

# Removal of Moisture Contamination from Porous Polymeric Low-k Dielectric Films<sup>#</sup>

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# Presentation Outline

- Sources and effects of molecular contamination
- Research objectives
- Experimental approach
- Results and discussion
  - Adsorption loading and transport of gases through low-k materials
  - Modeling and simulation of desorption
  - Effect of porosity and film thickness on outgassing rate
- Conclusions



# Sources and Effects of Molecular Contamination

## Moisture (H<sub>2</sub>O)

- Resist and via Poisoning
- Etch rate shifts due to incomplete wetting
- Wafer and optics hazing
- Counter-doping
- Delamination, non-uniform Cu-seed deposition
- Malfunction of epitaxial growth
- Photolithography

## Organics from

Chemicals and Personnel

Paints and Filters

Wafer Boxes and Equipment

- ✓ Isopropanol (IPA)
- ✓ Butylated Hydroxy toluene (BHT)
- ✓ Dioctylphthalate (DOP)
- ✓ Amines

Acknowledgment: Dr. Prashant Raghu



# Low-k Materials

Materials	Application	k value
SiO <sub>2</sub>	CVD	3.9 - 4.5
FSG	CVD	3.2 - 4.0
Black Diamond™ (SiCOH)	CVD	2.7 – 3.3
<b>p-MSQ</b>	<b>Spin-on</b>	<b>1.8 - 2.2</b>
Porous SiLK	Spin-on	1.5 - 2.0

- **Faster clock speeds and lower power consumption**
- **Reduce RC delay, power dissipation, crosstalk noise and number of metal level**
- **Number of options**

1. Introducing Low-k Dielectrics into Semiconductor Processing, Michael E. Clarke. Mykrolis



# Contamination Behavior of Low-k Materials

- **Low-k inter-layer dielectrics (ILD) are highly prone to molecular contamination, especially if it porous**
- **Potential issues associated with molecular contamination of low-k materials:**
  - **Their ability to absorb chemicals, such as contaminants containing polar O-H bonds due to their porous structure**
  - **Increase in k values**
  - **Signal propagation delays and cross-talk between interconnects**
- **Characterization of sorption behavior of new low-k films will assist in deciding their potential for successful integration in semiconductor processes**



