Fundamental Beam Studies of Radical Enhanced Atomic Layer CVD (REALCVD)

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Outline

- Discussion of Deposition Issues
- Description of REALCVD
- Description of Previous Work
- Description of Beam System
- Discussion of Proposed Experimental Procedure

New Materials Challenges

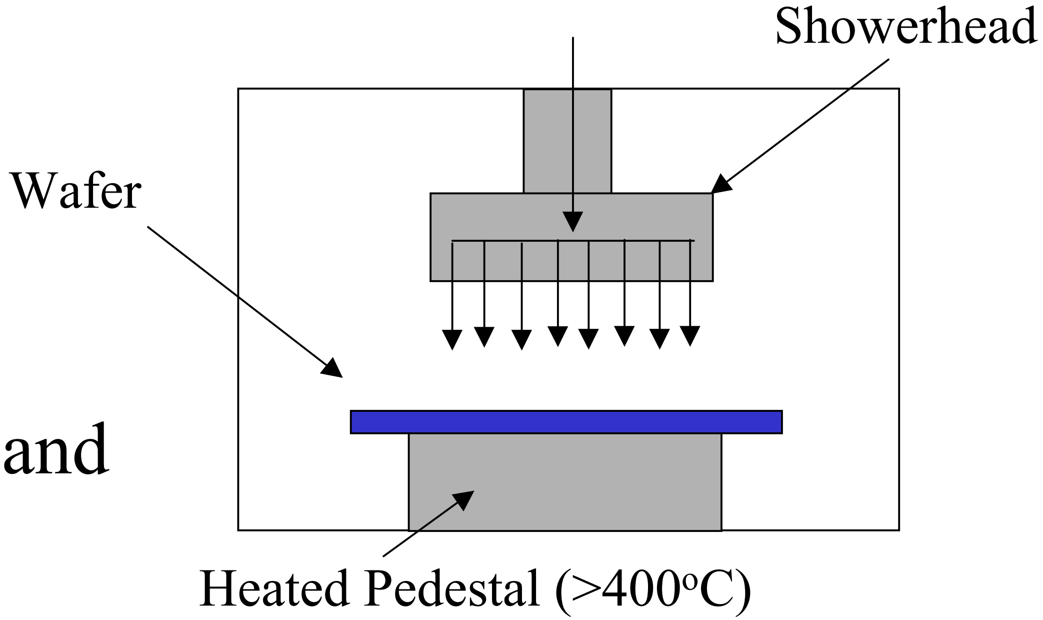
- High k materials
  - Potential replacement for SiO_2 as a gate dielectric
  - Capacitors in devices
- Diffusion barriers
  - Conductive
  - Thin
  - Pinhole free
  - Conformal in high aspect ratio features

Challenge: Develop materials and design processes while satisfying ESH objectives

Conventional Thermal CVD

- Use volatile organometallic precursor
- Heated wafer surface catalyzes precursor decomposition
- Products are oxide film and volatile compounds

$$\text{OM-Zr}_{(g)} + O_{2\,(g)} \rightarrow$$
$$ZrO_{2\,(s)} + CH_{4(g)} + CO_{2\,(g)} + H_{2\,(g)}$$

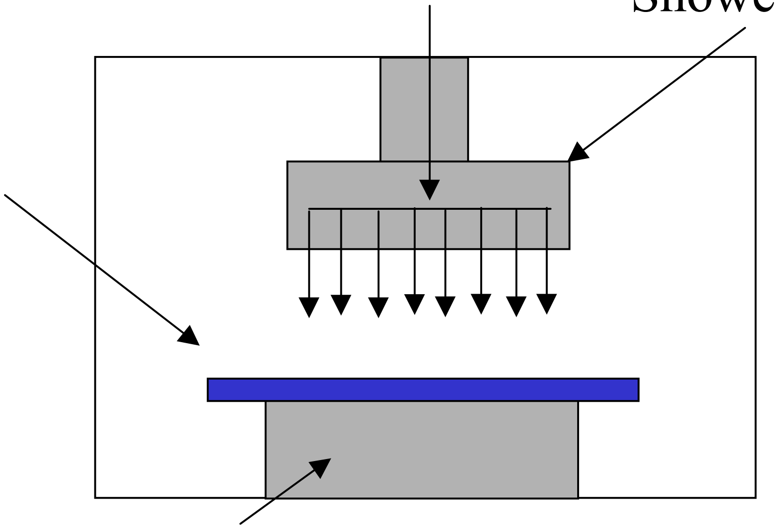


Atomic Layer Epitaxy (ALE)[1]

- Use volatile halide precursor and H_2O
- Reactants introduced in separate steps to achieve atomic layer control
- Heated wafer surface catalyzes precursor decomposition
- Products are oxide film and volatile halide compounds

Step 1: $ZrCl_{4(g)}$

Step 2: $ZrCl_{4(ab)} + 2H_2O_{(g)} \rightarrow$
$ZrO_{2\ (s)} + 4HCl_{(g)}$



Showerhead

Wafer

Heated Pedestal (>400°C)

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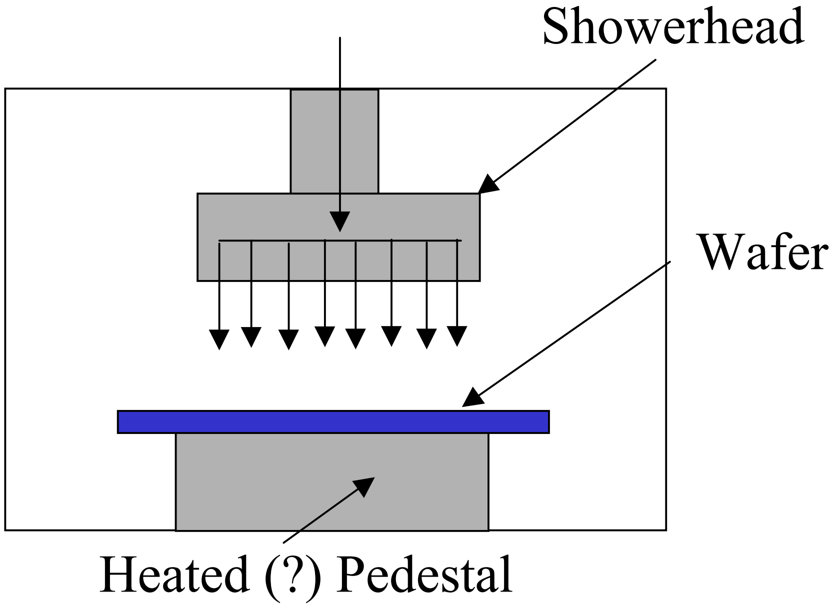
[1] S. George, et al. 1990-

Radical Enhanced Atomic Layer CVD (REAL CVD)[2]

- Use volatile organometallic precursor and a radical source
- Reactants introduced in separate steps to achieve atomic layer control
- Radical flux catalyzes precursor decomposition
- Products are oxide film and volatile organic compounds

Step 1: $\text{OM-Zr}_{(g)}$

Step 2: $\text{OM-Zr}_{(ab)} + 2\text{O}^*_{(g)} \rightarrow \text{ZrO}_{2\,(s)} + \text{CO}_{(g)} + \text{CO}_{2(g)} + \text{H}_2\text{O}_{(g)}$



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[2] A. Sherman 1999.

