Downstream Etching of Parylene-N Films

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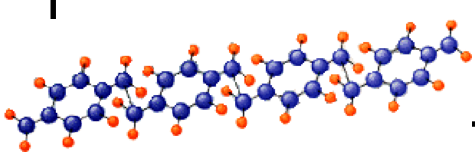
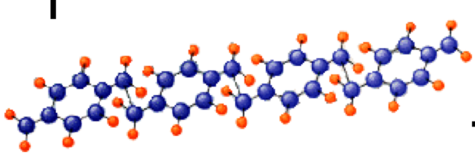


Significance of Research

- Performance advantage
  - Parylene’s lower dielectric constant, relative to silicon dioxide, offers increased performance
- Environmental advantage
  - Use of oxygen plasma as the dielectric etchant gas eliminates the need for perfluorinated compounds(PFCs) in IC manufacturing
    - ⇒ PFCs are undesirable greenhouse gases

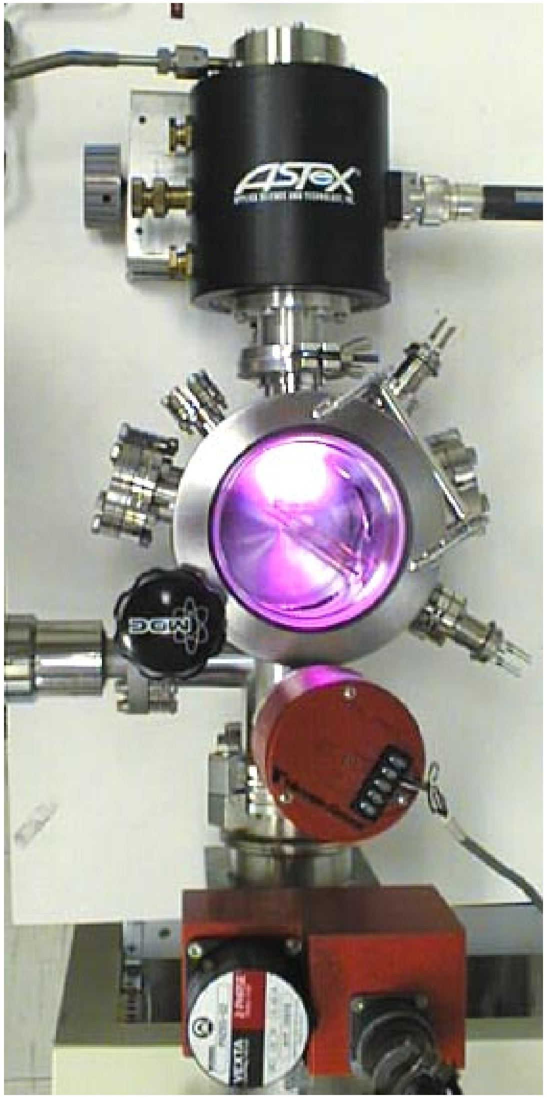


Research Goals

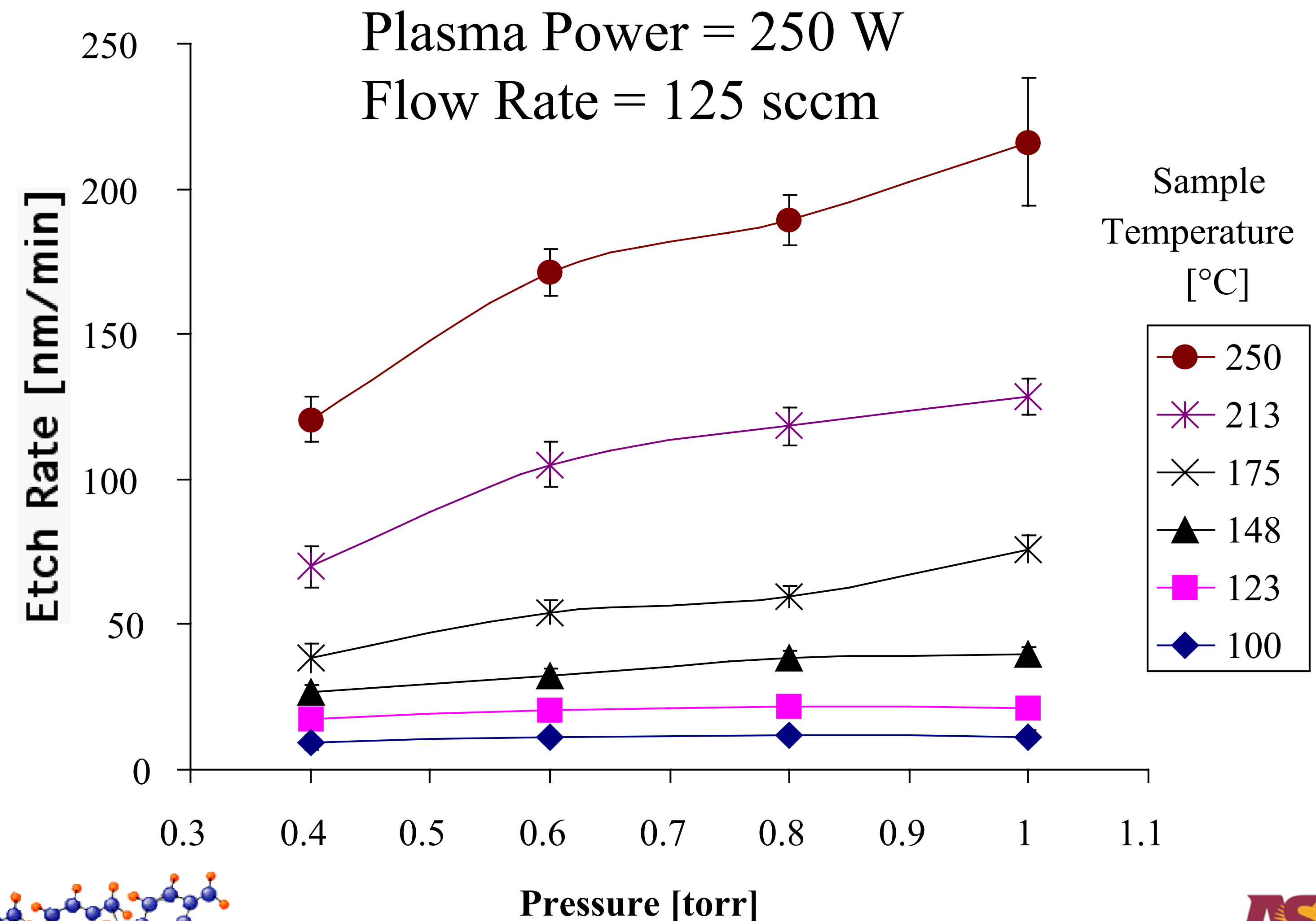
- Characterize downstream etching of parylene-n
  - Investigate effects of process variables on etch performance
    - Temperature
    - Pressure
    - Plasma power
    - Total gas flow
  - Develop experimentally-validated transport and reaction models