# Method of Approach

Identification of molecular contaminants



Adsorption characteristics

Adsorption loading

Transport/Kinetics

Mechanism of interaction



Variables

Temperature

Concentration

Film Physical Properties



Effect on Inter-layer dielectric quality



# Model Contaminants

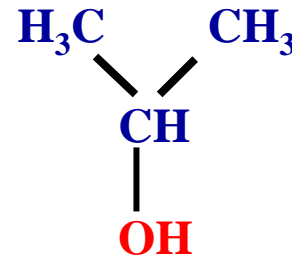
## Moisture



Ubiquitous impurity

$\mu = 1.8 \text{ D}$

## Isopropanol (IPA)



Used as solvent, drying agent

Mol.Wt : 60.10

B.P : 83 °C

$\mu = 1.7 \text{ D}$



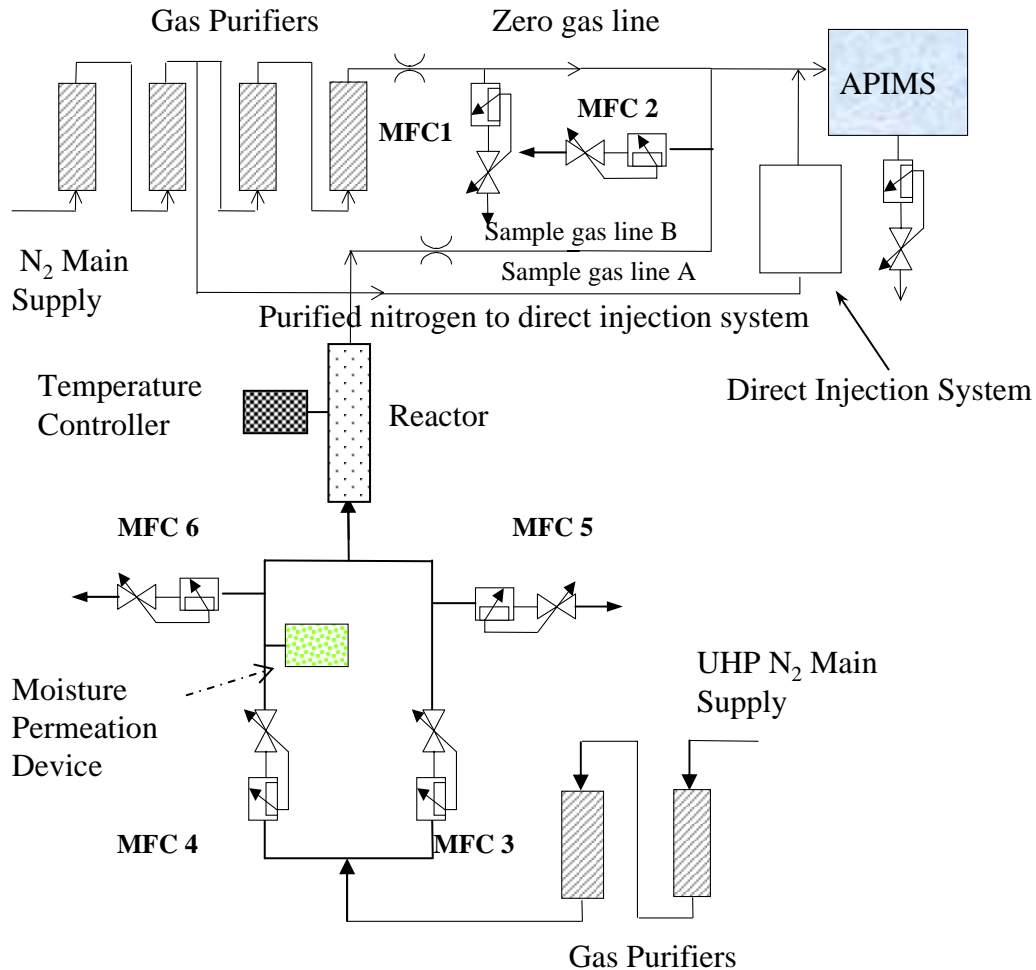
# Research Objectives

- **Study molecular contamination of low-k materials like p-MSQ and compare them with SiO<sub>2</sub>**
  - **Adsorption loading**
  - **Transport, Incorporation and removal of moisture in all forms in the matrix**
  - **Mechanism of interactions of moisture and organics with wafer surfaces**
- **Develop fundamental model based on adsorption/desorption mechanism to simulate adsorption loading and surface concentration profiles**





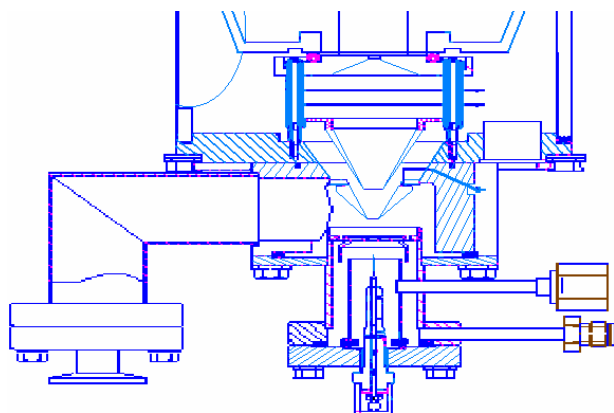
# Experimental Setup



- All metal MFCs
- Heated 316L EPSS tubing
- No dead volumes
- Research grade gases

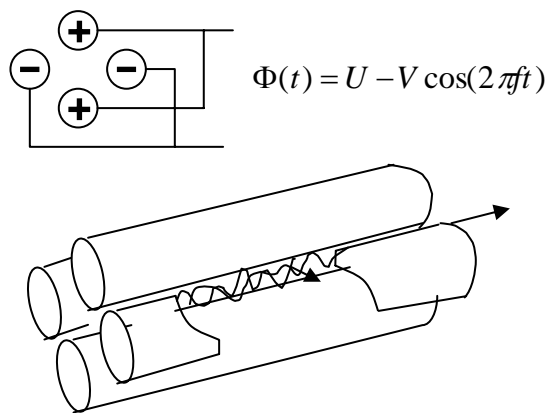
# Atmospheric Pressure Ionization Mass Spectrometry

## Ionization



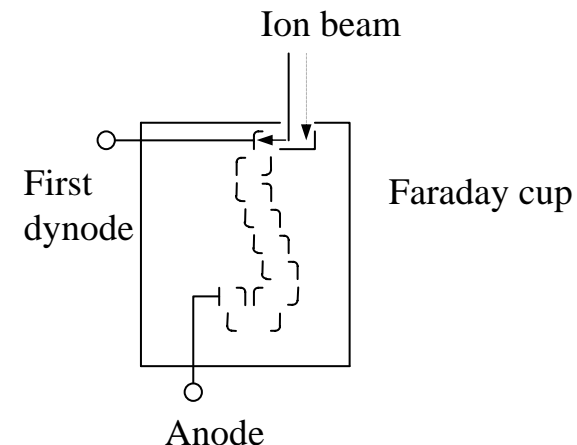
- Ionization by electron impact
- Atmospheric
- High rate of ionization
- High sensitivity (ppt levels)

## Separation



- Separation in quadrupole
- Based on m/e ratio
- 3 quadrupoles enable analysis of peaks with overlapping m/e

## Detection



- Electron multiplication by secondary electron emission

# Sample Preparation

Test samples for this study was porous methylsilsesquioxane (MSQ) low-k dielectrics (JSR 5109) with

Dielectric constant	2.2-2.3
Porosity	~ 48%,
Pore diameter	~ 3.4 nm

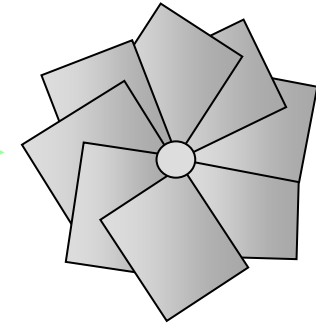
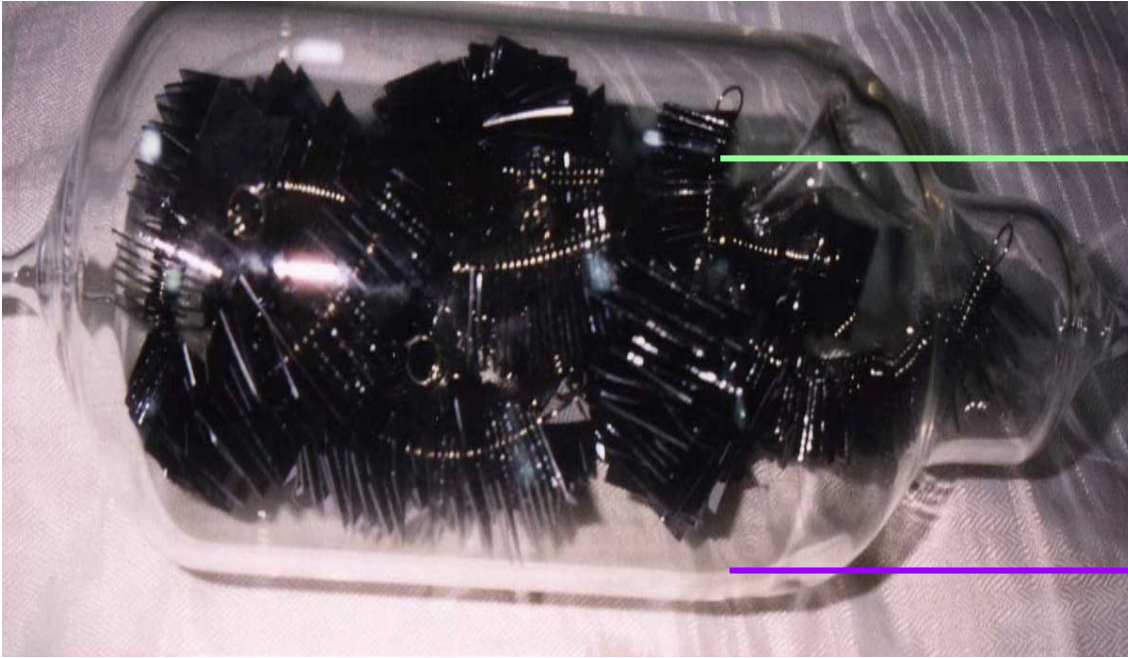
The Low-k wafers<sup>3</sup> were processed as follows:

- 5500 Å Thermal Oxidation (Wet Oxidation)
- 3500 Å LPCVD Nitride (Thermal Nitride – both sides of wafer)
- 4000 Å Blanket JSR 5109
- Standard JSR Cure
- Partial etch
- Partial ash

3. Wafers provided by Sematech



# Experimental Reactor

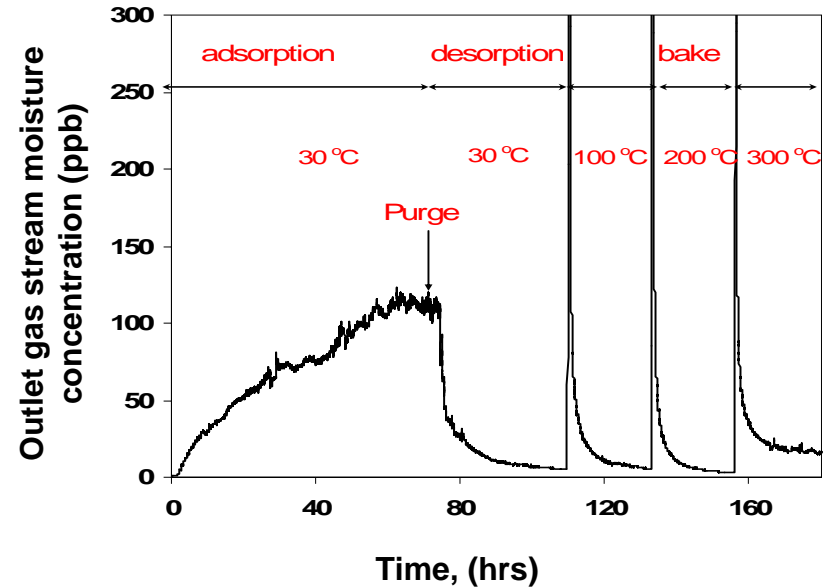
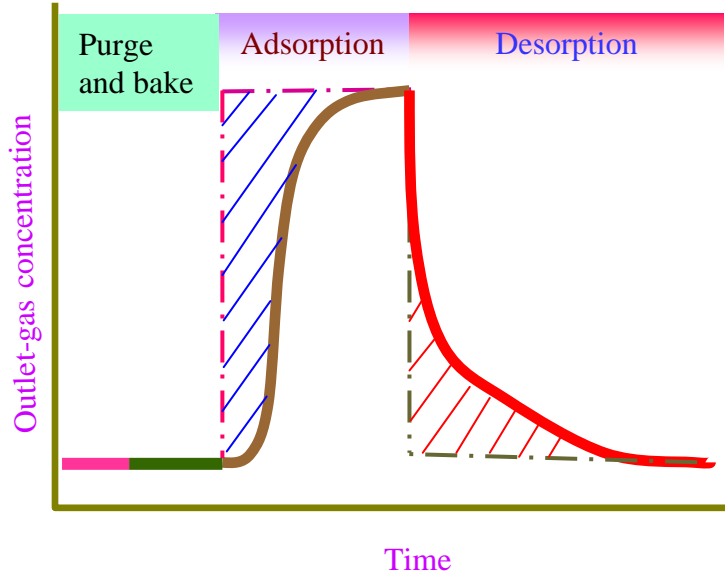


Wafer coupons  
loaded on springs

Pyrex reactor

- Wafers diced into 1 cm x 2 cm coupons
- Coupons loaded on nickel coated steel springs and densely packed into a Pyrex<sup>®</sup> glass reactor
- Random orientation and reactor geometry results in adequate gas mixing, allow this reactor to be treated as a differential reactor
- High wafer to glass surface area ratio