Potential Advantages of REALCVD over CVD and ALE

REALCVD vs. CVD

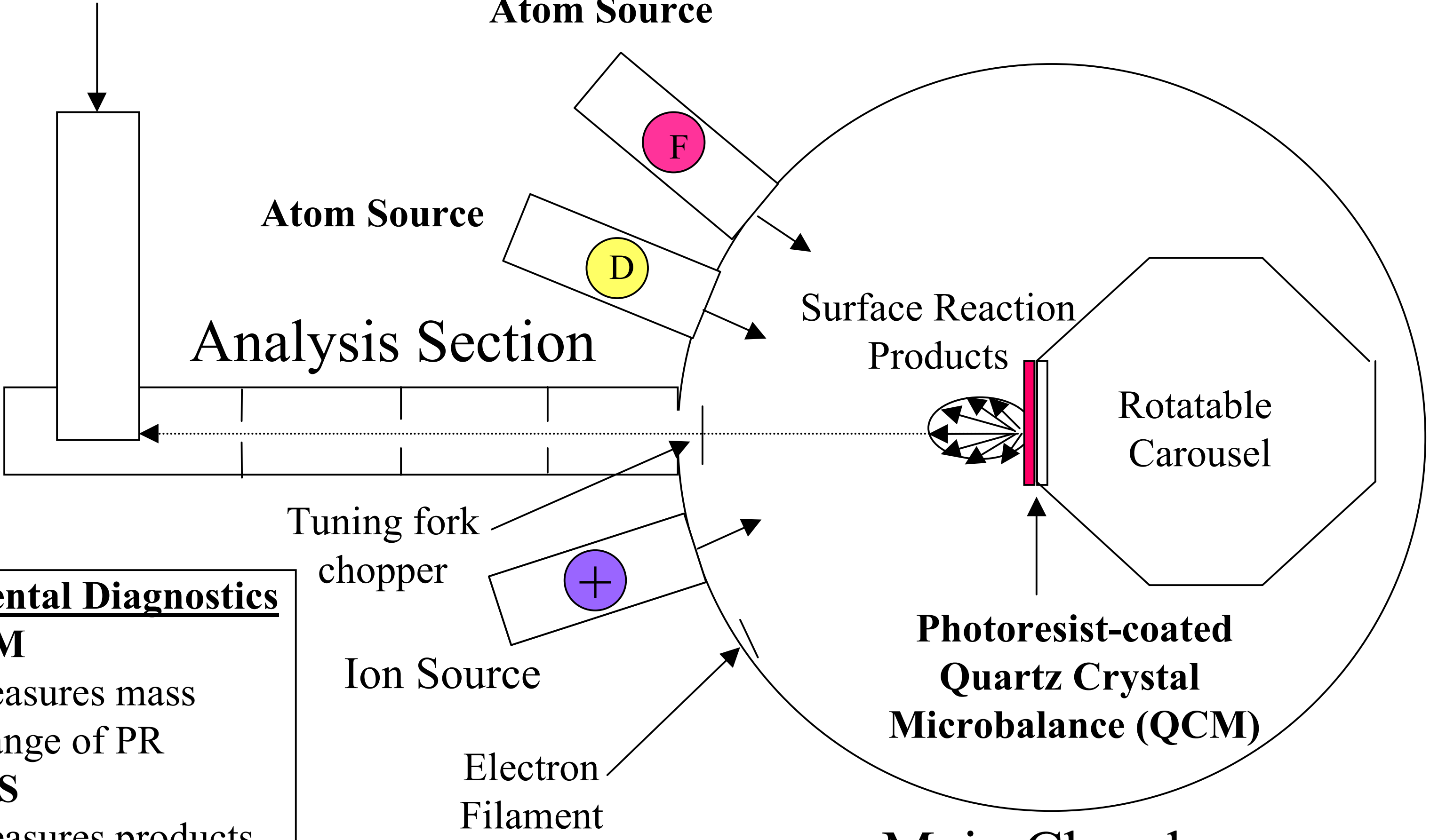
- Atomic Layer Control
  - Conformal step coverage
  - Wafer scale uniformity
- No gas phase nucleation
- Lower processing temperatures

REALCVD vs. ALE

- Lower processing temperatures
- Wider range of processing conditions
- Wider range of materials

- Little fundamental data exist to validate these statements

Schematic of the Beam Apparatus in Cross-section (Top View)



Quadrupole Mass Spectrometer (QMS)

Atom Source

Atom Source

Analysis Section

Surface Reaction Products

Rotatable Carousel

Tuning fork chopper

Ion Source

Electron Filament

Photoresist-coated Quartz Crystal Microbalance (QCM)

