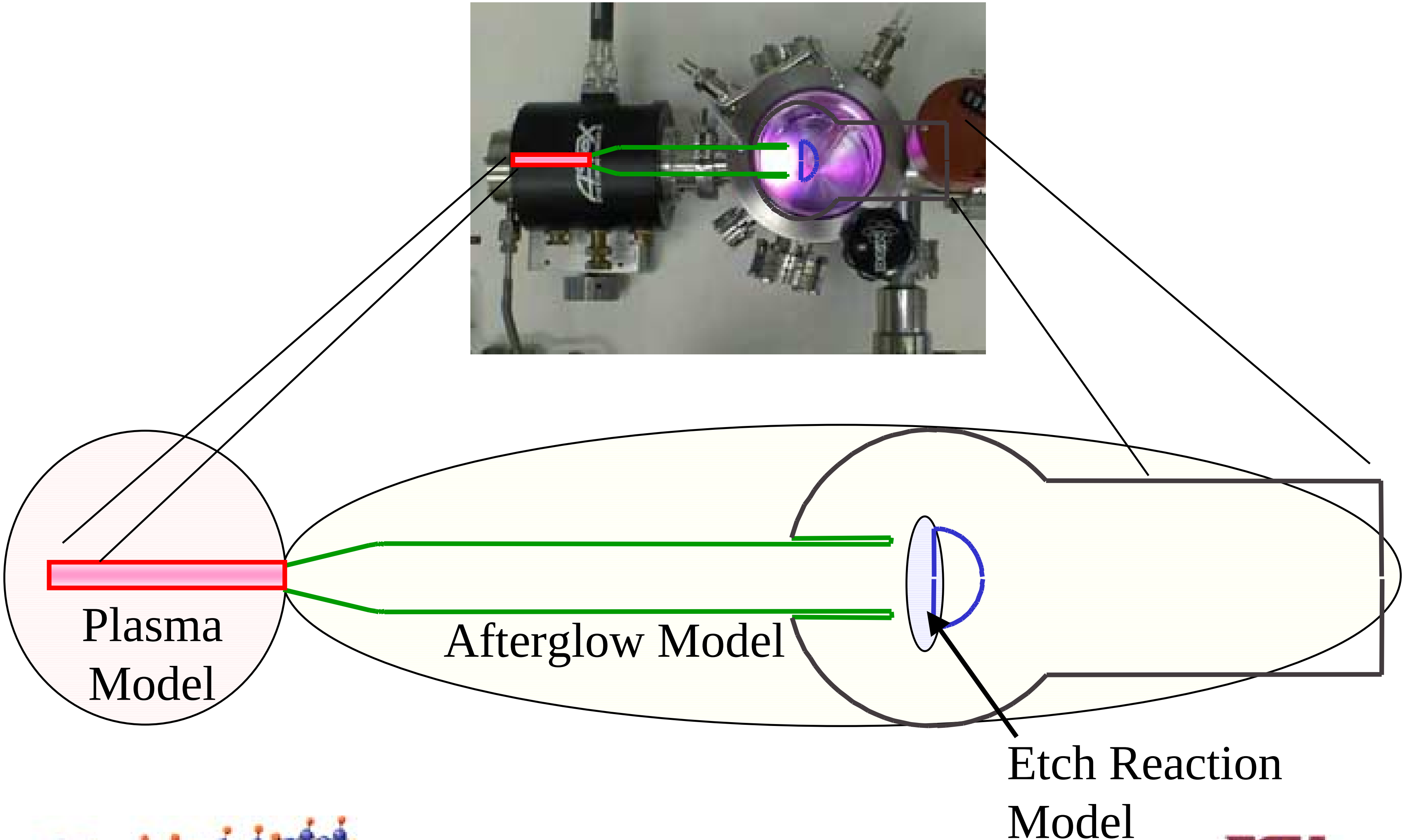


Activation Energies





Downstream Plasma Etch Model



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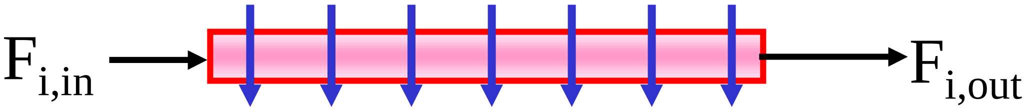
Plasma Model

- Well mixed reactor

$$F_{i,out} = F_{i,in} - (-r_i)V$$



  - Generation and recombination reactions

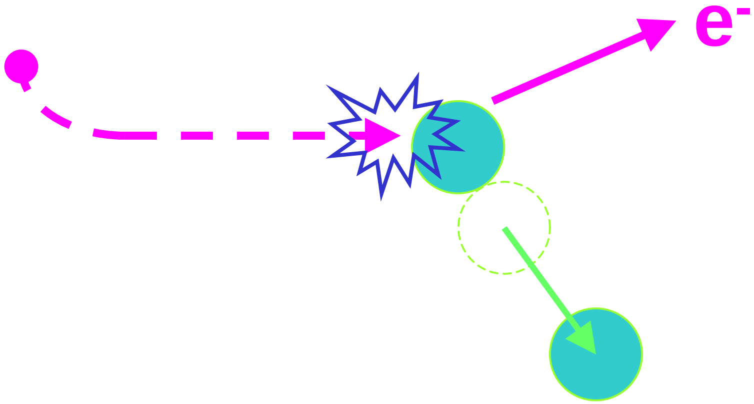
$$r_1: \quad O_2 + e \rightarrow 2O + e$$

