Interactions of Moisture with Dielectric Films

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Low-k Interlayer Dielectric

Outline

- Necessity to remove moisture from low-*k* dielectric films
- Research objectives
- Experimental procedure and model development
- Experimental results and model validation
- Comparison of moisture uptake and removal in two p-MSQ films
- Effect of cap layer on moisture uptake and removal
- Conclusion

Dielectric Materials as Candidates for Low-*k*

Oxide Derivatives

F-doped oxides (CVD)	k = 3.3-3.9
C-doped oxides (SOG, CVD)	k = 2.8-3.5
H-doped oxides (SOG)	k = 2.5-3.3

Organics

Polyimides (spin-on)	k = 3.0-4.0
Aromatic polymers (spin-on)	k = 2.6-3.2
Vapor-deposited parylene; parylene-F	k ~ 2.7; k ~ 2.3
F-doped amorphous carbon	k = 2.3-2.8
Teflon/PTFE (spin-on)	k = 1.9-2.1

Highly Porous Oxides

Xerogels/Aerogels	k = 1.8-2.5

Air k = 1

Source: Prof. Krishna Saraswat, Stanford University

Adverse Impacts of Moisture

- **Moisture (water *k* value ~ 80) could significantly deteriorate *k* value of a low-*k* film.**
- **Moisture outgassing degrades device reliability.**
- **Moisture adsorbed on low-*k* film surface may cause metal corrosion and delamination of a cap layer.**