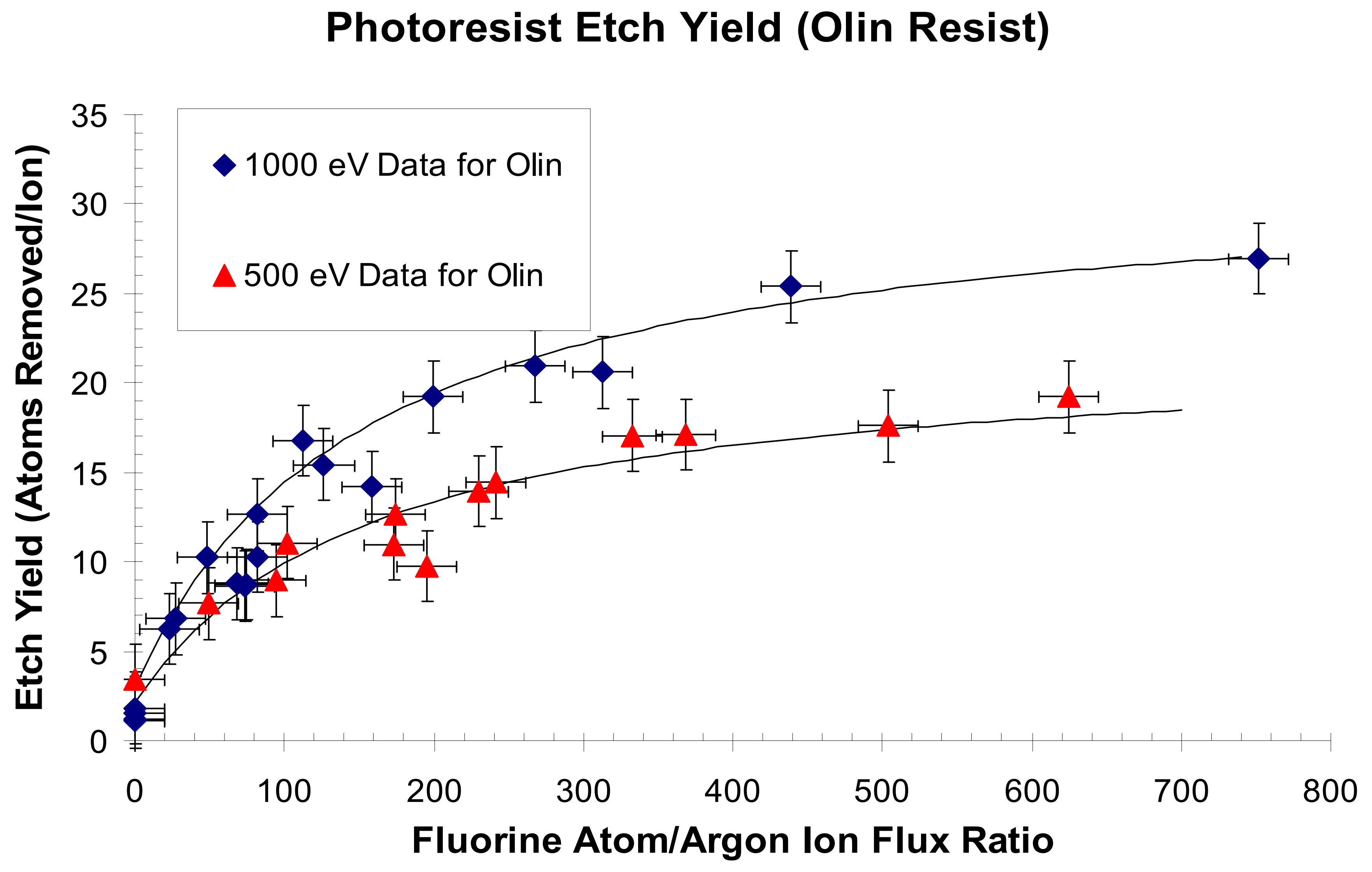
Main Chamber

Experimental Diagnostics

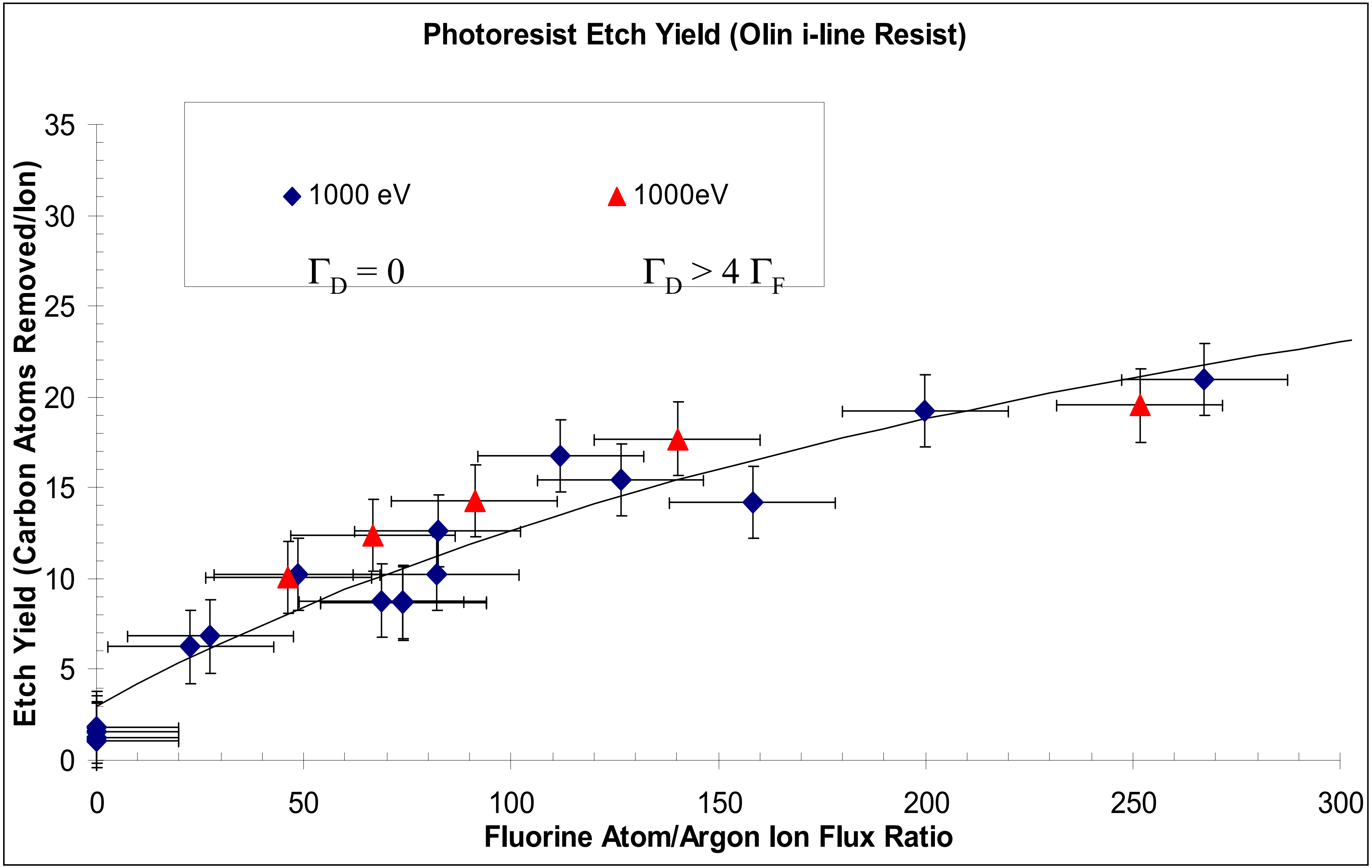
- **QCM**
  - Measures mass change of PR
- **QMS**
  - Measures products formed on PR