Downstream Etching Apparatus

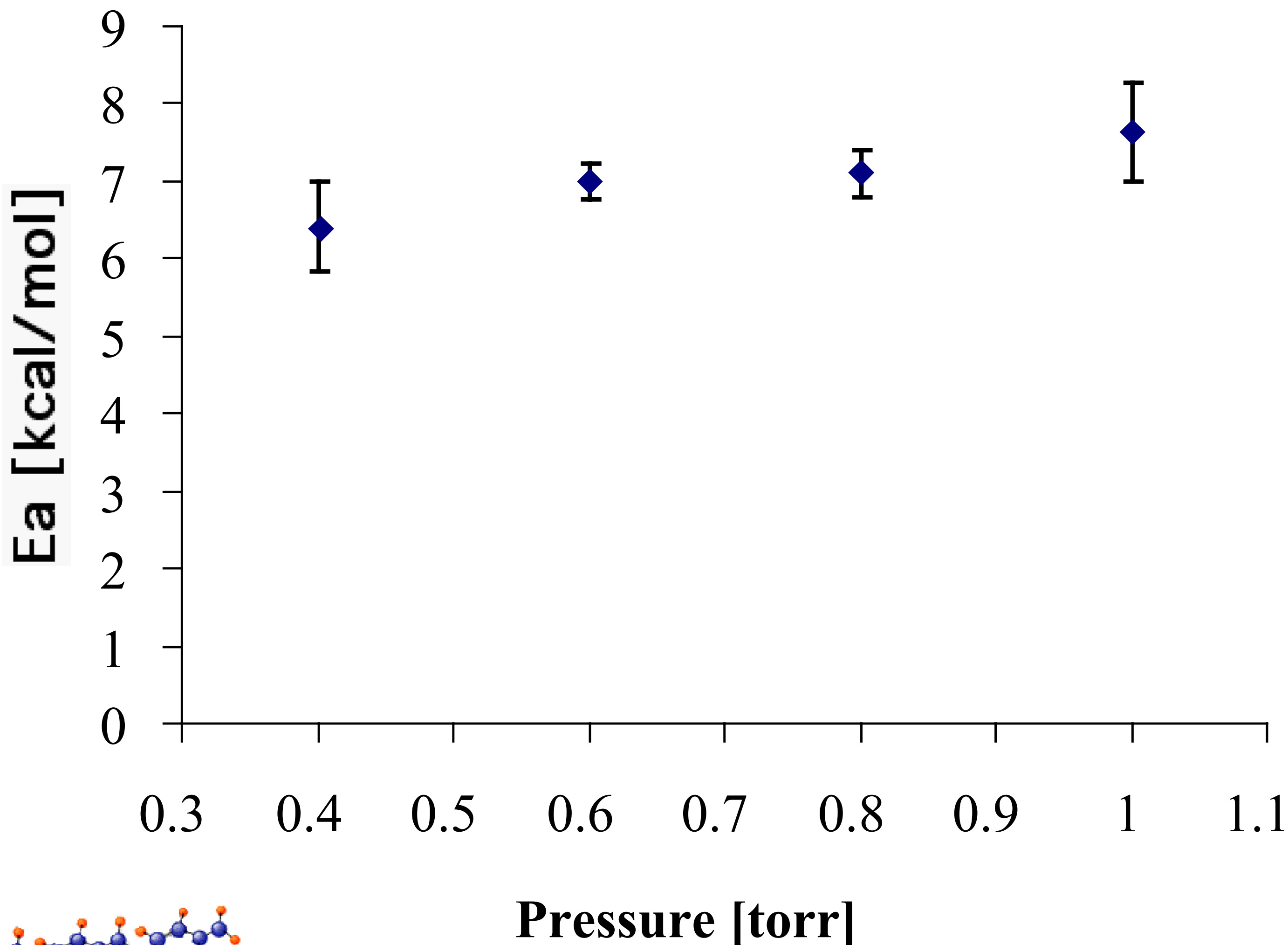
- 250 W Astex microwave generator to create downstream oxygen plasma
- Base pressure = 4×10^{-7} Torr
- Temperature controlled substrate holder



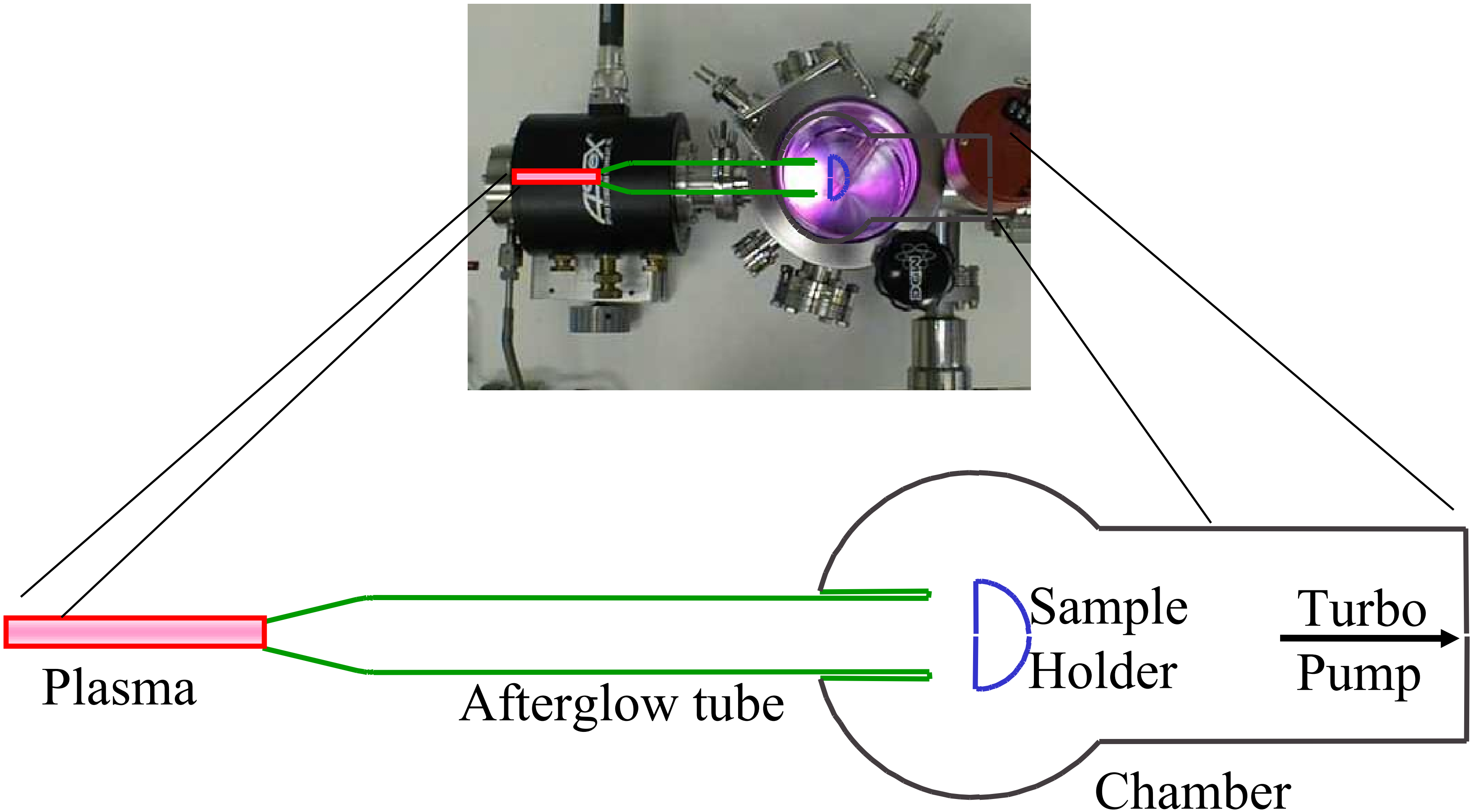
Experimental Results: Etch Rate as a Function of Temperature and Pressure