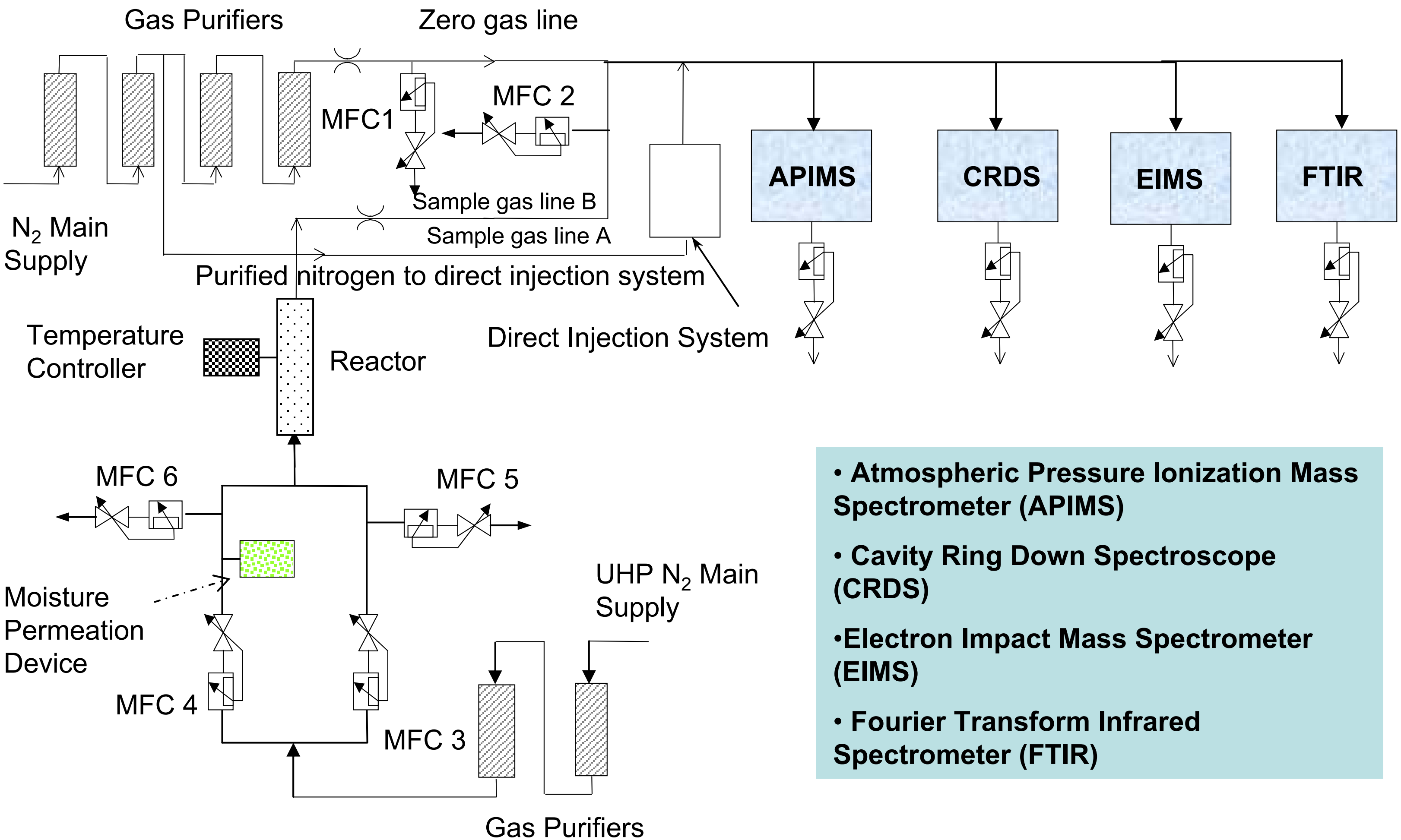
Objectives

- Determine the fundamentals of moisture interactions with blanket, and patterned porous low-*k* films:
  - Loading
  - Outgassing Dynamics

- Develop a process model that could be used to design a more efficient purging and drying process for contaminated low-*k* films

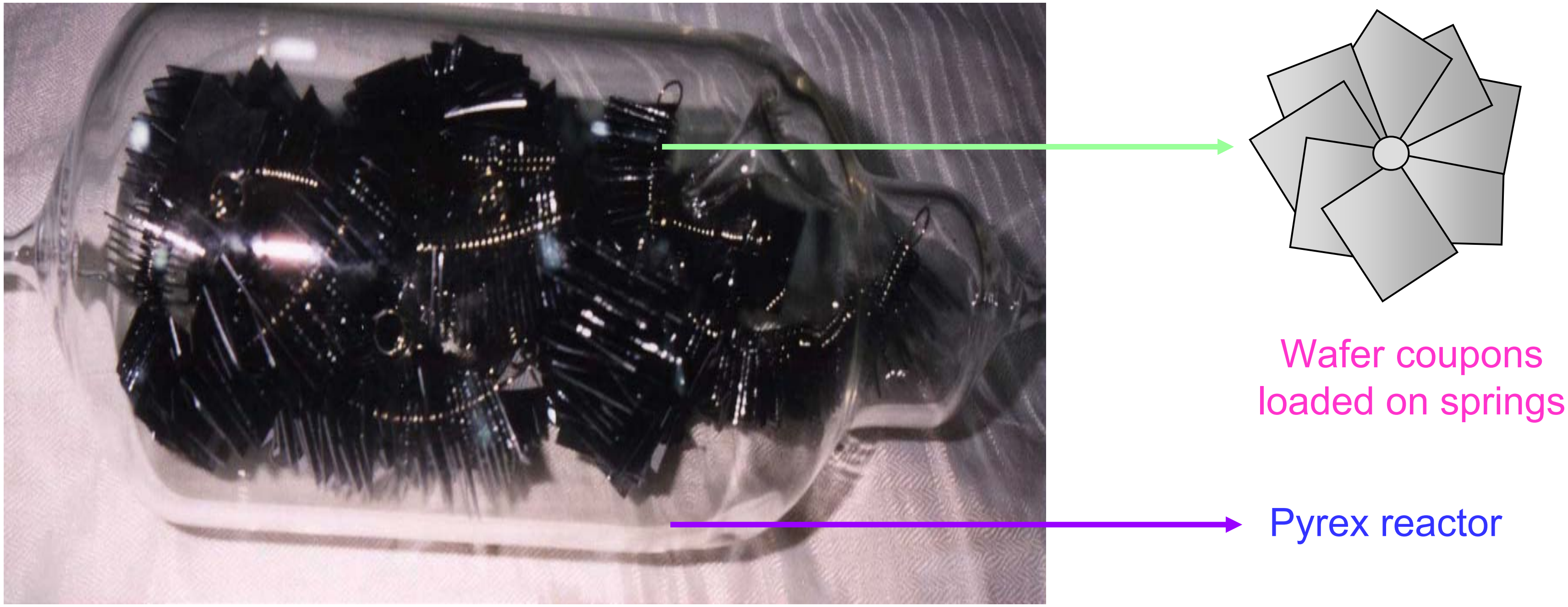
- Study the effect of a cap layer on moisture adsorption and desorption in porous low-k films