$$r_2: \quad 2O + O_2 \rightarrow 2O_2$$

$$r_3: \quad 3O \rightarrow O + O_2$$

$$r_4: \quad O + 2O_2 \rightarrow O_3 + O_2$$

$$r_5: \quad 2O + S \rightarrow O_2 + S$$



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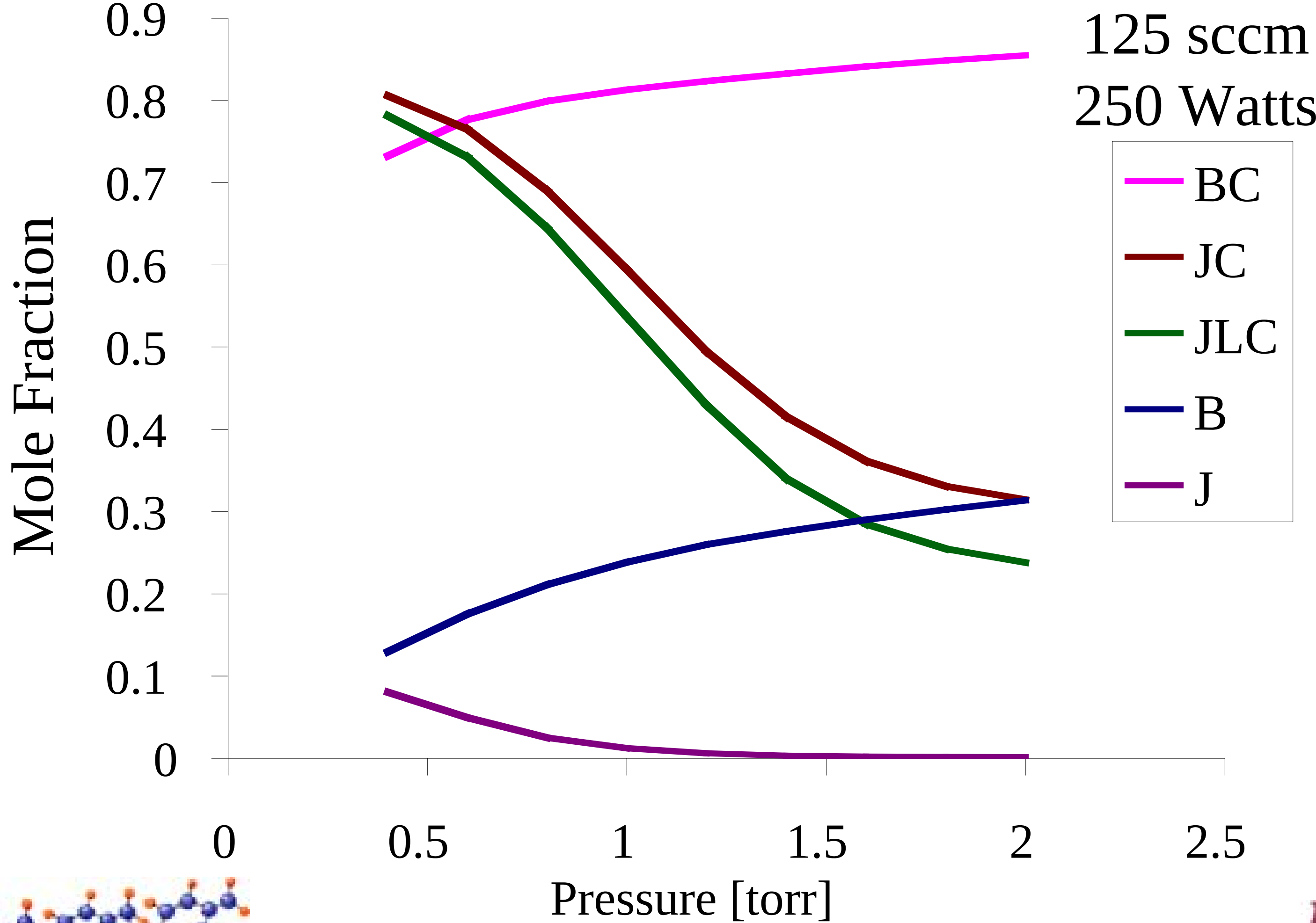
Oxygen Plasma Models

- One plasma model
  - A.T. Bell and K. Kwong, AIChE J. **18,** 990 (1972).
- Three sets of dissociation cross-sections
  - P.E. Luft, Joint Inst. For Lab. Astrophysics, Univ. of Colorado, Boulder, Report 14, 1975.
  - P.C. Cosby, J. Chem. Phys. **98,** 9560 (1993).
  - M.A. Lieberman and A.J. Lichtenberg, *Principles of Plasma Discharges and Materials Processing* (John Wiley & Sons, New York, NY, 1994).

Predicted Atomic Oxygen Mole Fraction at Plasma Outlet



Afterglow Model: Simultaneous Transport and Reaction

- Dimensionless momentum equations

$$\mathrm{Re}\left(v_r^* \frac{\partial v_z^*}{\partial r^*} + v_z^* \frac{\partial v_z^*}{\partial z^*} \right) = \frac{1}{r^*}\frac{\partial}{\partial r^*}\left(r^* \frac{\partial v_z^*}{\partial r^*} \right) + \frac{\partial^2 v_z^*}{\partial z^{*2}} - \mathrm{Re}\frac{\partial P^*}{\partial z^*}$$

$$\mathrm{Re}\left(v_r^* \frac{\partial v_r^*}{\partial r^*} + v_z^* \frac{\partial v_r^*}{\partial z^*} \right) = \frac{\partial}{\partial r^*}\left(\frac{1}{r^*}\frac{\partial}{\partial r^*}(r^* v_z^*) \right) + \frac{\partial^2 v_r^*}{\partial z^{*2}} - \mathrm{Re}\frac{\partial P^*}{\partial r^*}$$

- Dimensionless Mass Balance

$$\left(\frac{1}{r^*}\frac{\partial}{\partial r^*} r^* \frac{\partial y_o}{\partial r^*} + \frac{\partial^2 y_o}{\partial z^{*2}} \right) - \mathrm{Pe}\left(v_r^* \frac{\partial y_o}{\partial r^*} + v_z^* \frac{\partial y_o}{\partial z^*} \right) -$$

$$2\,\mathrm{Da}_2 y_o^2 (1 - y_o) - 2\,\mathrm{Da}_3 (y_o)^3 - \mathrm{Da}_4 y_o (1 - y_o)^2 = 0$$

Boundary Conditions

Location	v_z^*	P*	y_O
z*=0	$2\left(1-4r^{*2}\right)$	Determined from iteration	From plasma model
r*=0	$\frac{\partial v_z^*}{\partial z^*}=0$	$\frac{\partial P^*}{\partial z^*}=0$	$\frac{\partial y_O}{\partial z^*}=0$
z*=L(exit)	$\frac{\partial v_z^*}{\partial r^*}=0$	$P^*=0$	$\frac{\partial y_O}{\partial r^*}=0$
any physical surface i	$v_z^*=0$	$\frac{\partial P^*}{\partial n^*}=0$	$\frac{\partial y_O}{\partial n^*}=-\mathrm{Da}_i \cdot y_O$
n is the normal direction to the boundary			