# Experimental Procedure



## Experimental procedure

Adsorption at 30°C

Desorption at 30°C

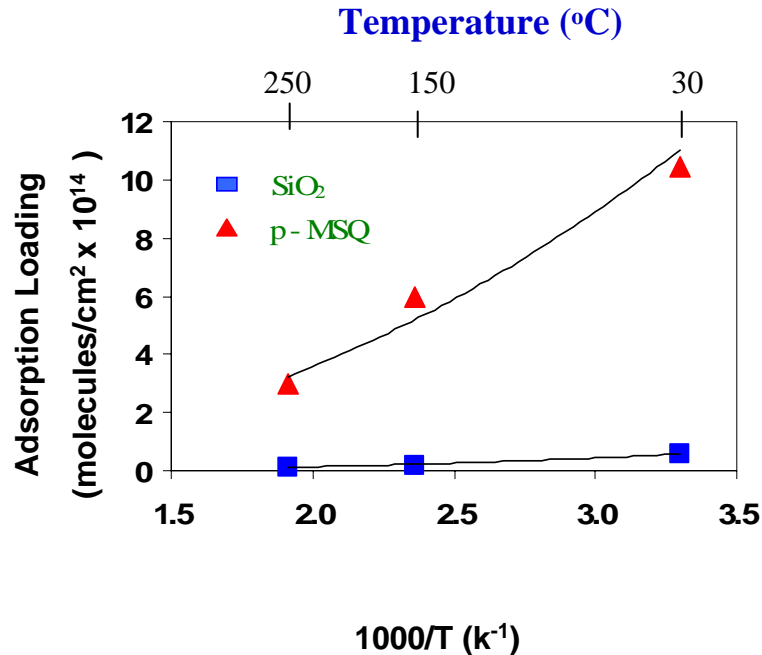
Bake-out at 100, 200 & 300°C

Temporal profile of adsorption (challenge 110 ppb moisture), followed by temperature-programmed desorption as measured by mass spectrometer



# Moisture Adsorption Loading

Gas-phase H<sub>2</sub>O conc.: 56 ppb



• p-MSQ have much higher adsorption loading than SiO<sub>2</sub>

SiO<sub>2</sub>

Δ Electronegativity 1.7

-OH site density 4.6 x 10<sup>14</sup>  
(#/cm<sup>2</sup>)

p-MSQ

$$C_{film0} = C_{gp0} \varepsilon + C_{s0} (1 - \varepsilon)$$

$$C_{s0} = C_{gb0} * S$$

$C_{gb0}$  = challenge moisture concentration

$C_{gp0}$  = equilibrium moisture conc in the pore

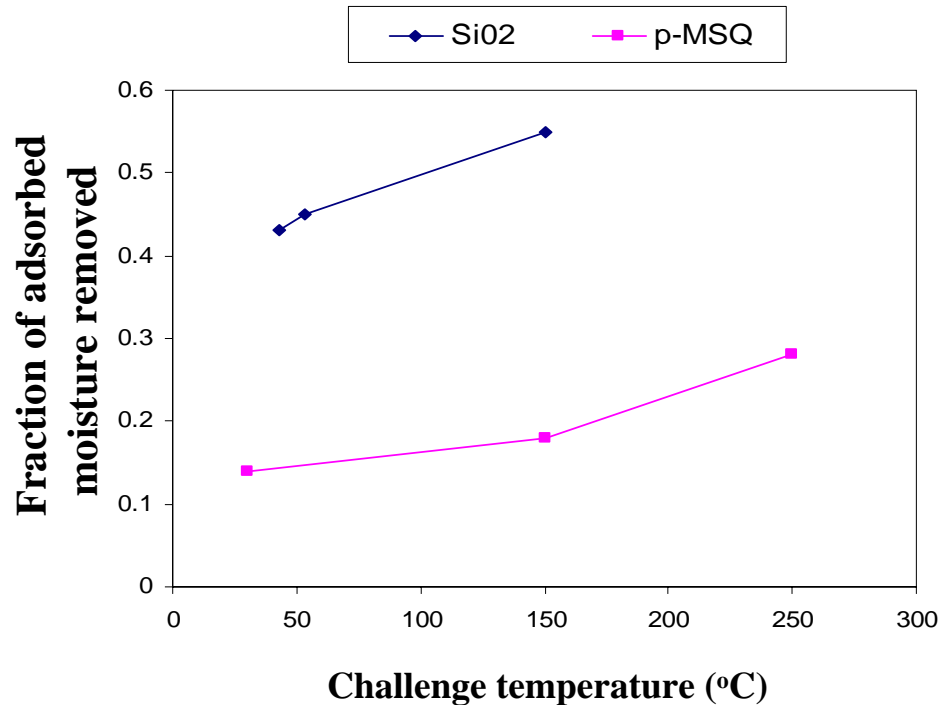
$C_{s0}$  = equilibrium moisture conc in the matrix

$C_{filmo}$  = total moisture loading in molecules per unit volume of the film

$\varepsilon$  = porosity,  $S$  = Solubility



# Moisture Retention after Isothermal N<sub>2</sub> Purge



Gas-phase H<sub>2</sub>O conc.: 56 ppb

Purge Time : 10 hrs

- 45-50 % of adsorbed moisture removed from SiO<sub>2</sub> during isothermal N<sub>2</sub> purge
- Around 15-25 % of adsorbed moisture removed from p-MSQ