Apparent Activation Energy



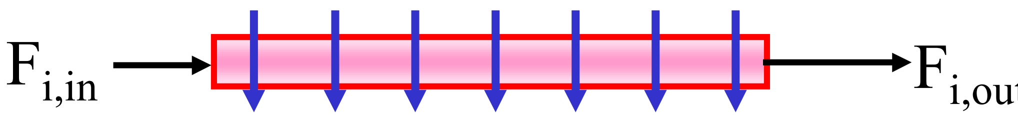
Modeling: System Geometry



Plasma Model

- CSTR reactor
  - Assumes uniform microwave intensity

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



  - Generation and recombination reactions

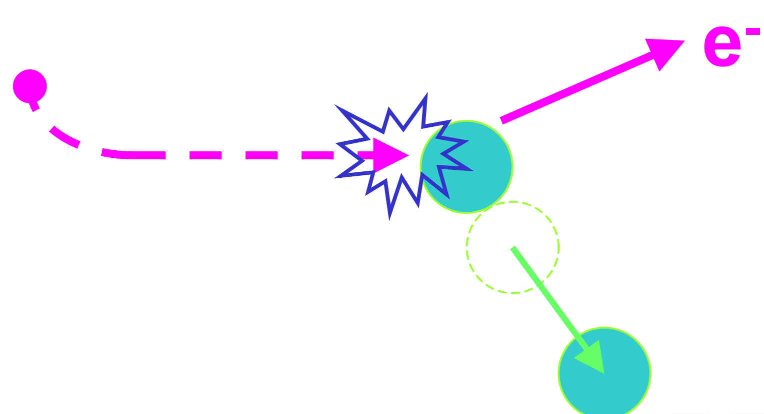
$r_1 : \quad O_2 + e \rightarrow 2O + e$

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

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

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

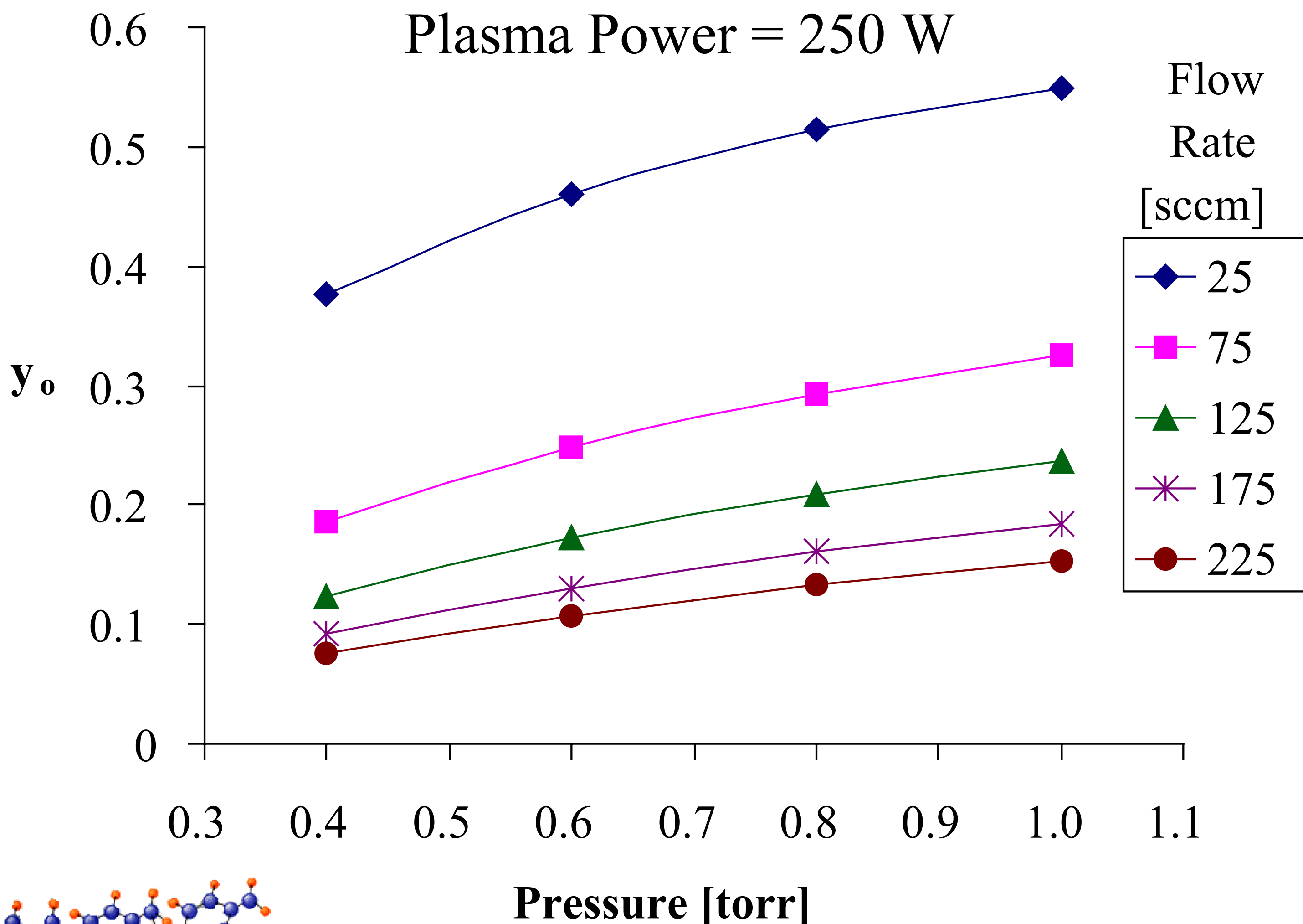
$r_5 : \quad 2O + S \rightarrow O_2 + S$