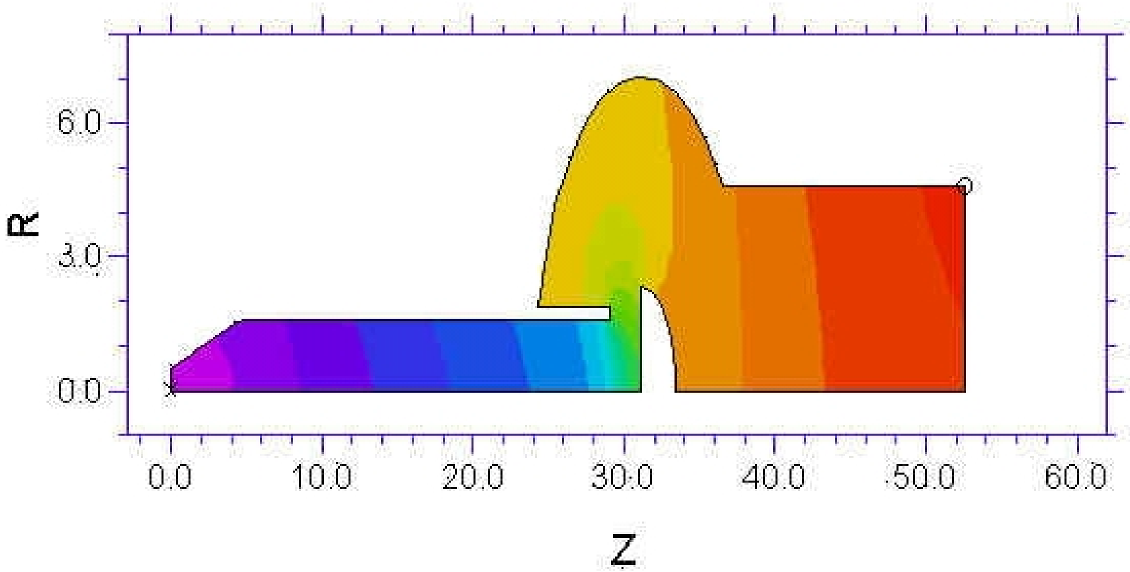
v_r*=0 at every boundary

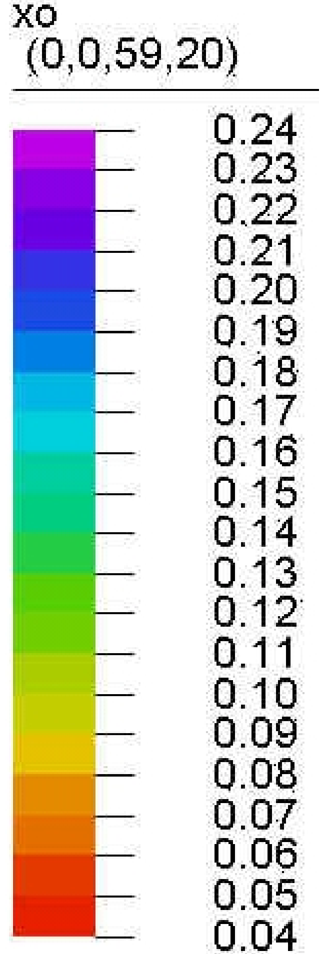
Afterglow Model Result: Atomic Oxygen Mole Fraction