- Deuterium used to avoid confusion with Ar^{2+} (m/c ratio = 20) signal in QMS

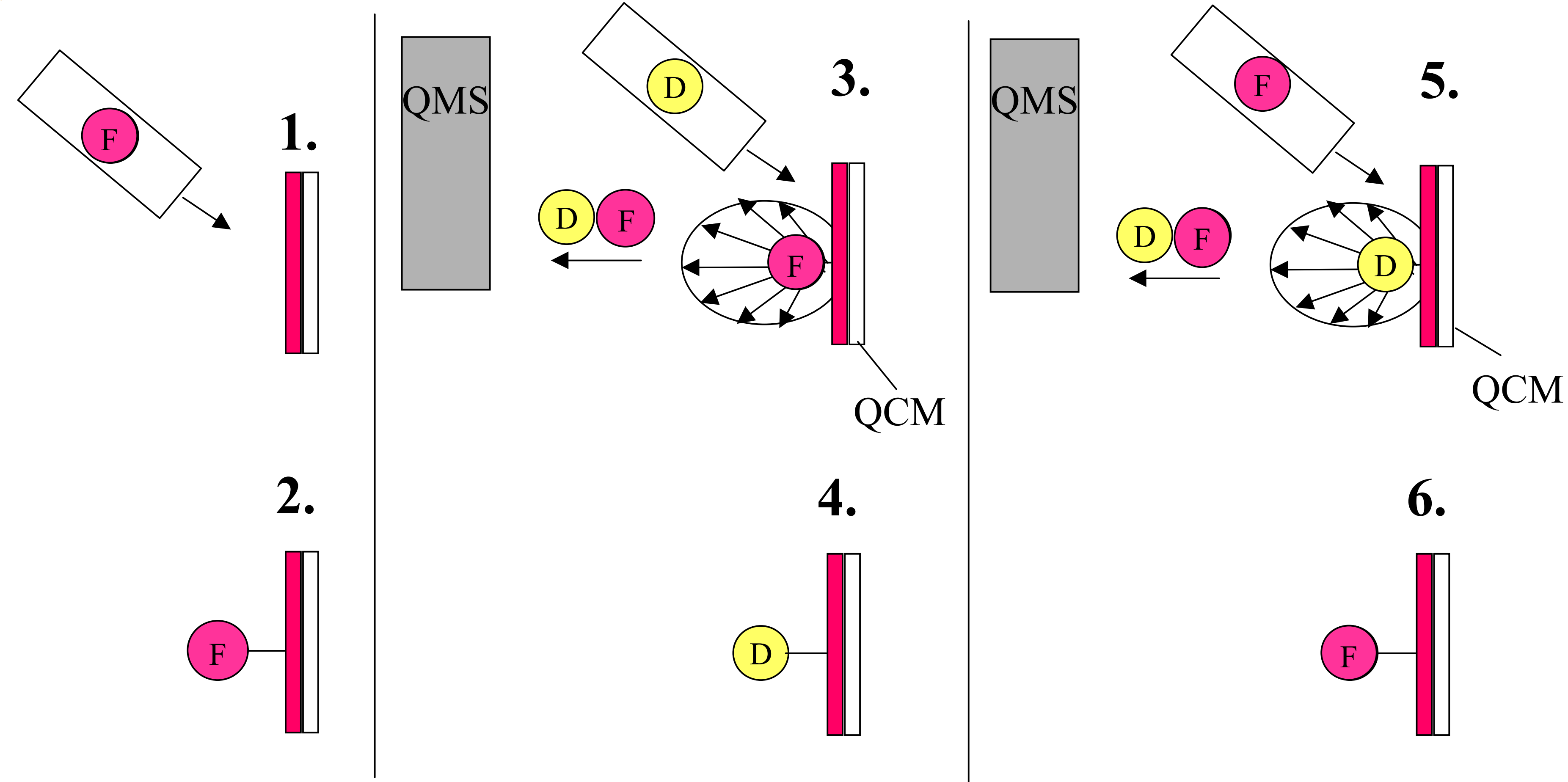
Etch Yield Results for Olin i-line Resist



Effect of Large Hydrogen Fluxes During Etching



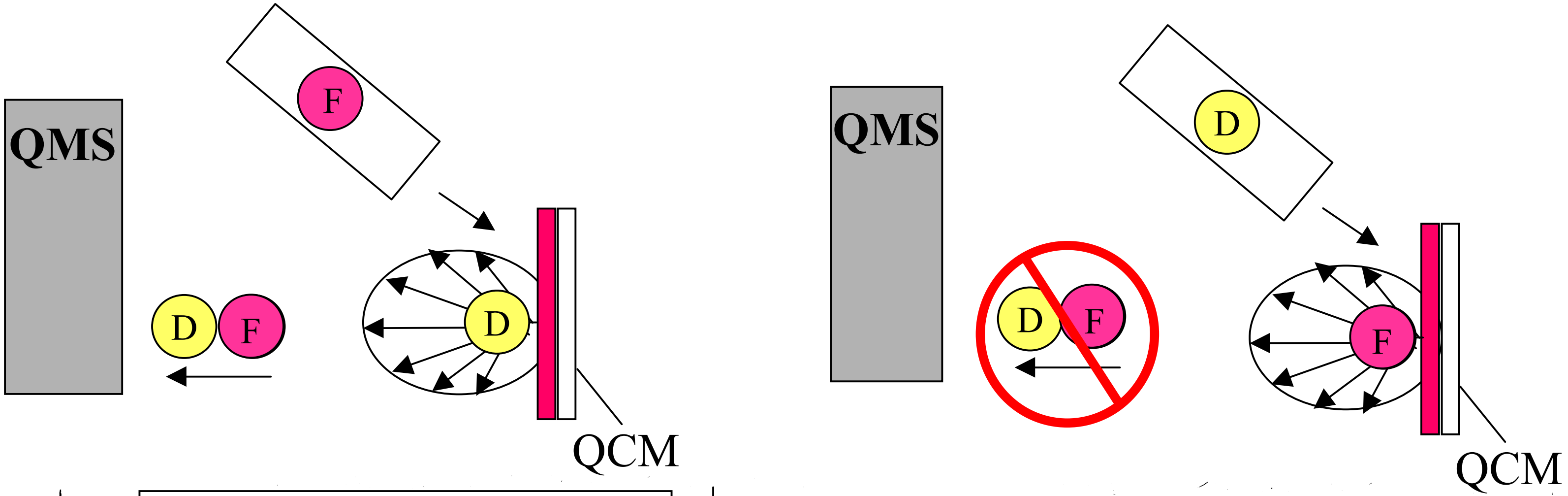
Why is there no effect of D flux on PR etch rate?

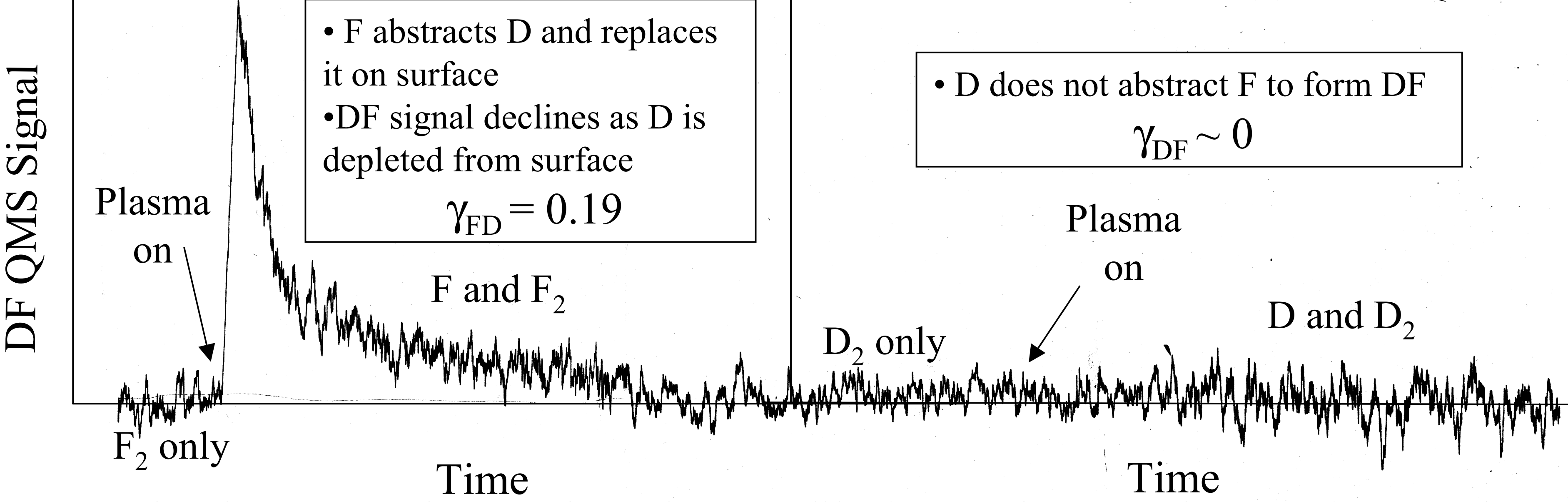


Abstraction Kinetics Experiments

1. Expose virgin PR to F atoms
2. Pump out fluorine from system
3. Expose PR to D atoms (Measure DF, Δmass)
4. Pump out deuterium from system
5. Expose PR to F atoms (Measure DF, Δmass)
6. Return to step 2