Plasma Model

- Rate constants taken from literature
- Four equations;
  - three species balances
  - molar balance ($\Sigma y_i=1$)
- Used result as a boundary condition for the transport model

Results: Atomic Oxygen Mole Fraction as a Function of Pressure and Flow Rate



Transport Model

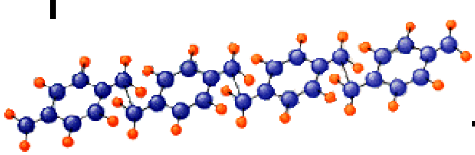
- Dimensionless quantities

$$v_r^* = \frac{v_r}{V}, v_z^* = \frac{v_z}{V}, z^* = \frac{z}{D}, r^* = \frac{r}{D}, y_o = \frac{n_o}{N}, P^* = \frac{(P - P_o)}{\rho V^2}$$

- Dimensionless momentum equations

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

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



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Transport Model, con't

- Dimensionless mass balance

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

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

- Pressure distribution

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

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

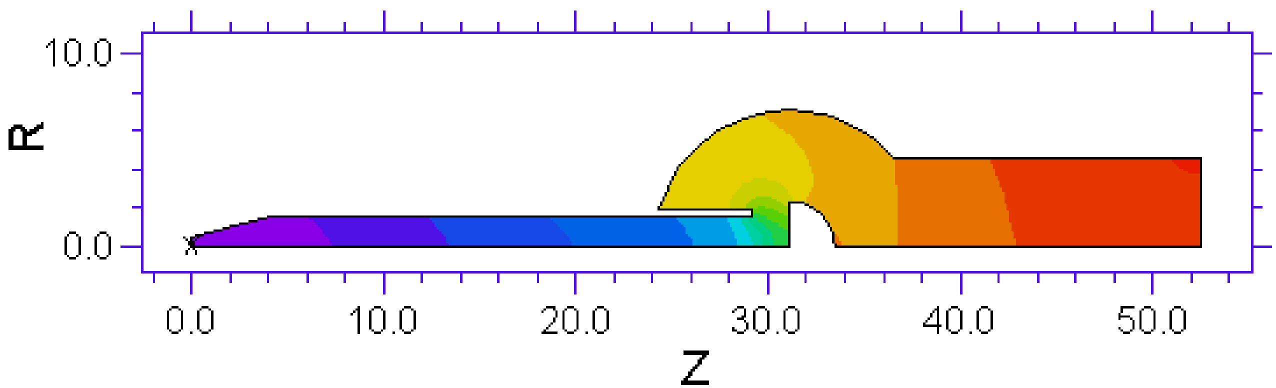
$$\mathrm{Constant}\cdot\left(\frac{1}{r^*}\frac{\partial}{\partial r^*}(r^* v_r^*) + \frac{\partial v_z^*}{\partial z^*}\right)$$

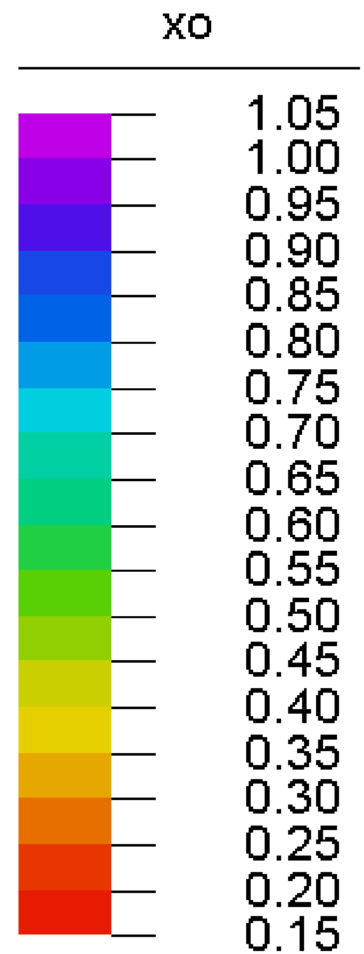
Boundary Conditions

- Flow is developed at entrance
- No-slip at surfaces
- Mass flux at surfaces due to recombination
- Outlet dimensionless pressure is zero
- Inlet dimensionless pressure is determined by checking the velocity profiles