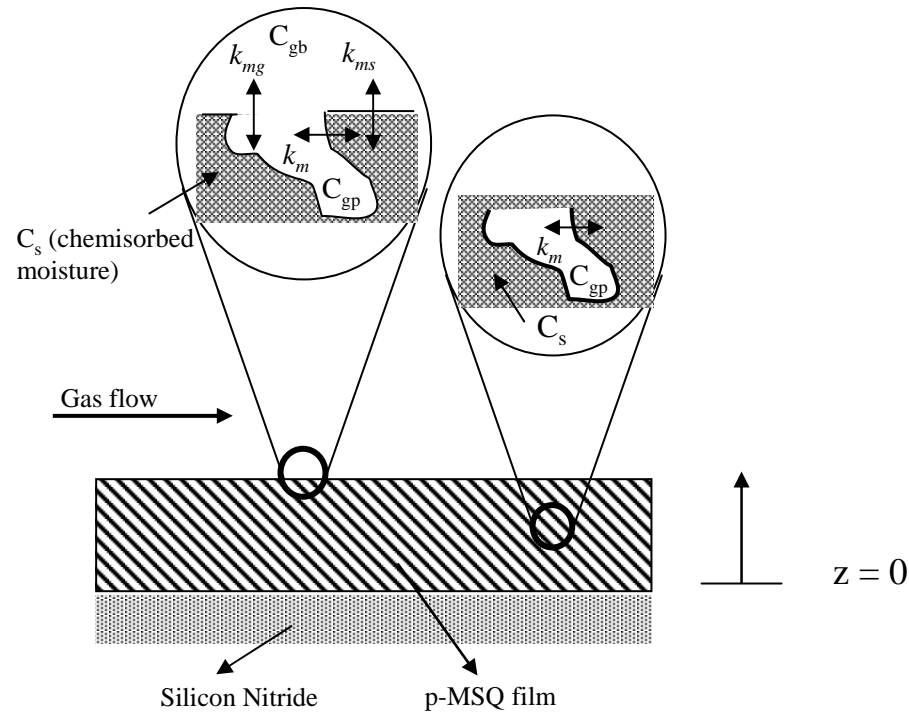
# Simulation of Adsorption/Desorption Profiles

- **Study mechanism and interaction**
- **Develop process model**
- **Experimental validation of model**
- **Parameter Estimation**
- **Applications:**
  - **Simulate concentration profiles and adsorption loading**
  - **Effect of porosity and film thickness**
  - **Optimization of process conditions**





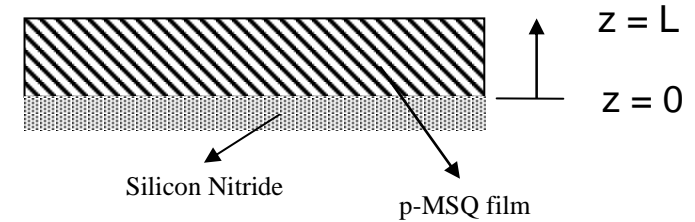
# Schematic of Moisture Transport and Interactions



## Transport and Interaction pathways:

- Transport in solid matrix by permeation (dissolution and diffusion)
- Transport in pore following micro pore diffusion
- Exchange between matrix and pores

# Development of Desorption Model



**Governing Equation for transport of moisture in porous matrix is:**

$$D_s \frac{\partial^2 C_s}{\partial z^2} - \frac{S_p \varepsilon}{(1 - \varepsilon)} k_m (C_s - C_{gp} S) = \frac{\partial C_s}{\partial t}$$

**The initial and boundary conditions are:**

I.C:  $C_s = C_{gb0} S,$  at  $t = 0$

B.C.1  $\frac{\partial C_s}{\partial z} = 0$  at  $z = 0$

B.C.2  $-D_s \frac{\partial C_s}{\partial z} = k_{ms} (C_s - C_{gb} S)$  at  $z = L$

**Governing Equation for transport of moisture in pore is given by:**

$$D_g \frac{\partial^2 C_{gp}}{\partial z^2} + S_p k_m (C_s - C_{gp} S) = \frac{\partial C_{gp}}{\partial t}$$

**The initial and boundary conditions are:**

I.C:  $C_{gp} = C_{gb0}, \quad \text{at } t = 0$

B.C.1  $\frac{\partial C_{gp}}{\partial z} = 0 \quad \text{at } z = 0$

B.C.2  $-D_g \frac{\partial C_{gp}}{\partial z} = k_{mg} (C_{gp} - C_{gb}) \quad \text{at } z = L$

### CSTR (Mixed Reactor) Model

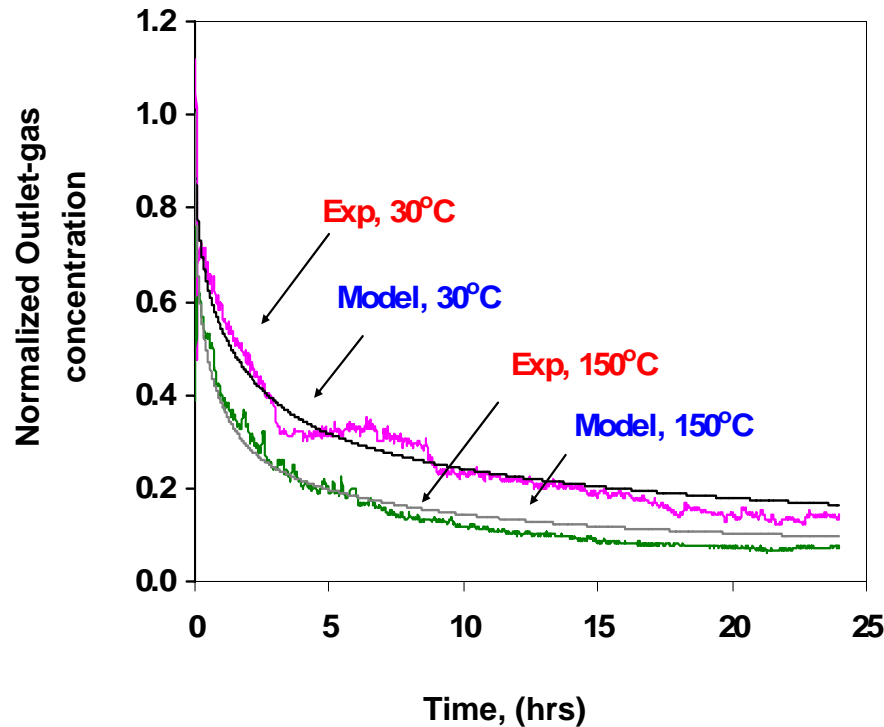


$$V \frac{dC_{gb}}{dt} = Q(C_{gb,in} - C_{gb}) + (1 - \varepsilon)A_{tot} k_{ms} (C_s - C_{gb} S) \Big|_{z=L} + \varepsilon A_{tot} k_{mg} (C_{gp} - C_{gb}) \Big|_{z=L}$$