- Solved system of equations using a finite element method

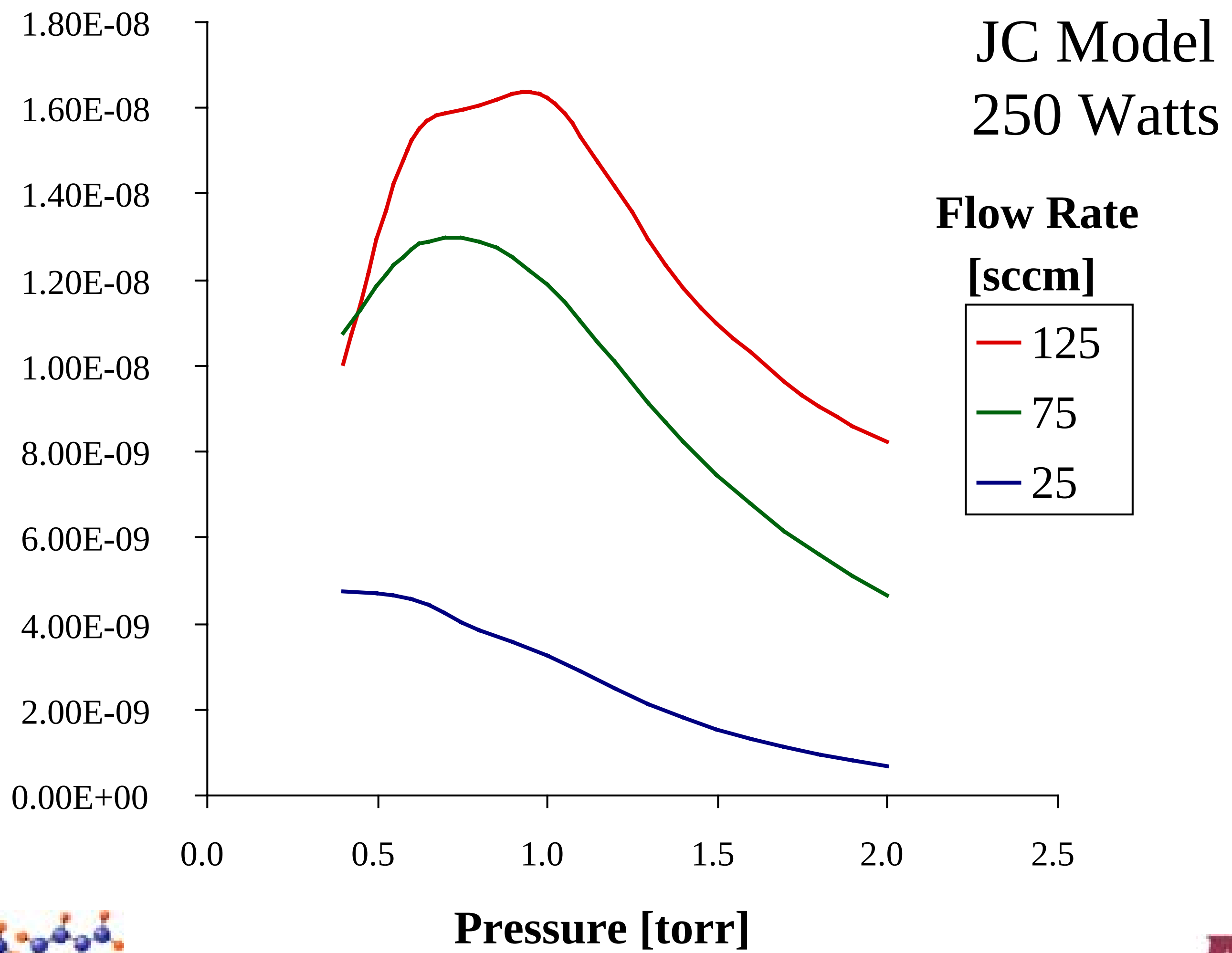
Pressure = 1.0 Torr

Flow Rate = 125 sccm





Atomic Oxygen Concentration at Sample Surface as a Function of Pressure and Flow Rate



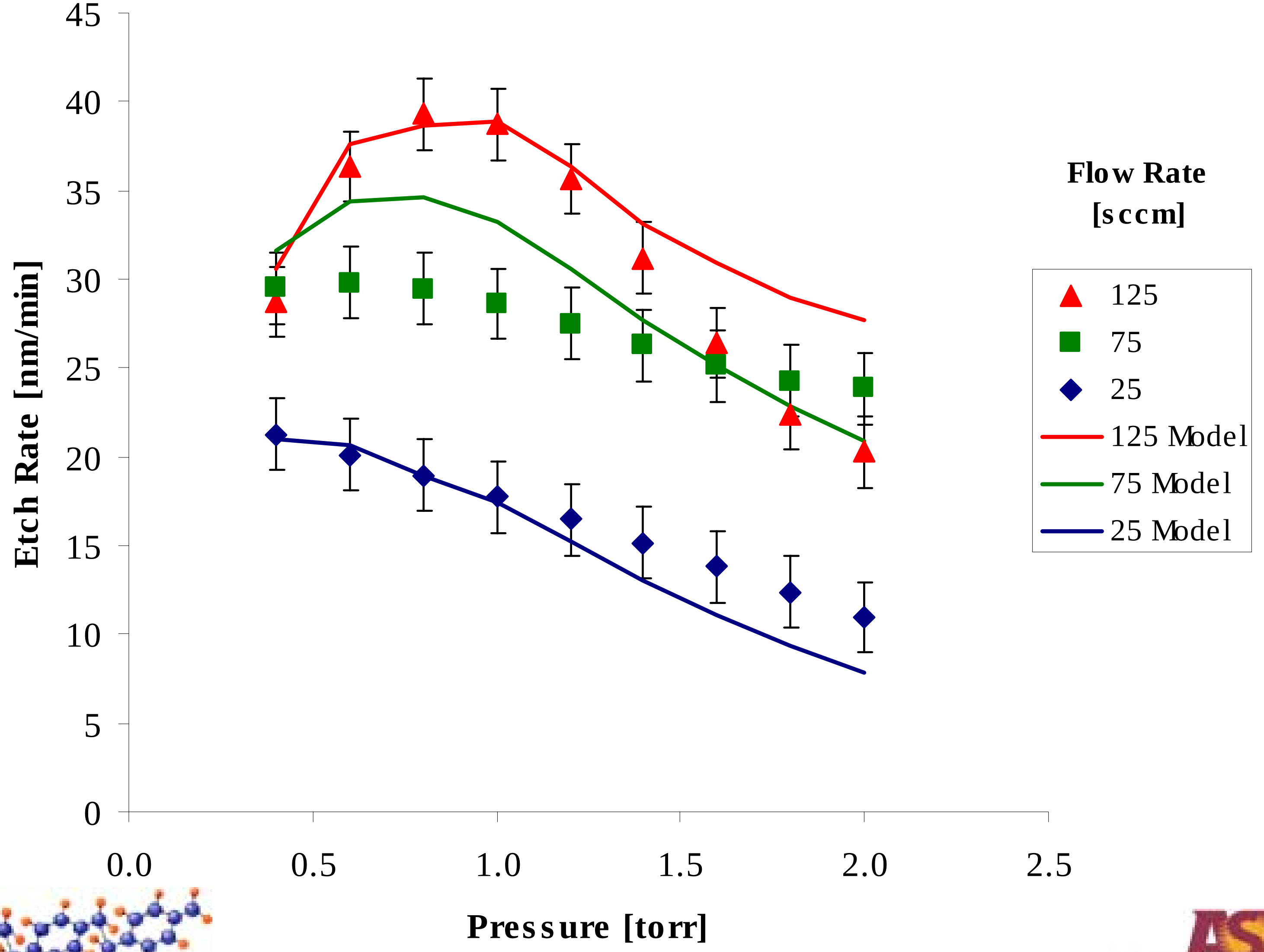
Parylene-N Etch Model

- Etch rate is dependent on oxygen atom concentration

$$\text{Etch Rate} = k_o \exp(-E_a / RT) N^{\alpha} y_o^{\alpha}$$

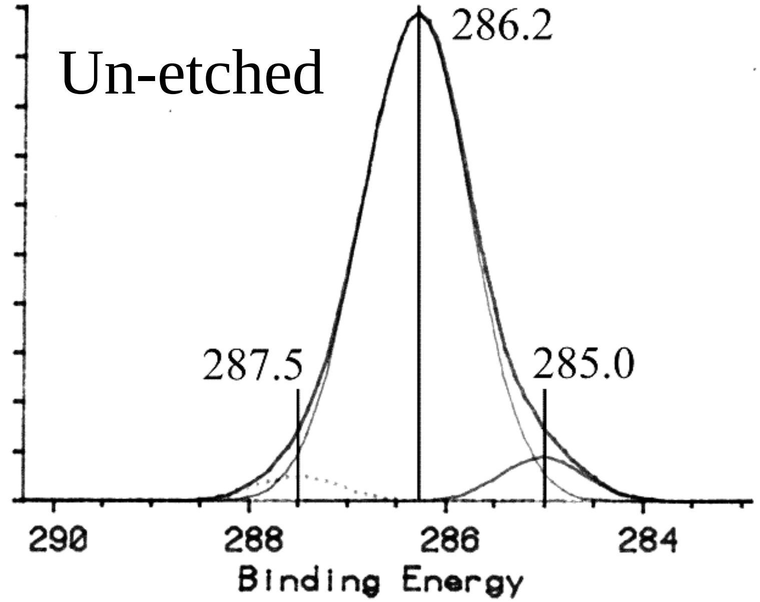
- α is the reaction order
- Used average k_o and E_a to generate etch rate model