Atomic Oxygen Mole Fraction

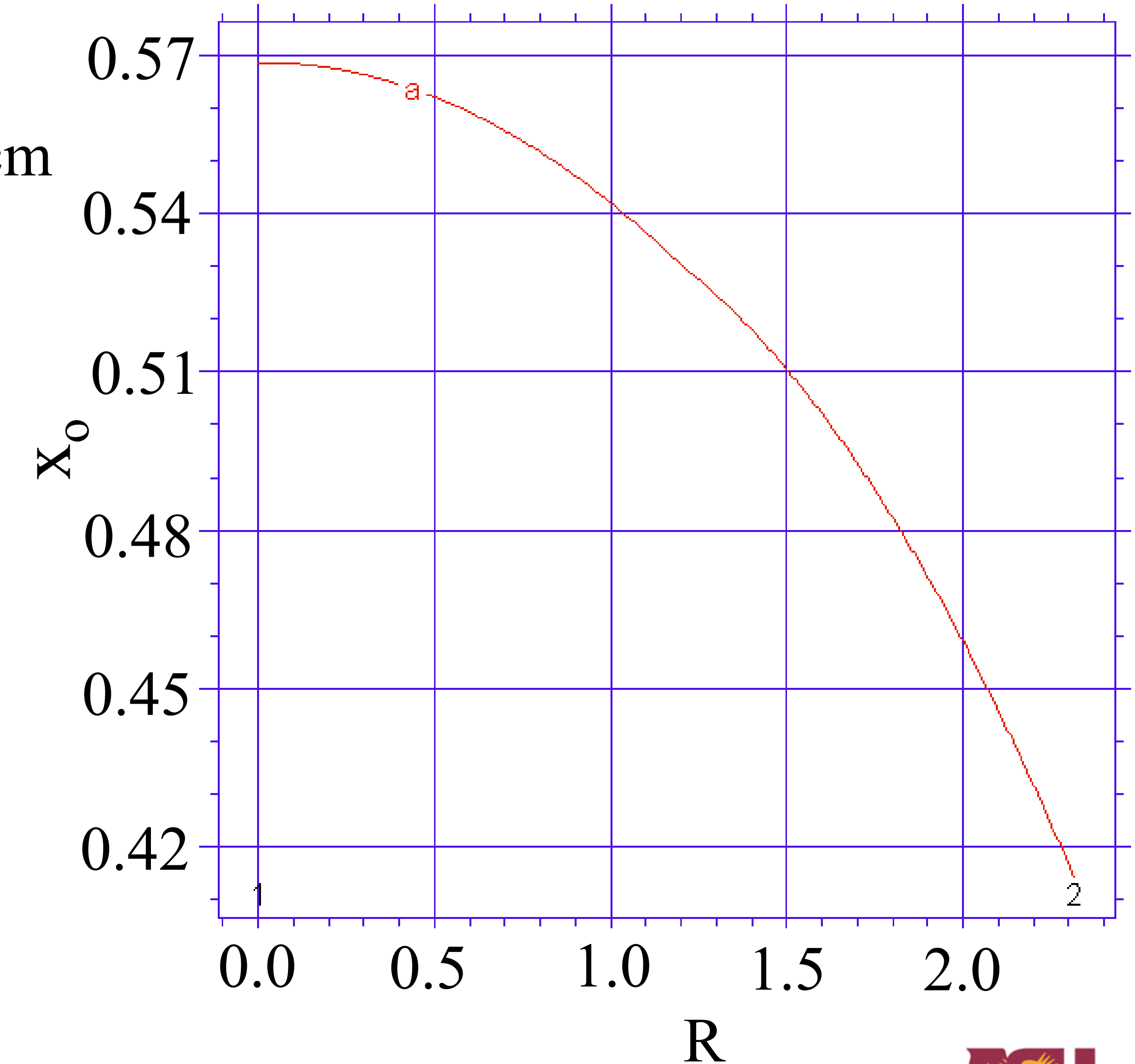
Pressure = 1.0 Torr
Flow Rate = 125 sccm
100% Dissociation





Atomic Oxygen Profile Along Sample

Pressure = 1.0 Torr
Flow Rate = 125 sccm
100% Dissociation



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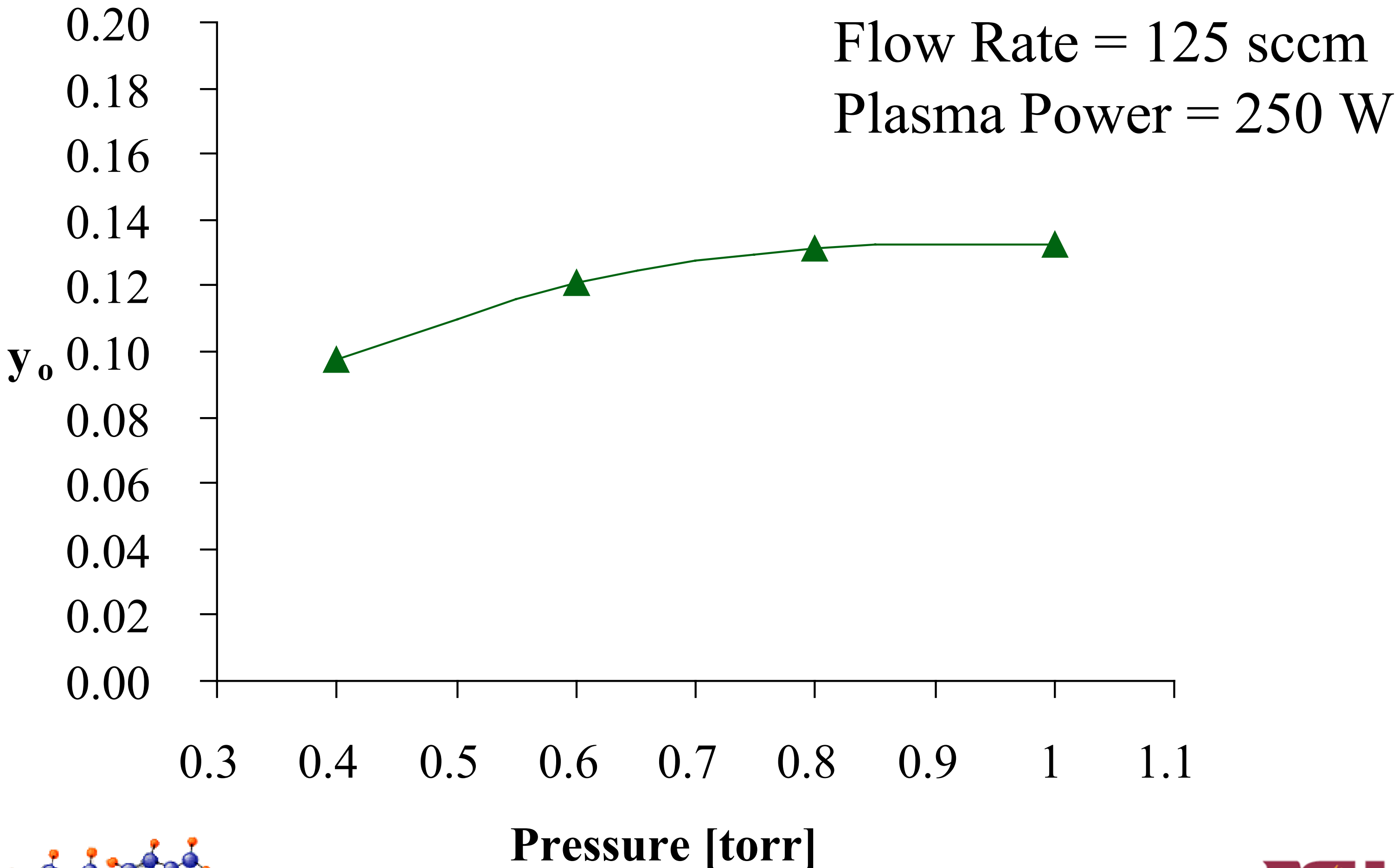
Results: Average Atomic Oxygen Mole Fraction on Sample as a Function of Pressure