# Validation of Model

- 30 °C experimental data on p-MSQ
- 30 °C Model fit
- 150 °C experimental data on p-MSQ
- 150 °C Model fit



Gas-phase Moisture conc.: 56 ppb

Desorption



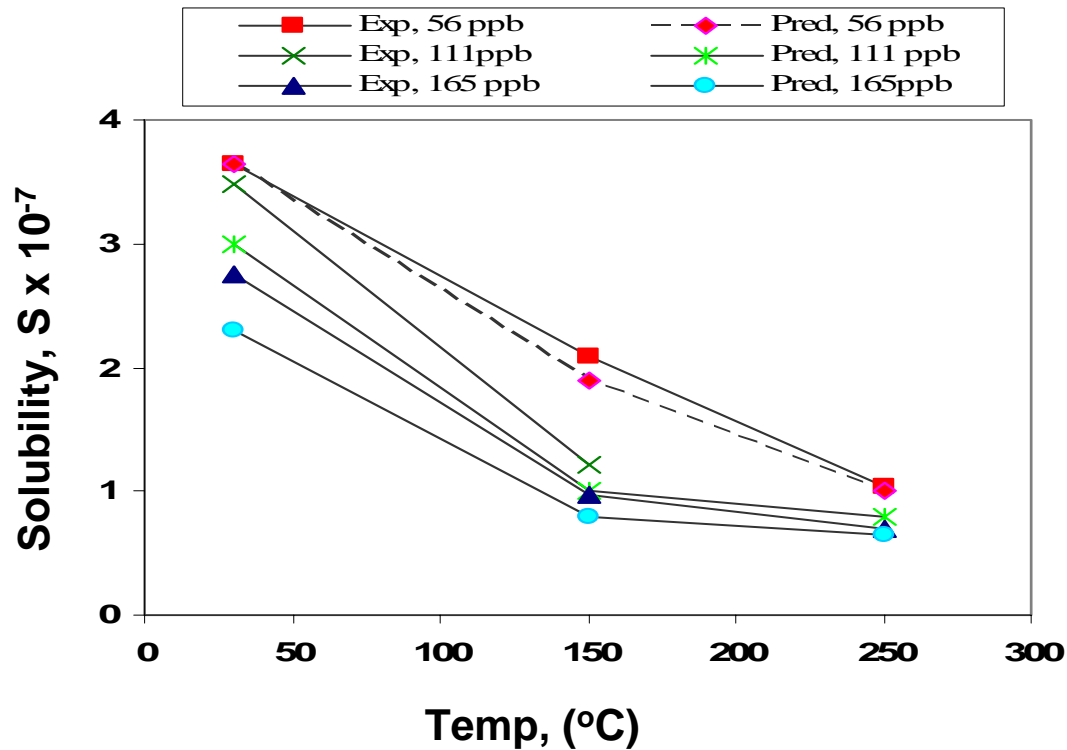
# Estimated Parameters

Parameters	Units	30 °C	150 °C	250 °C
$D_s$	cm <sup>2</sup> /s	1.4e-15	1.7e-15	3.5e-15
$D_g$	cm <sup>2</sup> /s	8.5e-10	1.0e-9	3.0e-9
$S$		3.65e7	1.9e7	1.0e7
$k_m$	cm/s	5.0e-13	5.0e-13	5.0e-13
$k_{ms}$	cm/s	1.0e-8	1.0e-8	1.0e-8
$k_{mg}$	cm/s	1.0e-7	1.0e-7	1.0e-7

- Diffusion in matrix is primarily through molecular or intra-lattice cavities
- Transport through pores is micro pore diffusion
- Exchange coefficients  $k_m$ ,  $k_{ms}$  and  $k_{mg}$  are weak functions of temperature and are constant for all cases