Abstraction Kinetics Results





- F abstracts D and replaces it on surface
- DF signal declines as D is depleted from surface

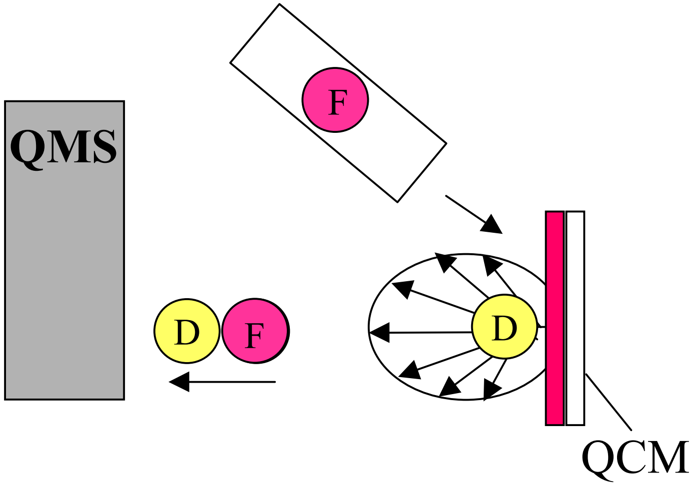
$\gamma_{FD} = 0.19$

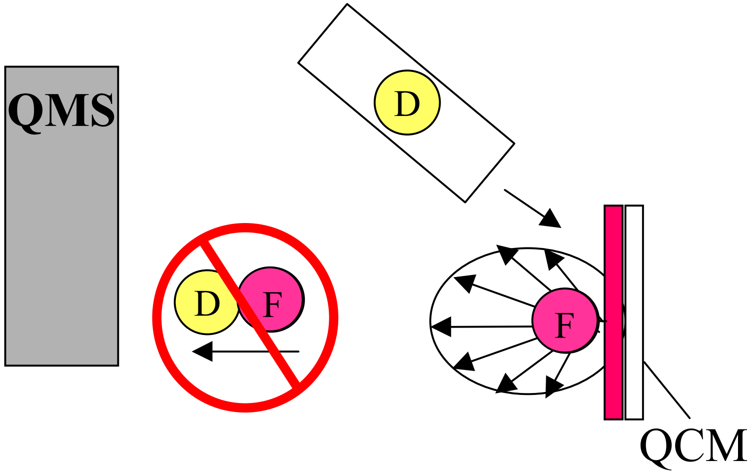
- D does not abstract F to form DF

$\gamma_{DF} \sim 0$

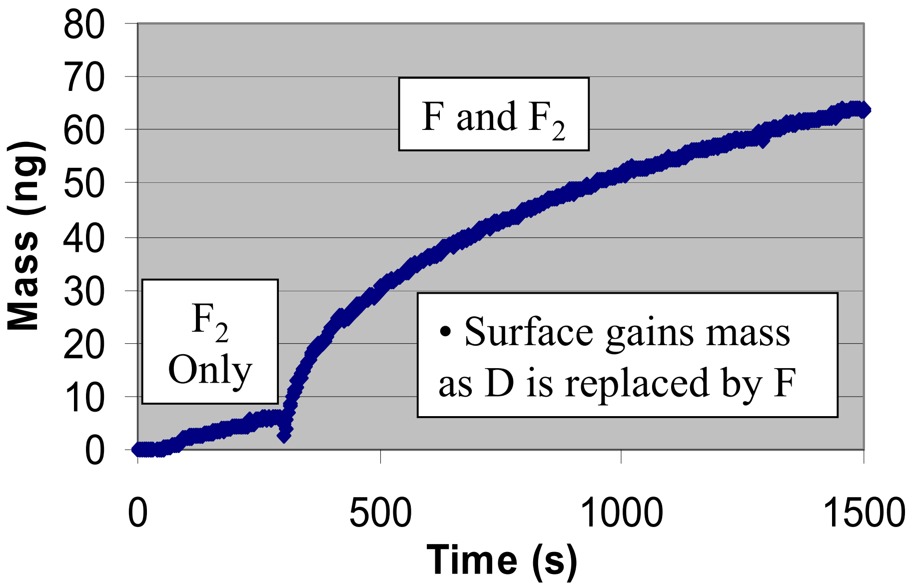
- Fluorine atoms abstract deuterium readily from a deuterated PR surface
- Deuterium atoms DO NOT abstract fluorine from a fluorinated PR surface