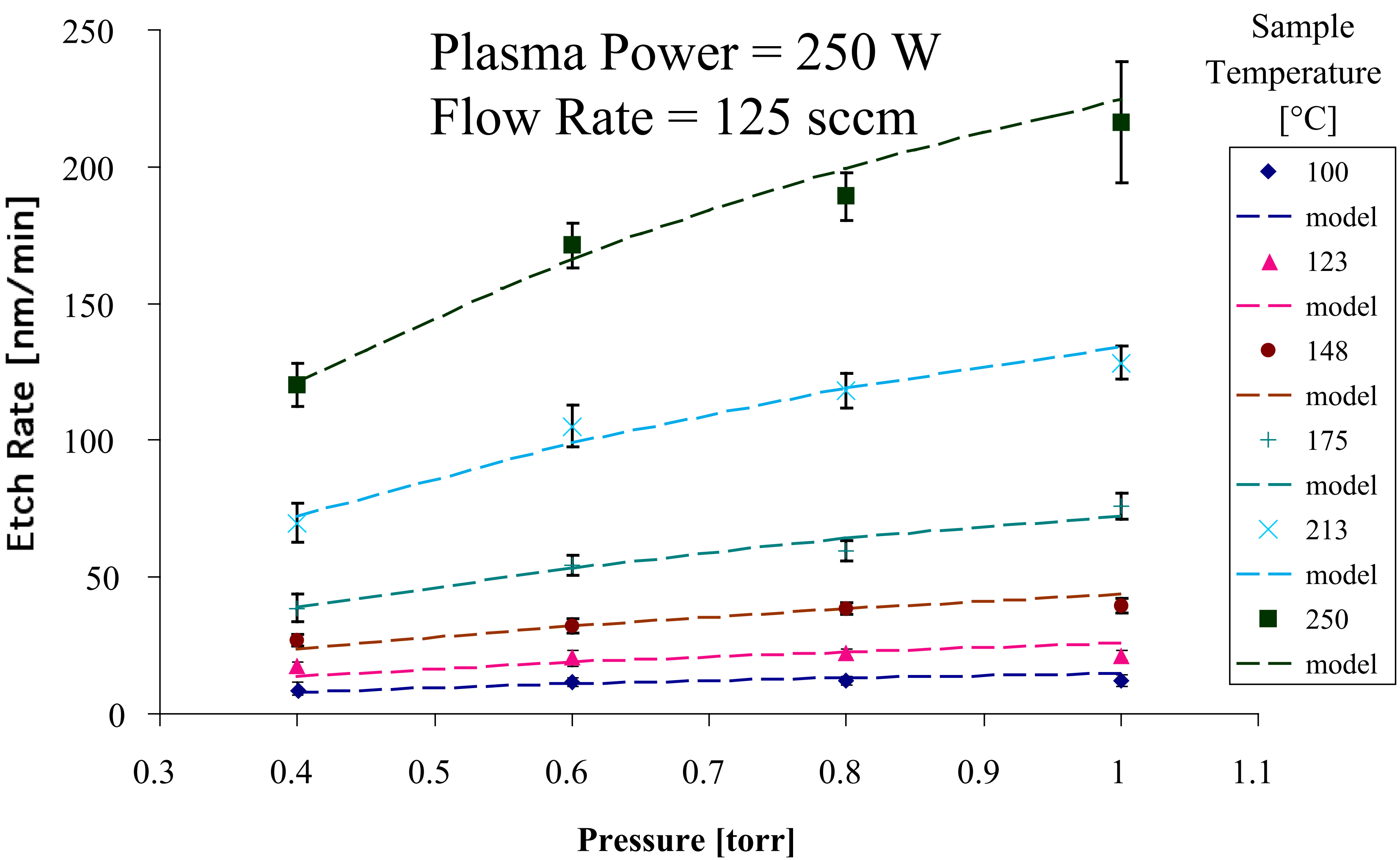
Etch Model

- Etch rate is dependent on oxygen atom concentration

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

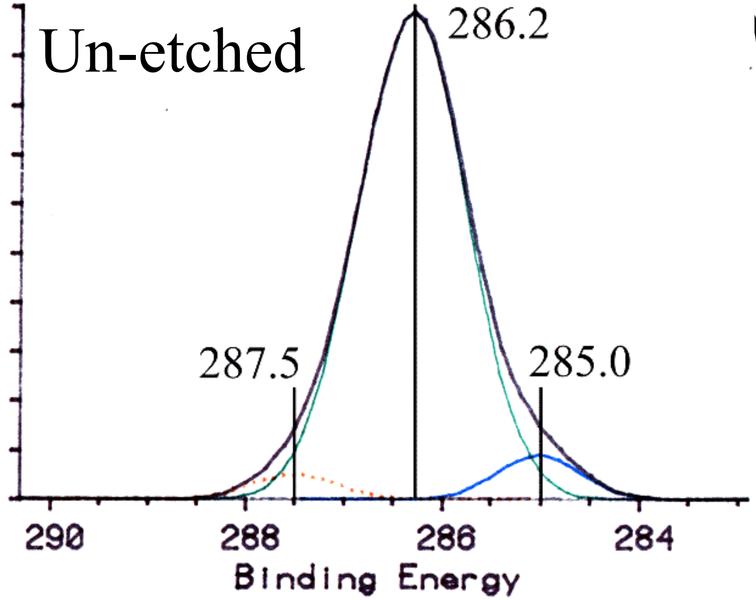
  - k_o is a pre-exponential factor from experiment
  - E_a is the activation energy from experiment
  - N is the gas density
  - y_o is the atomic oxygen mole fraction
  - α is the reaction order