Experimental Setup



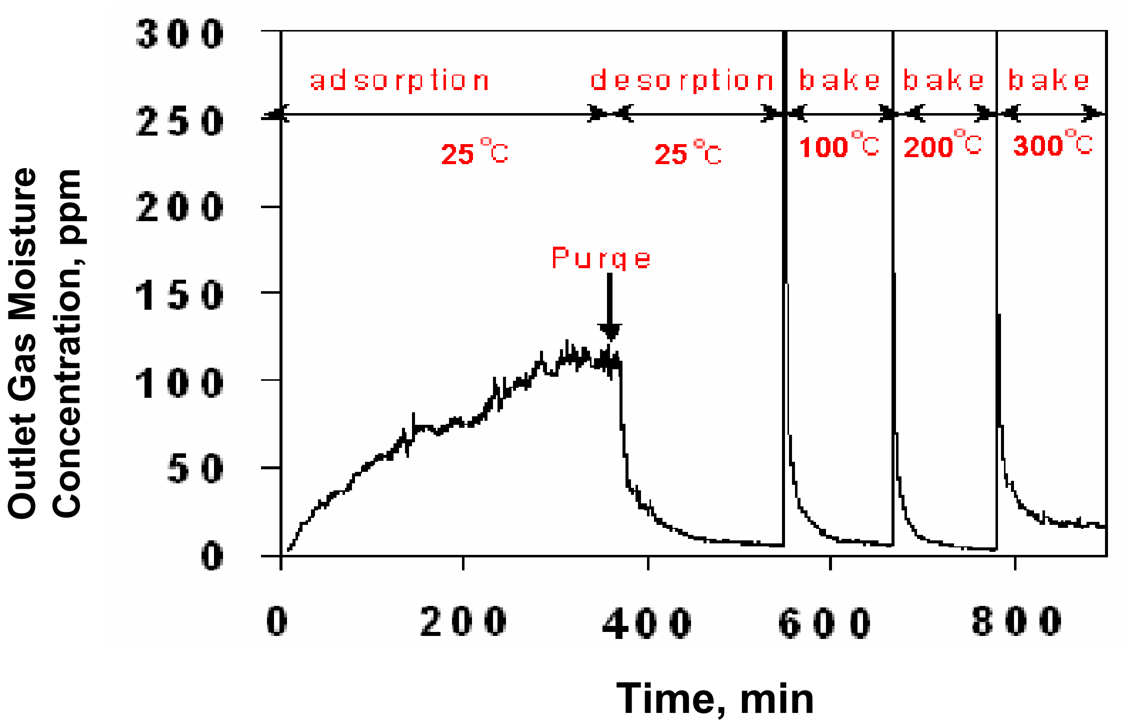
- **Atmospheric Pressure Ionization Mass Spectrometer (APIMS)**
- **Cavity Ring Down Spectroscope (CRDS)**
- **Electron Impact Mass Spectrometer (EIMS)**
- **Fourier Transform Infrared Spectrometer (FTIR)**

Experimental Reactor



- 1 x 2 cm coupons
- Random orientation results in adequate gas mixing
- High wafer to glass surface area ratio