Abstraction Kinetics Results



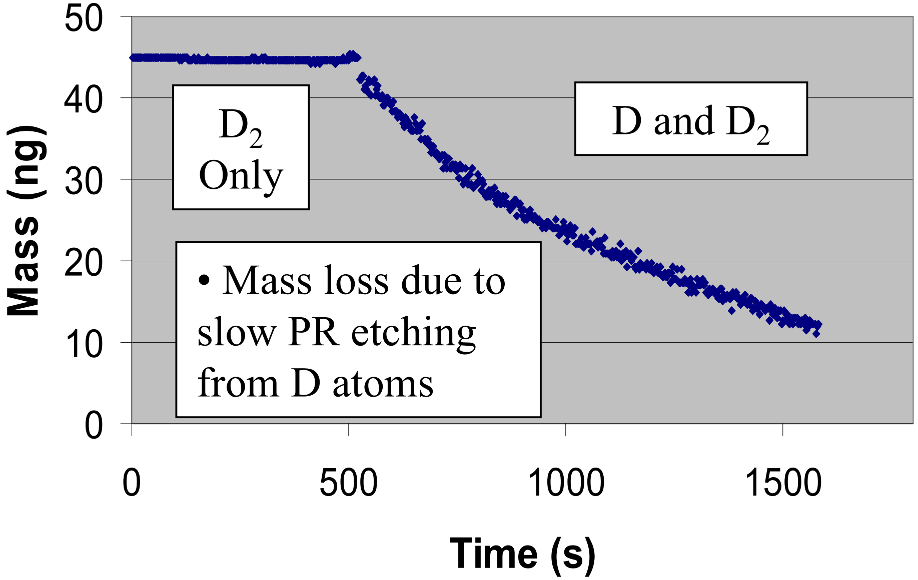


Mass Change Upon Exposure to Fluorine



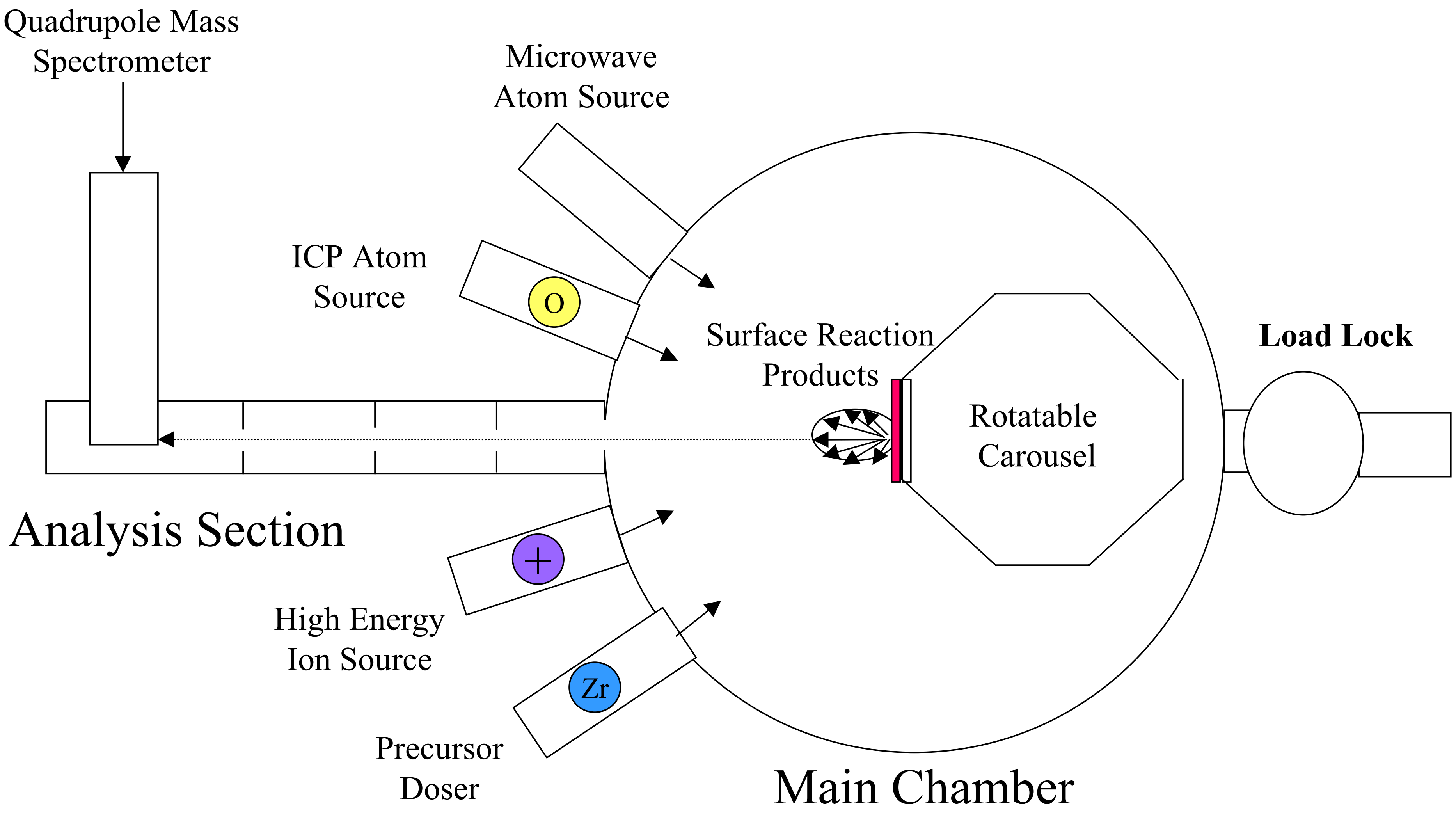
- Surface gains mass as D is replaced by F

Mass Change Upon Exposure to Deuterium



- Mass loss due to slow PR etching from D atoms

Schematic of the Beam Apparatus in Cross-section



REALCVD Issues

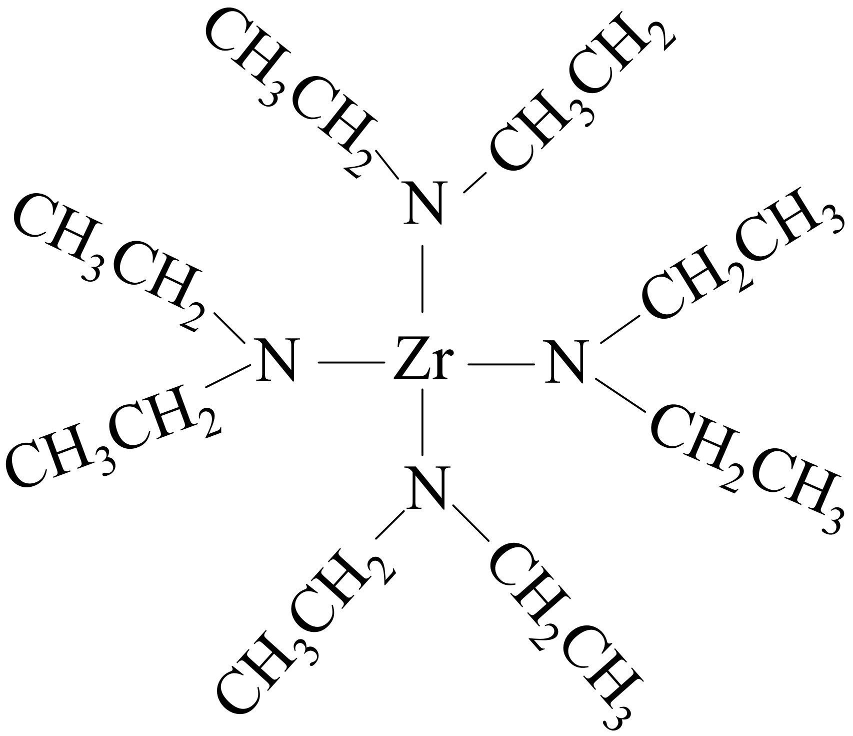
- Precursor Choice
  - Reactivity
  - Toxicity
- Precursor Delivery
  - Source temperature
  - Delivery method
- Film Characterization
  - Composition
  - Interface structure/composition
  - Electrical properties
- ESH Concerns