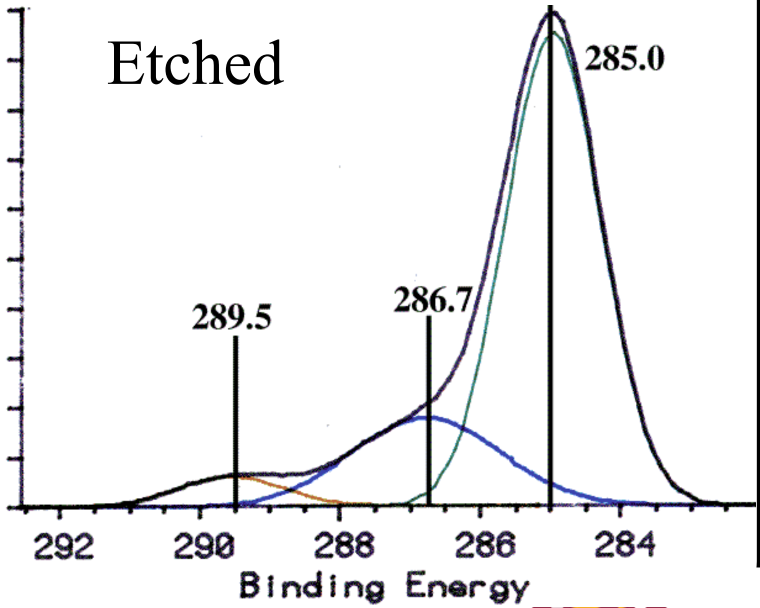
Comparison of Model and Experiments for α=0.5

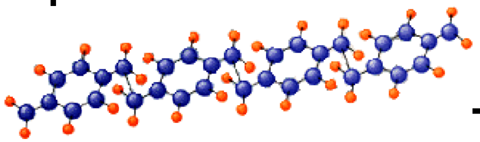


XPS Analysis

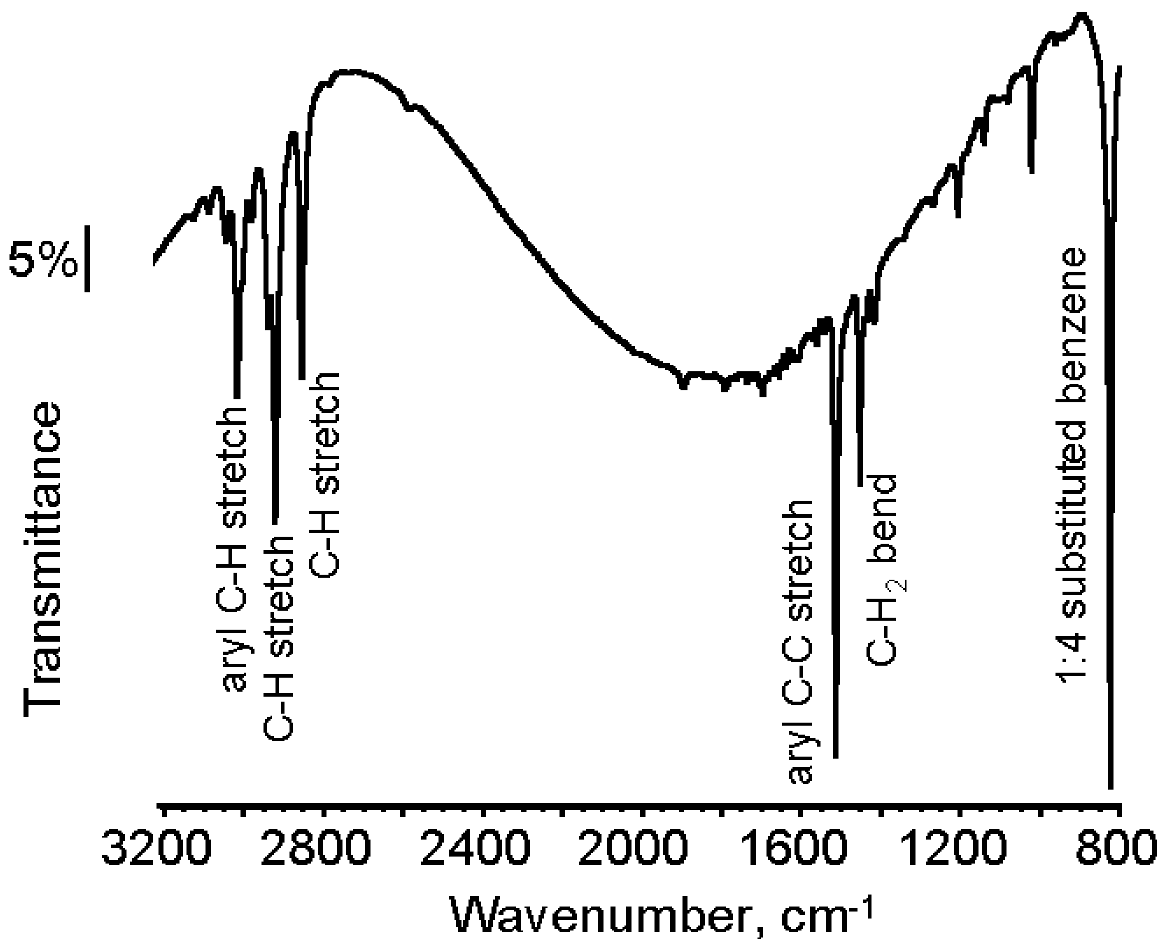
- Peak identification
  - 285.0 saturated carbon
  - 286.2-286.7 aromatic carbon
  - 287.5 oxygen contamination
  - 289.5 carboxylic acid
- Post-etch XPS shows the ratio of aromatic carbon to saturated carbon has been reduced
- Relative ratio information gives evidence of mechanism pathway