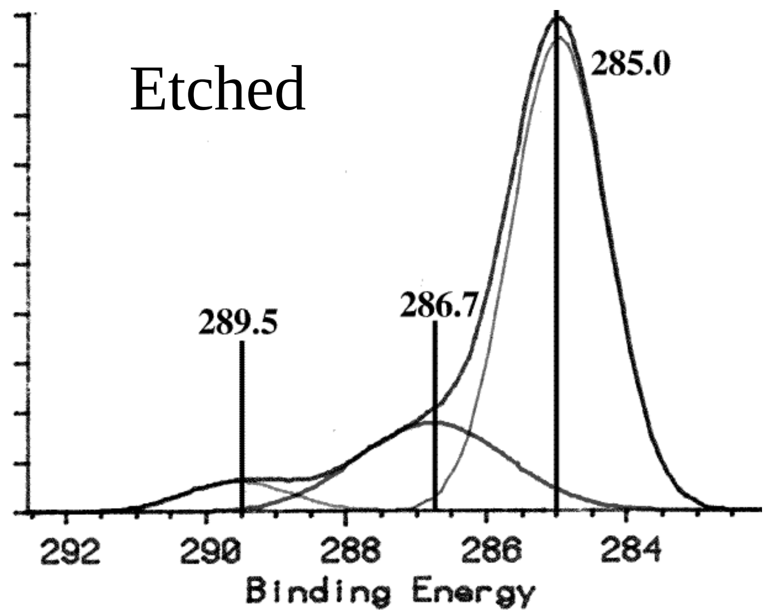
Comparison of Model and Experiment Using Etch Rate Model

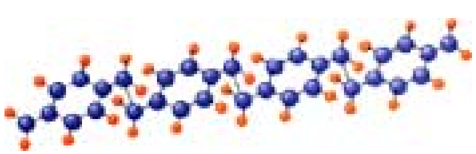


XPS Analysis for Pa-N

- Peak identification
  - 285.0 saturated carbon
  - 286.2-286.7 aromatic carbon
  - 287.5 oxygen contamination
  - 289.5 carboxylic groups
- Post-etch XPS shows the ratio of aromatic carbon to saturated carbon has been reduced