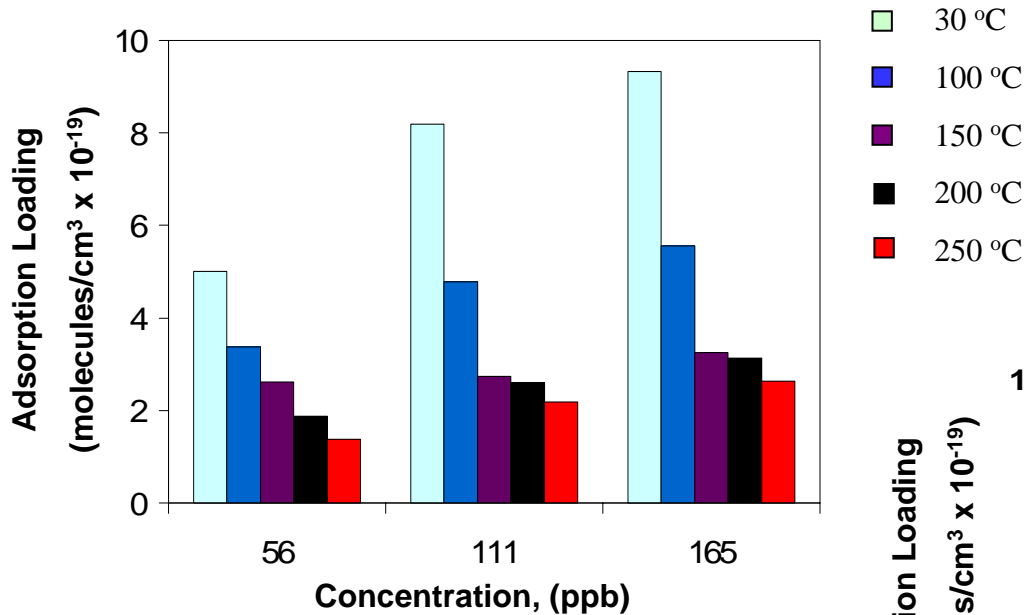
# Solubility of moisture in p-MSQ



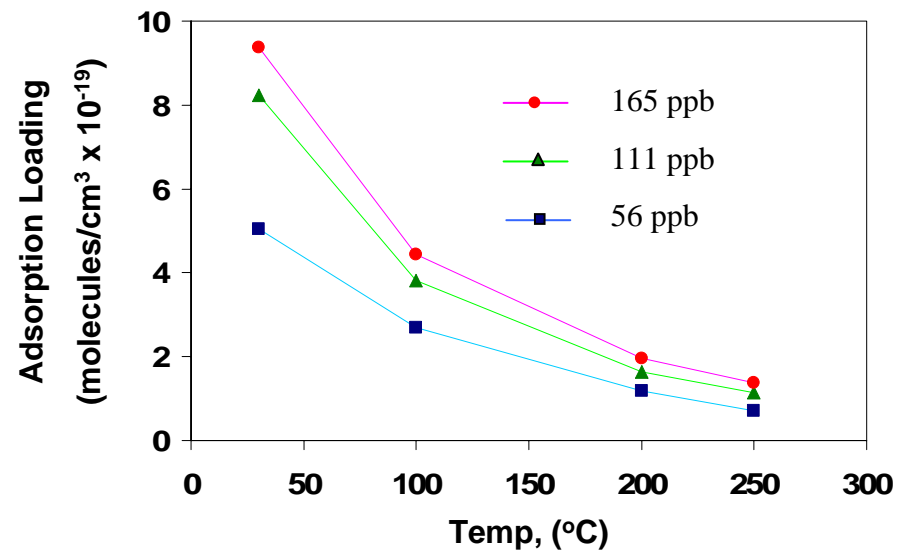
- $S$  values are in good agreement with the values of  $S$  determined by fitting the model to desorption data
- Slight dependence of  $S$  on moisture concentration



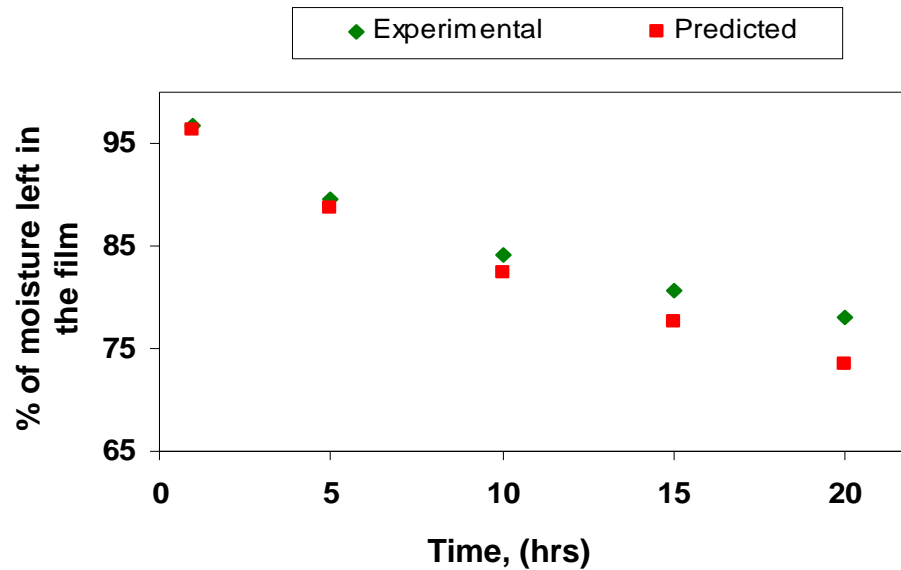
# Loading Comparison



- The total amount of moisture adsorbed for a particular concentration decreases with increasing temperature
- At a constant temperature the total moisture loading increases with increase in the challenge concentration



# Percentage clean up



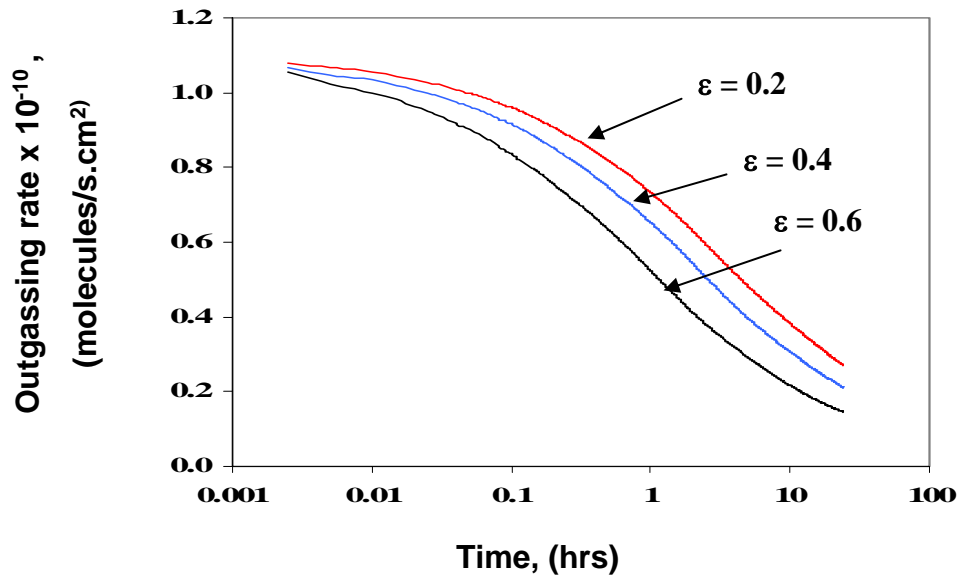
Gas-phase H<sub>2</sub>O conc.: 56 ppb  
T = 150 °C