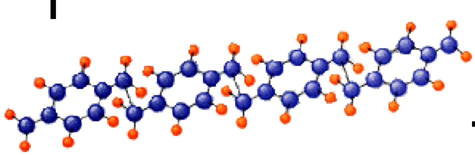




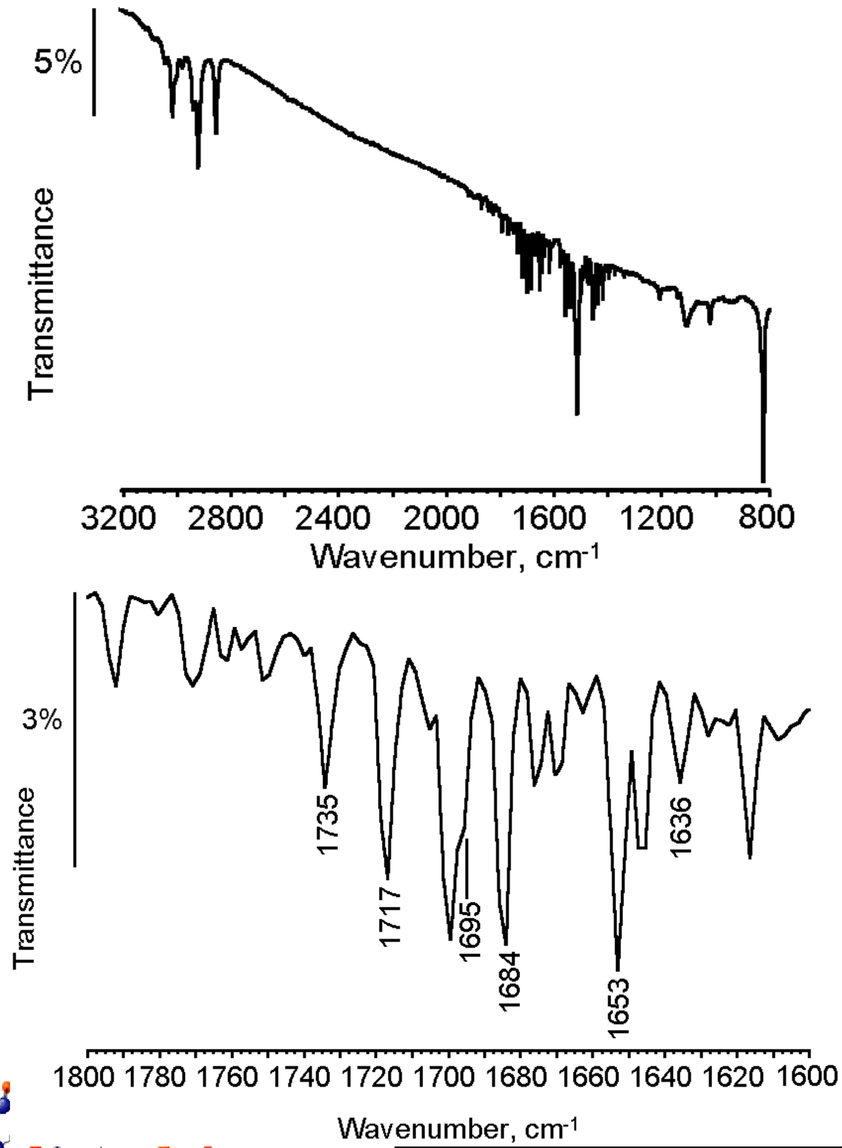
Infrared Analysis



Parylene-n IR spectrum



IR of Etched Sample



- IR spectrum of etched sample shows evidence of carbonyl formation
- The evidence being new absorption peaks around 1700 cm^{-1}

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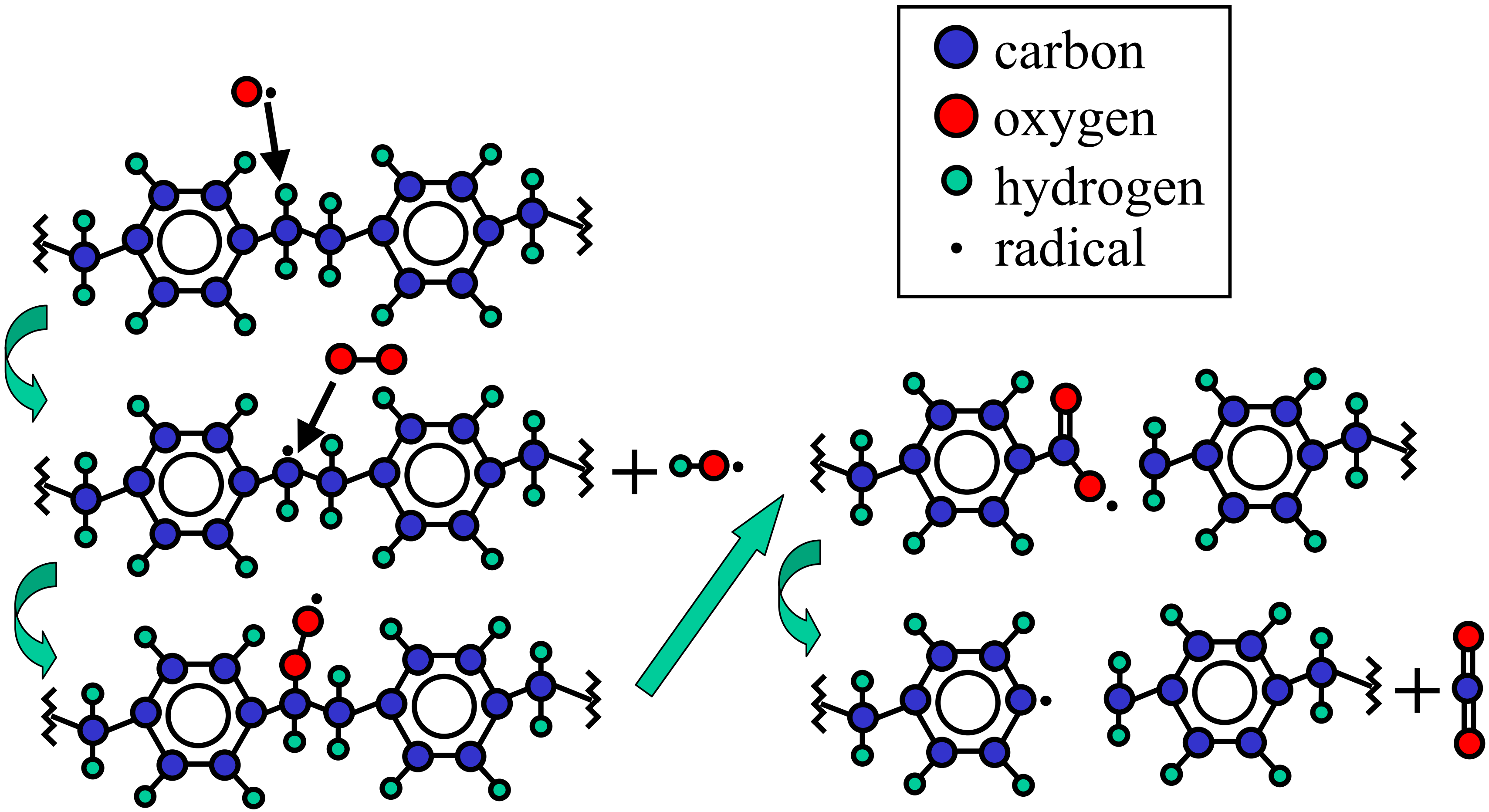
Possible Etching Mechanism



Conclusions

- Fundamental model for generation, transport and reaction in microwave system developed and validated
- Preliminary data suggests etch rate reaction order is 0.5 in oxygen atoms at conditions studied
- XPS and IR suggest carbonyl formation on the surface is one of the steps of the etching mechanism

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