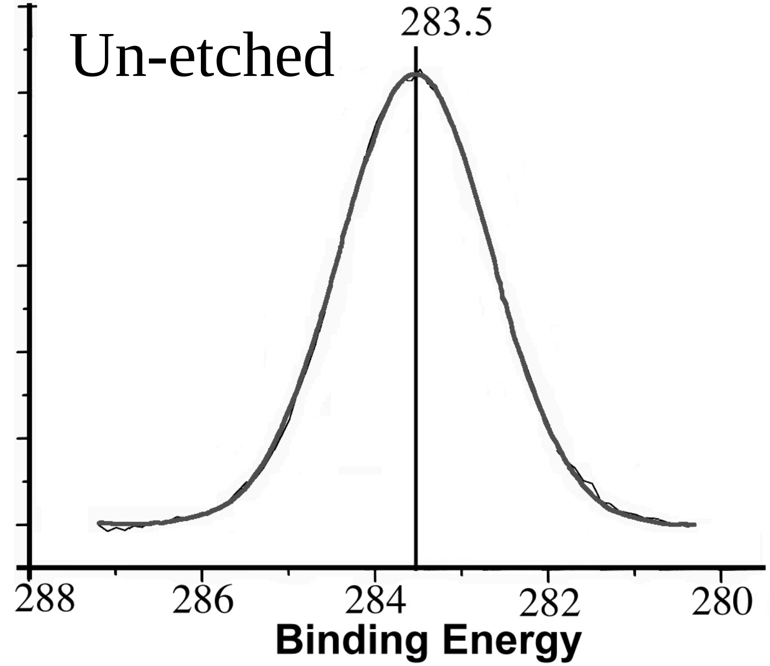


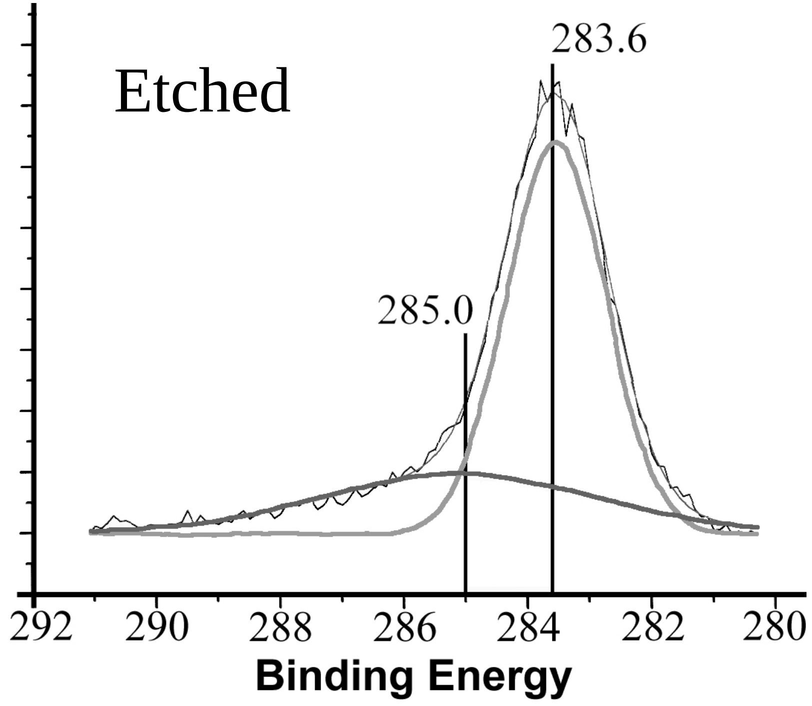




XPS Analysis for Pa-C

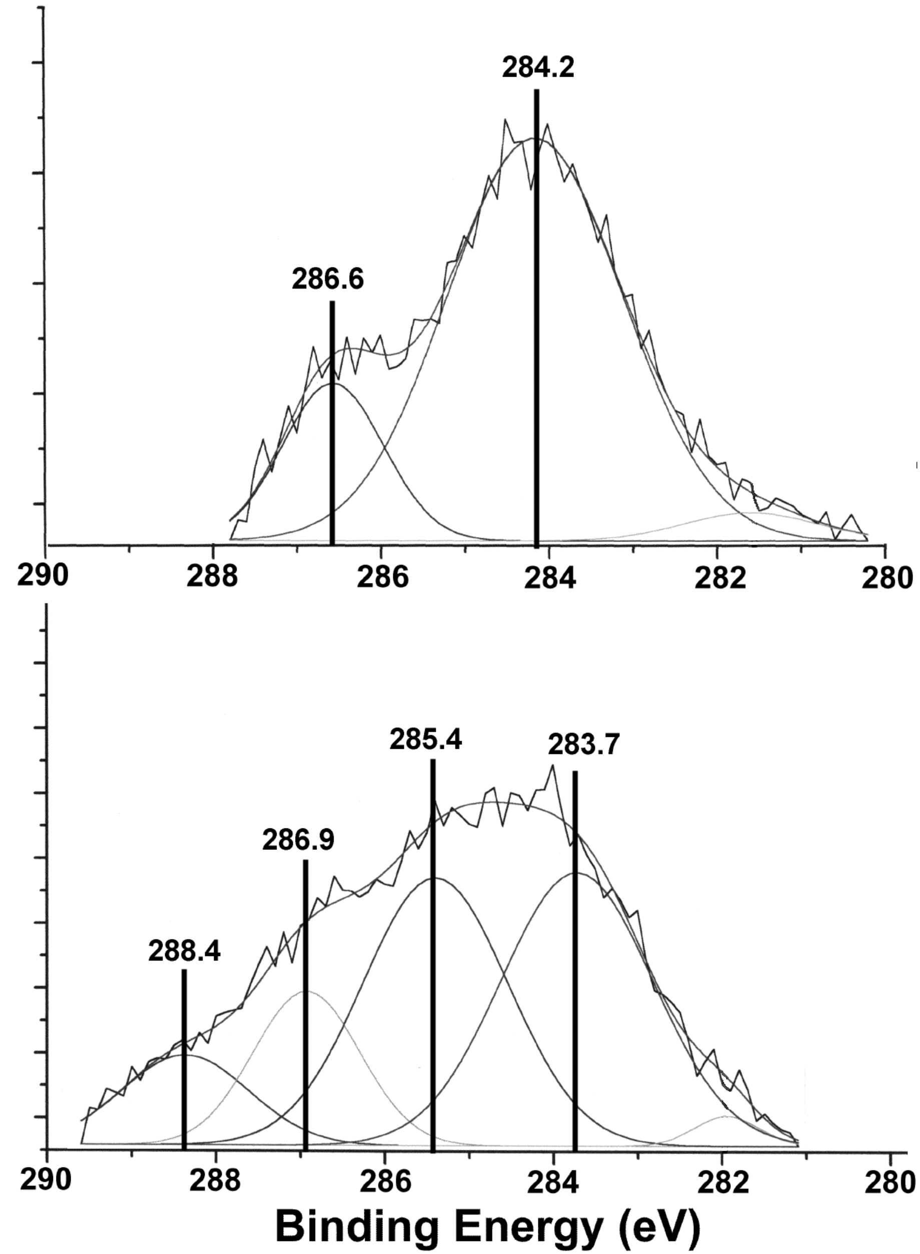
- Peak identification
  - 283.5 aromatic carbon
  - 285.0 saturated carbon
- Evidence of saturated carbon after etching