Precursor Issues

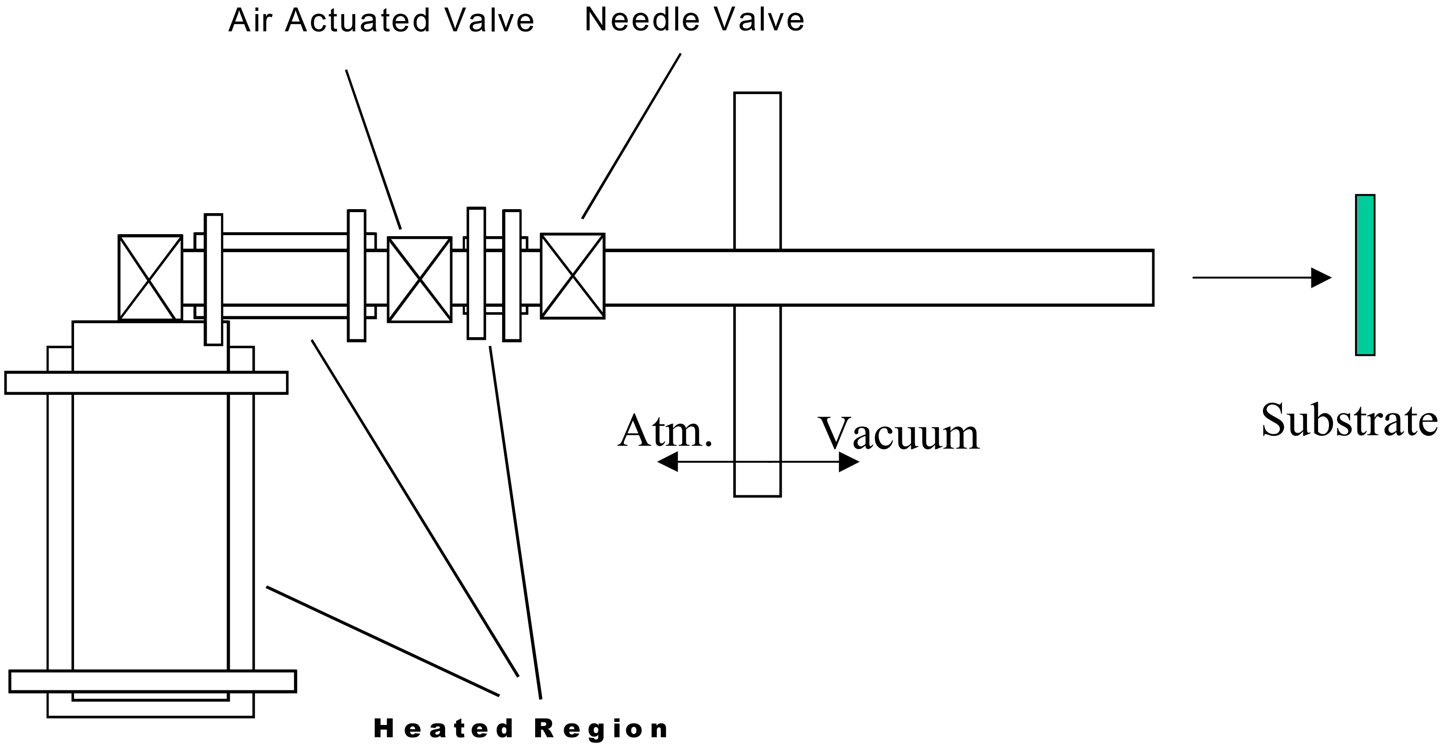
- Want both oxides and nitrides from same precursor
  - Oxygen in precursor may lead to oxynitrides
- Want liquid precursor
  - Solid precursors difficult to heat and somewhat incompatible with vacuum
- Want low toxicity and non-corrosive precursor

Tetrakis(diethylamides)

- Organometallic Precursor
- Potential candidate for deposition of oxides and nitrides
- Non-toxic
- Non-corrosive



Precursor Delivery



Issues: 1). Flux characterization

2). Supersonic Expansion

3). Throttling

Experimental Plan

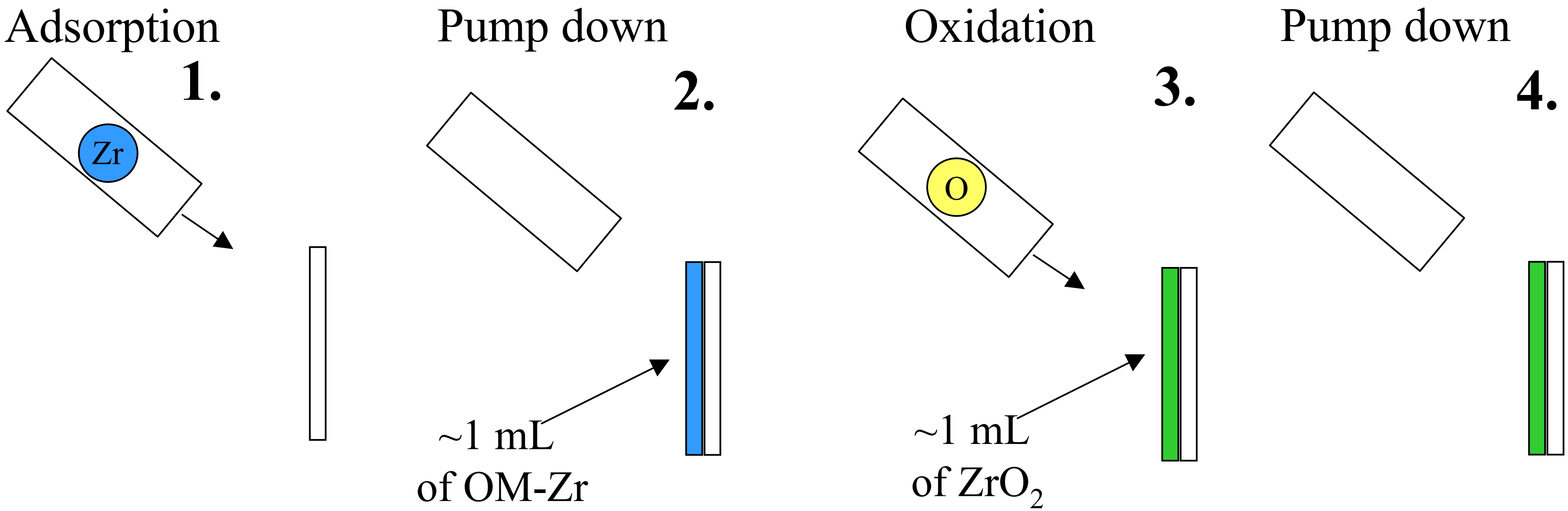
- Use Si QCM’s to perform 25^{o}C-100^{o}C REALCVD of oxides
- Oxides may be simpler due to possible film reaction with trace oxygen background
- Move to higher surface temperatures later

Requires:

- – new sample holder
- – Inductive or resistive heating of Si

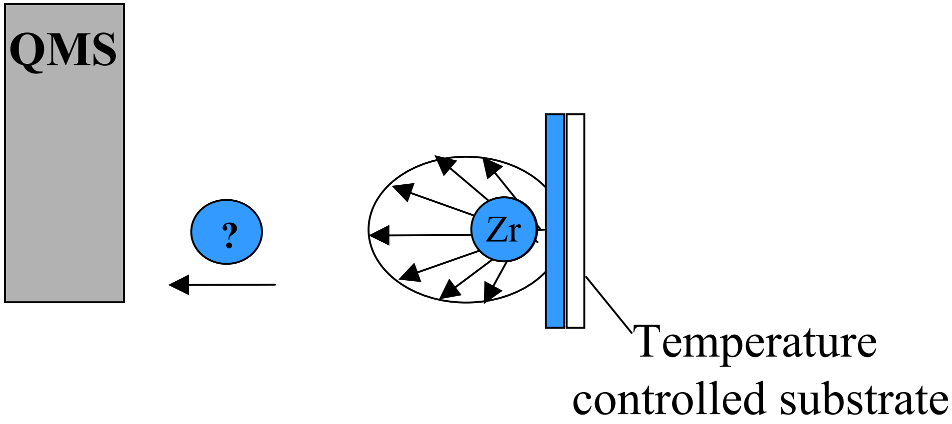
Experimental Plan

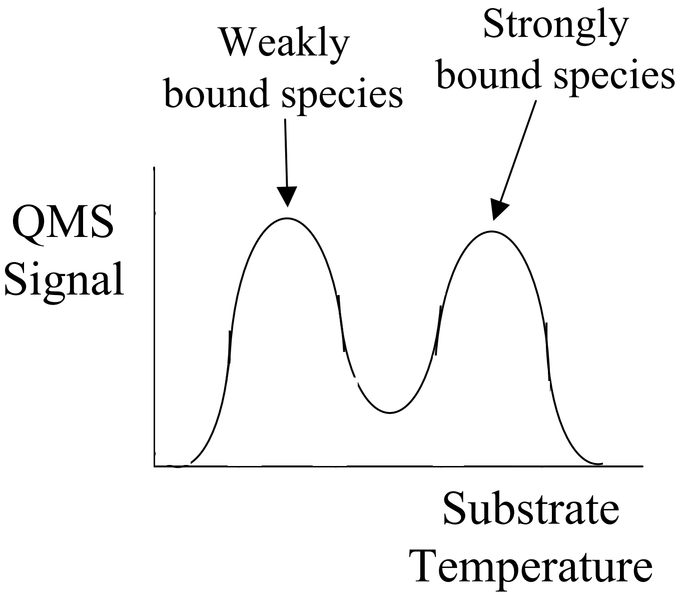
- Quartz Crystal Microbalance (QCM) Studies:
  - Uptake rate (molecules/sec/L of source gas)
  - Number of monolayers (amu/dose) ads. vs. temperature
  - Number of monolayers deposited per dose vs. temperature (amu remaining/dose)



Experimental Plan

- Quadrupole Mass Spectrometer (QMS) Studies:
  - Reaction rate and product distributions
  - Temperature Programmed Desorption (TPD)



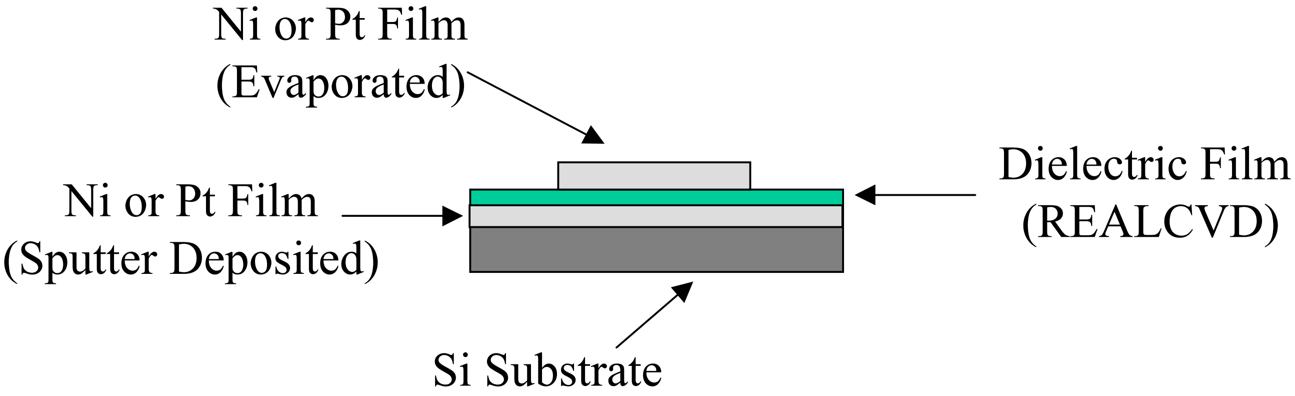


Long Range Plans

- REALCVD of high-k dielectrics
- Deposit on Pt or (Ni or Pt)/Si films

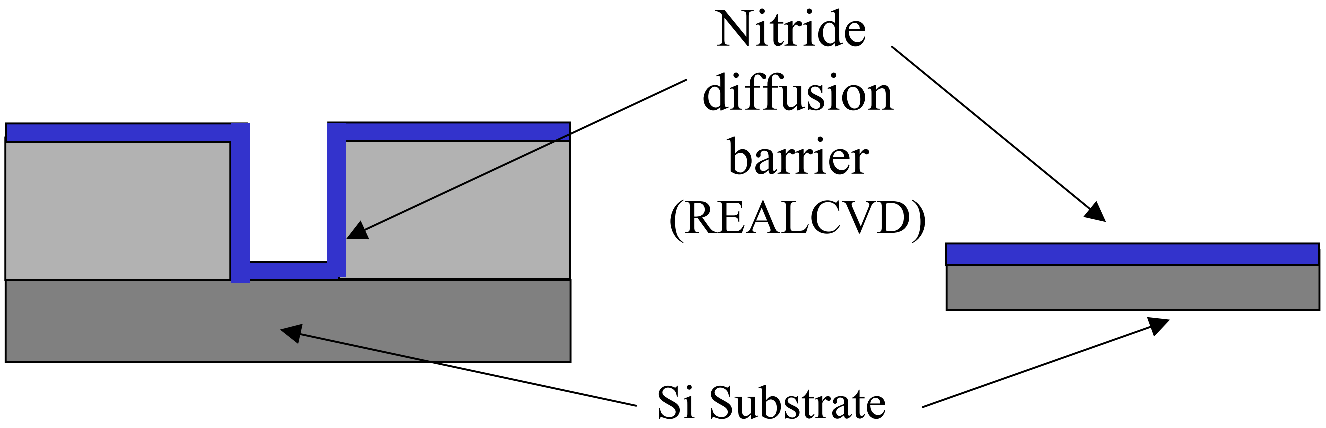
- Characterize film dielectric properties

$$C = \frac{kA}{Thickness}$$



Long Range Plans

- REALCVD of Nitrides for barrier applications
- Test for conformality and conductivity



Conformality

Conductivity

Nitride diffusion barrier (REALCVD)

Si Substrate

ESH Evaluation of REALCVD

- Comparison of REALCVD Precursors
  - Performance
  - Toxicity
  - Efficiency
    - Energy usage
    - Materials consumption
    - Consumables required
- Comparison of Processes
  - Thermal CVD
  - ALE
  - Reactive Sputtering

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