- After one hour of desorption; only around **5%** of the total moisture is removed. Even after 20 hrs, **~75%** of total moisture remains in the dielectric film.
- Very slow and highly activated overall removal of moisture could be a significant problem in the integration of such porous dielectric films in semiconductor processing





# Effect of porosity on outgassing rate

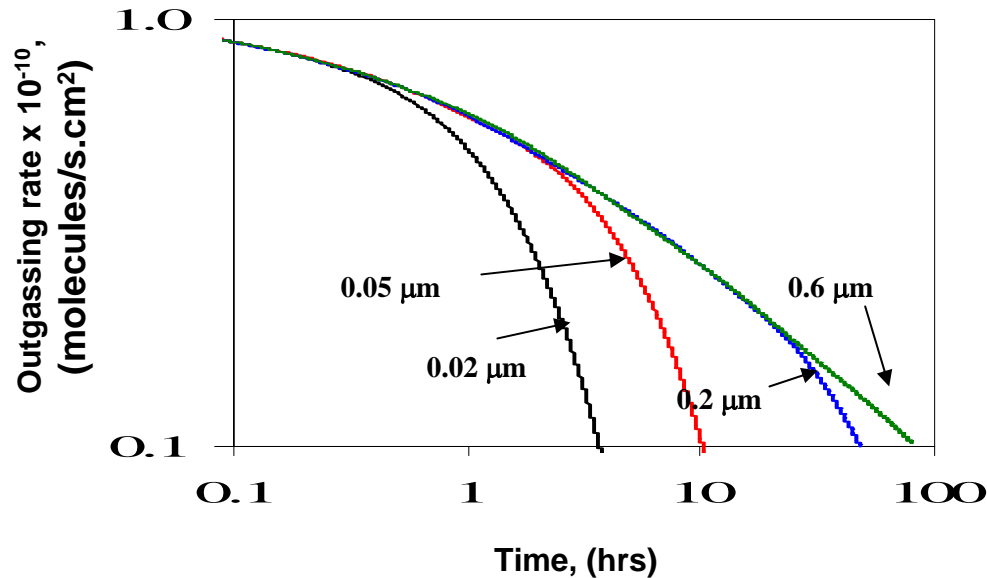


Gas-phase H<sub>2</sub>O conc.: 56 ppb  
T = 30 °C

- Two competing factors: film loading and mass transport rate
- The total amount of moisture adsorbed in the film decreases with increase in porosity
- The overall mass transfer between the film and bulk gas depends on the mass transfer between the pore and bulk gas; porosity increase leads to an increase in the mass transport by pores



# Effect of thickness on outgassing rate



Gas-phase H<sub>2</sub>O conc.: 56 ppb

T = 30 °C

- The thickness affects both the film mass and the overall diffusional resistance .
- Decrease in diffusional resistance increases the outgassing rate
- Decrease in total amount of moisture adsorbed decreases the outgassing rate



# Practical Applications of Model

- **Model describes actual processes and explains experimental results**
- **It is a practical tool for**
  - **estimation of surface contamination and**
  - **optimization of process conditions to minimize effects of molecular contamination**
  - **valuable tool for designing a desorption recipes (temperature, gas flow, and gas purity) to assure effective and efficient clean up of the dielectric films**



# Conclusions

- **Moisture adsorption and desorption rates in p-MSQ are sensitive to temperature, moisture concentration as well as the film thickness, moisture solubility and the fundamental properties of moisture transport in the dielectric materials, in the pores and across the solid gas interphase.**
- **Moisture incorporation in MSQ matrix involves many intermediates (a wide spectrum of physical and chemical interactions).**
- **A process model is developed to elucidate the interactions of moisture with porous films.**
- **The results show that interphase transport and the pore diffusion coefficients are much smaller than those predicted by bulk or Knudsen diffusion mechanism.**
- **Diffusion through matrix is very slow and activated process**
- **The low outgassing rates also indicate that porous films such as p-MSQ are highly susceptible to moisture contamination**



# Future Work

- **Development of models to simulate competitive adsorption / desorption profiles of multiple molecular contaminants**
- **Adsorption of molecular contaminants on other low-k materials.**



# Nomenclature

$A_{\text{tot}}$  = total exposed surface area available for moisture to adsorb

$C_{\text{gb}}$  = concentration of moisture in surrounding medium

$C_{\text{gb,in}}$  = concentration of moisture in inlet gas stream

$C_{\text{gp}}$  = concentration of moisture in voids

$C_{\text{s}}$  = concentration of moisture in matrix

$D_{\text{s}}$  = diffusivity of moisture in the matrix

$D_{\text{g}}$  = gas phase diffusivity of moisture in pores

$k_{\text{m}}$  = mass transfer coefficient between matrix and voids

$k_{\text{ms}}$  = mass transfer coefficient between matrix and gas phase in the surrounding medium

$k_{\text{mg}}$  = mass transfer coefficient between pores and gas phase in the surrounding medium

$L$  = thickness of the film

$Q$  = volumetric flow rate

$S$  = solubility of moisture in the film

$S_{\text{p}}$  = specific surface area of the porous film

$V$  = volume of the reactor

$\varepsilon$  = Film porosity



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