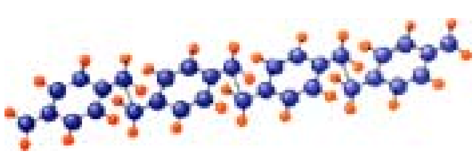




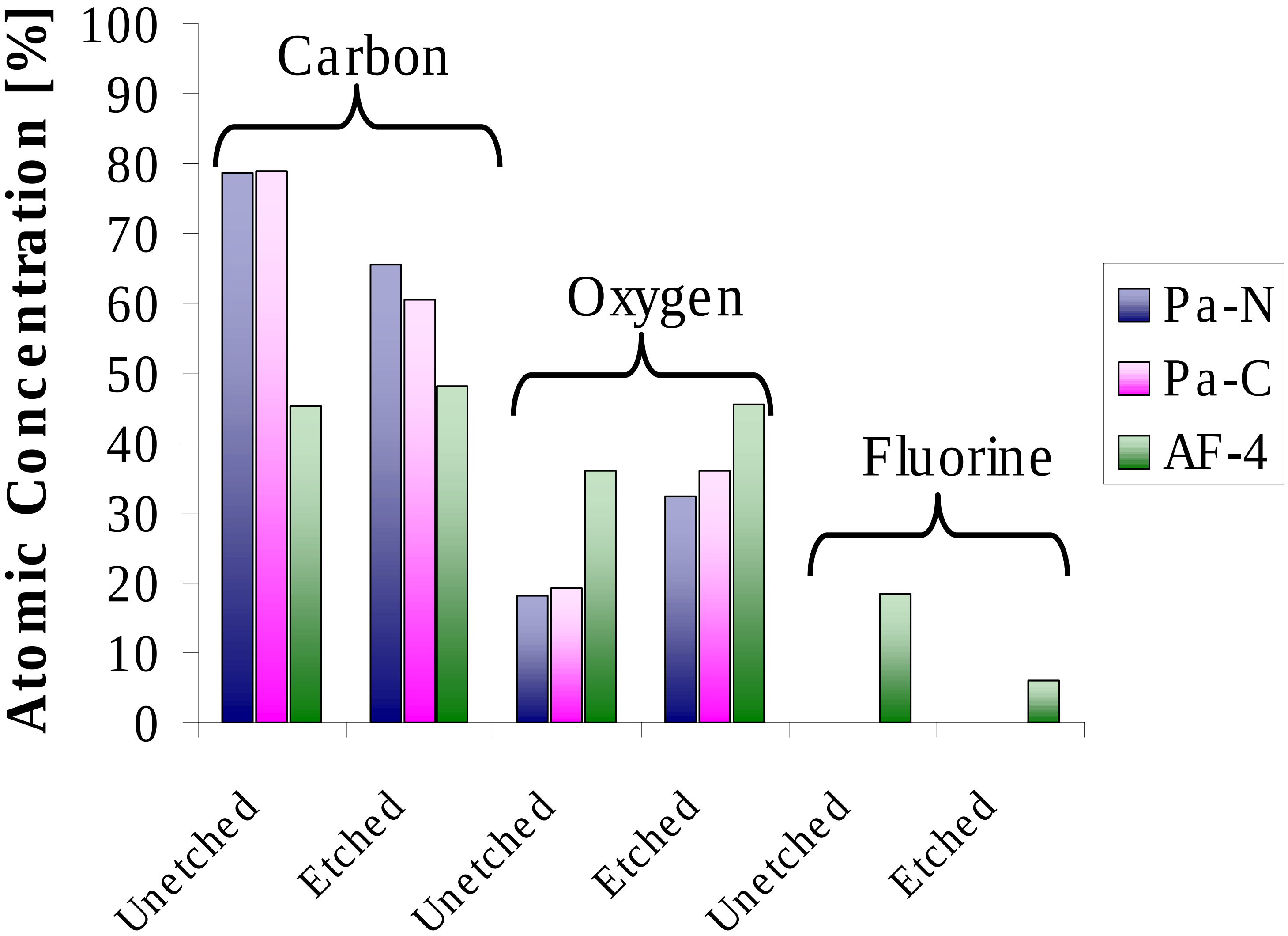
XPS Analysis for AF-4

- Peak identification
  - 283.7-284.2 aromatic carbon
  - 285.4 saturated carbon
  - 286.6-286.9 carbon bonded to fluorine
  - 288.4 carbon bonded to oxygen
- Evidence of saturated carbon after etching and carbonyl formation





Atomic Composition of Etched Films



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Bond Strengths

Bond Dissociation Energies for Typical Bonding Found in Parylene-N

Bond Broken	Bond Dissociation Energy [kcal/mol]
C_6H_5—H	110
C_6H_5—Cl	86
$C_6H_5CH_2$—H	85
CH_3-CH_3	83
$C_6H_5CH_2$—$CH_2C_6H_5$	47

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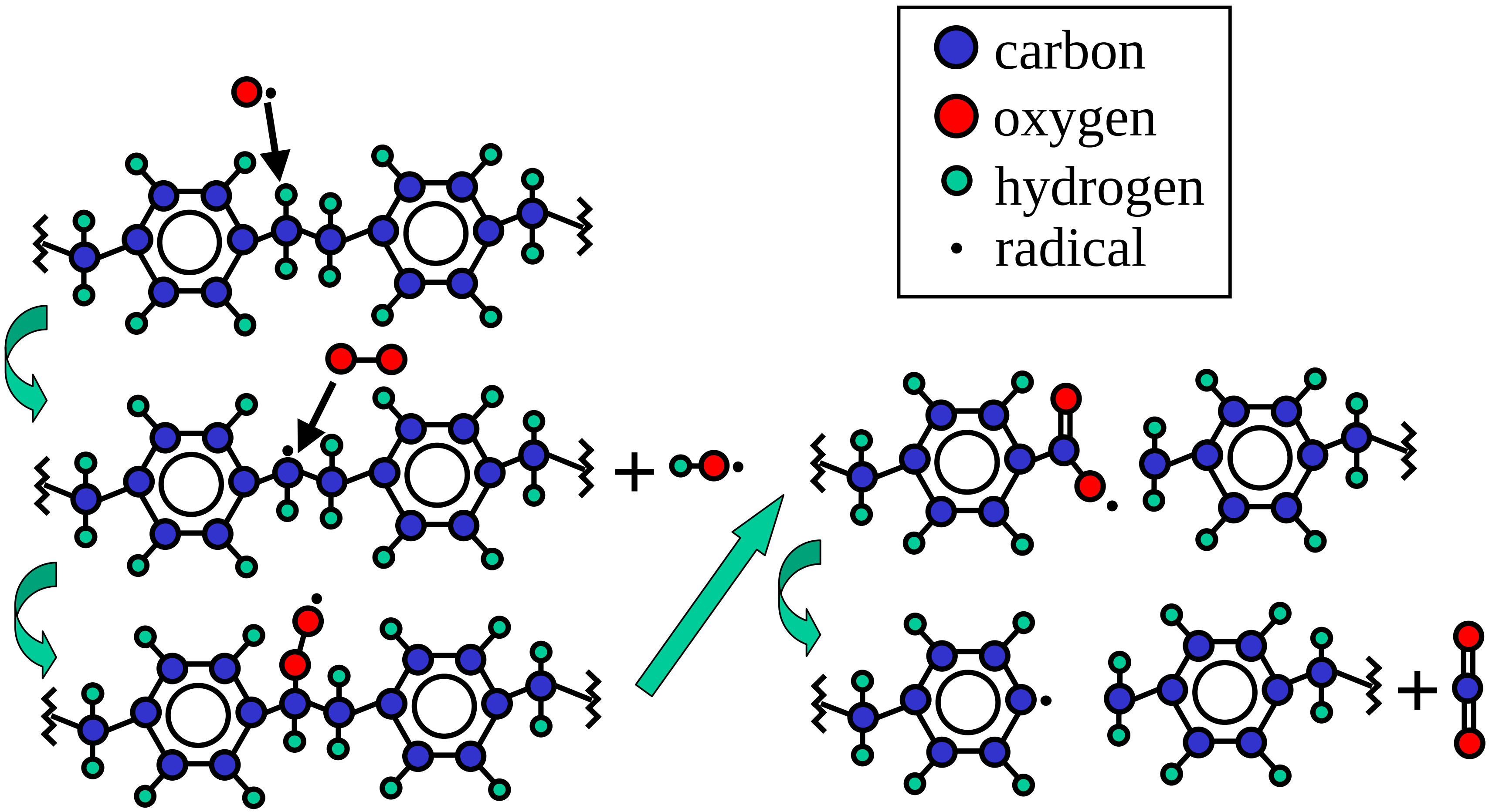
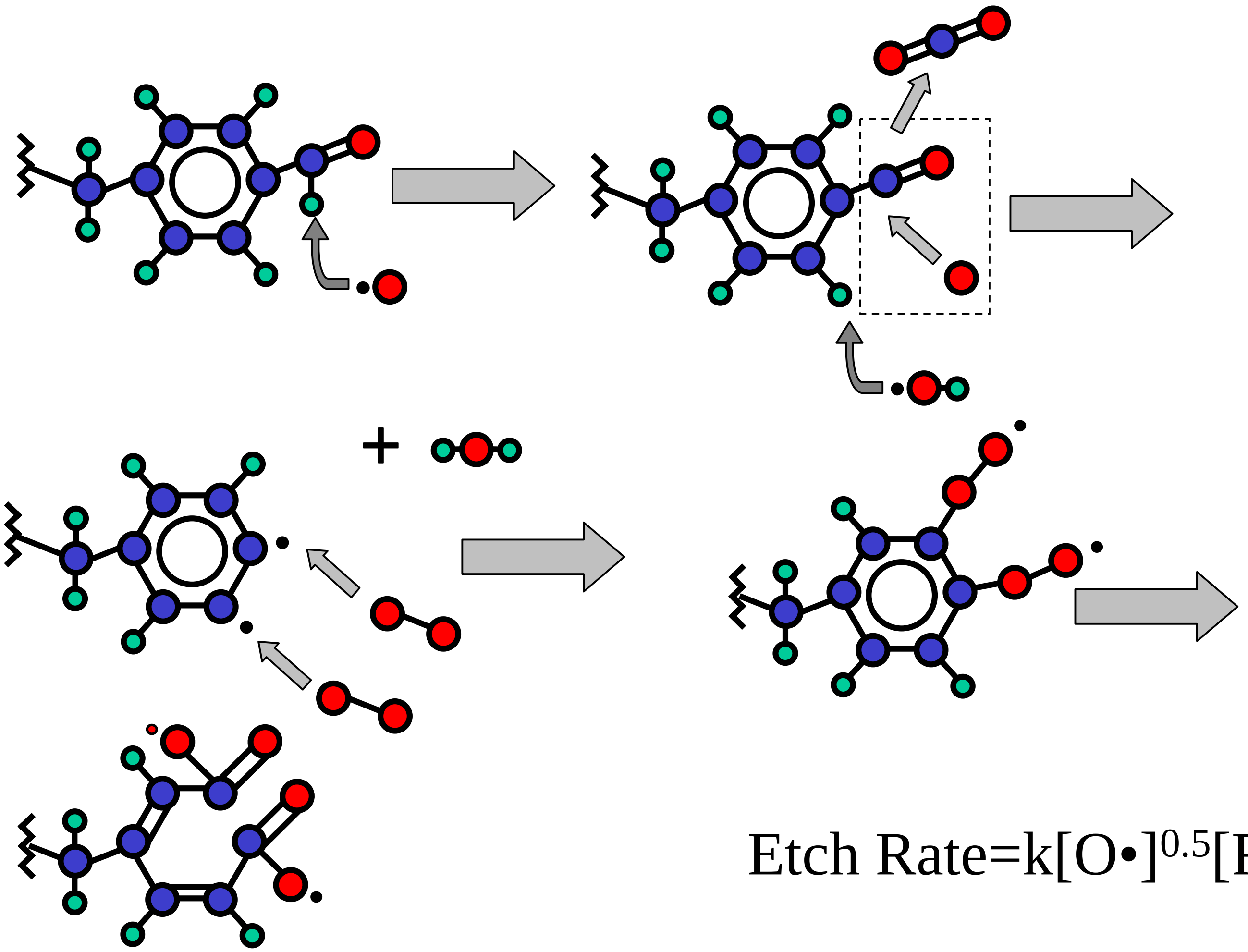
Chain Break Mechanism

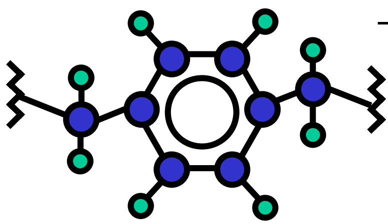
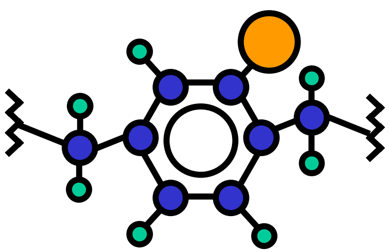
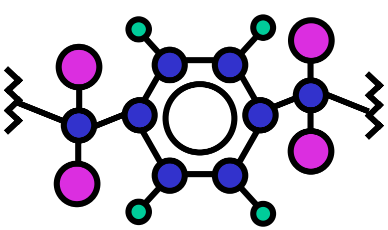


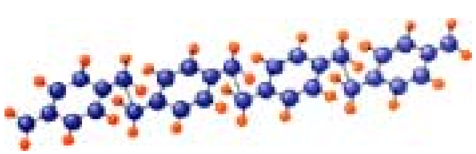
Etch Reaction Mechanism



Etch Rate=k[O•]$^{0.5}$[RH]

Comparison of Relative Etch Rates

	Number of sites available for ring opening	Theoretical relative etch rate to pa-N	Measured relative etch rate to pa-N
	6		
	5	5/6 (0.83)	0.86
	4	4/6 (0.66)	0.61



Conclusions

- Parylenes etch at different rates in a remote oxygen plasma afterglow
- The apparent activation energies for etching each polymer are equivalent
- A plasma model and transport model were combined to predict the oxygen atom concentration at the polymer surface
- A reaction order of 0.5 yielded good agreement between experimental and model data

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Conclusions

- Film analysis indicates carbonyl formation and ring openings after films are exposed to the remote plasma
- A possible etch mechanism was proposed which was based on the model and film analysis results
- The rate limiting step involved the ring opening

Acknowledgements

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- Kaustubh Gadre for assistance with XRD
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