Experimental Procedure



Adsorption at 25°C

Desorption at 25°C

Bake-out at 100, 200 & 380°C

Temporal profile of adsorption /desorption

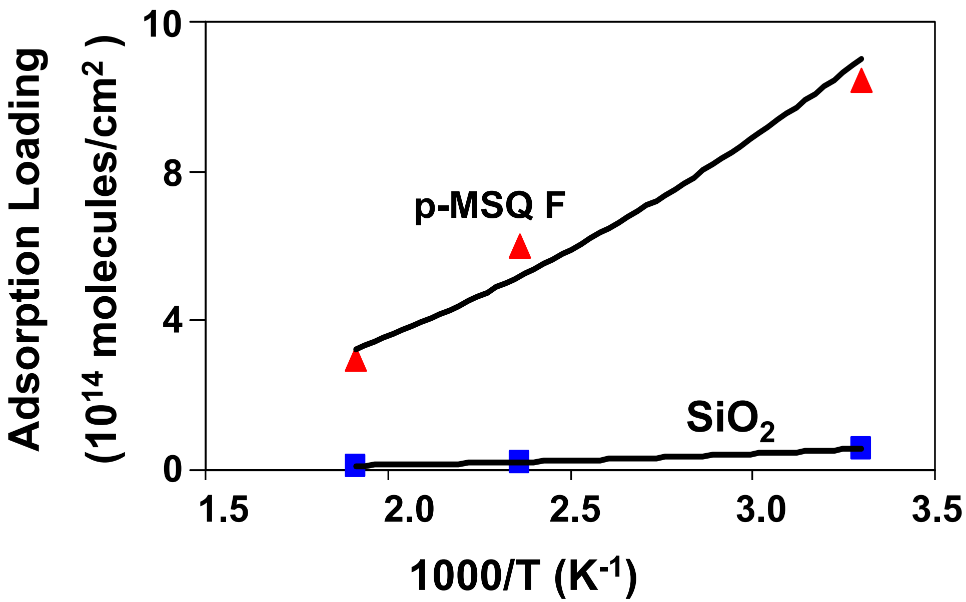
Test Samples

p-MSQ	Processing Conditions	Contact angle
A	Partial etch @ 10s, N_2H_2 ash @ 20s	102^o
B	Partial etch @ 10s, HeO_2 ash @ 20s	50^o
C	Partial etch @ 10s, H_2 ash @ 20s	90^o
D	Partial etch @ 10s, no ash	48^o
E	Blanket and cure only	105^o
F	JSR LKD 5109. Standard JSR cure, partial etch and partial ash	——

* Samples provided by Sematech

Moisture Absorption Loading in SiO_2 and p-MSQ

Challenge Concentration: 56 ppb; p-MSQ F: JSR LKD 5109. Standard JSR cure, partial etch and partial ash.



p-MSQ F has much higher sorption loading than SiO_2

SiO_2

Δ Electronegativity	1.7
-OH site density	4.6×10^{14} (#/cm²)

p-MSQ

$$C_{film0} = C_{g0}\varepsilon + C_{s0}(1-\varepsilon)$$

$$C_{s0} = C_{g0} * S$$

C_{go} = equilibrium moisture concentration in the pore

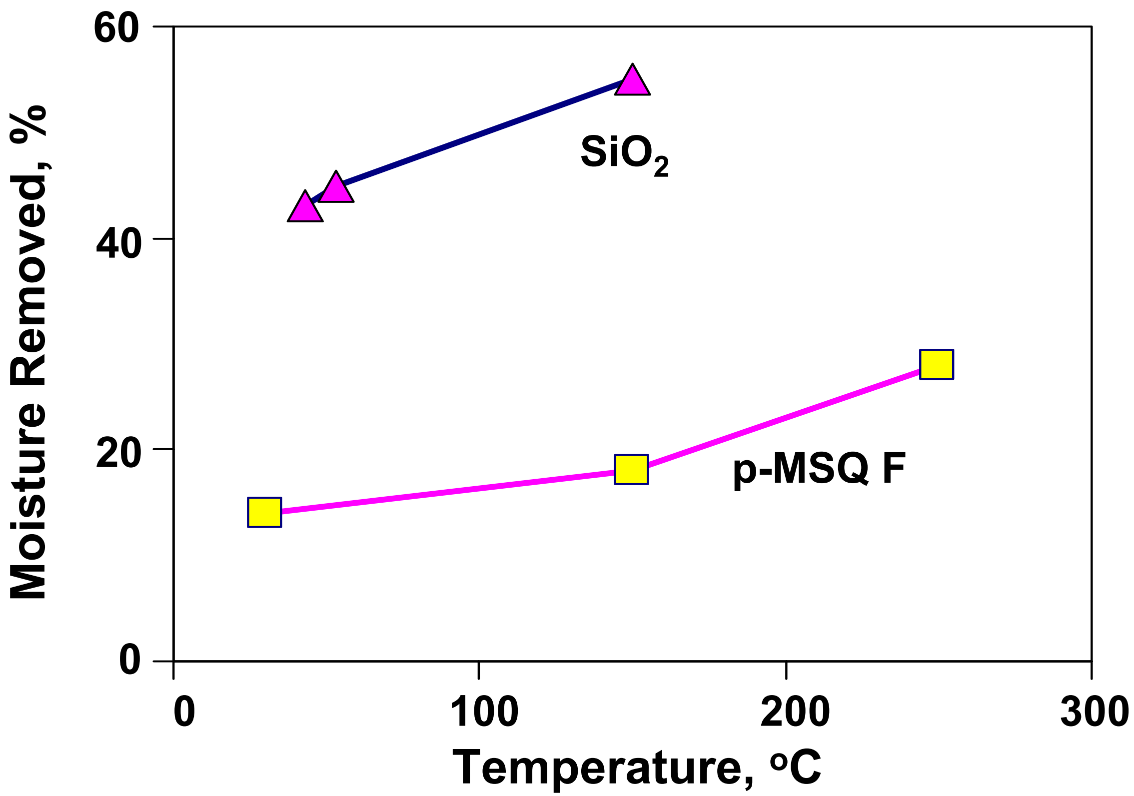
C_{so} = equilibrium moisture concentration in the matrix

C_{filmo} = total moisture loading

ε = porosity, *S* = solubility

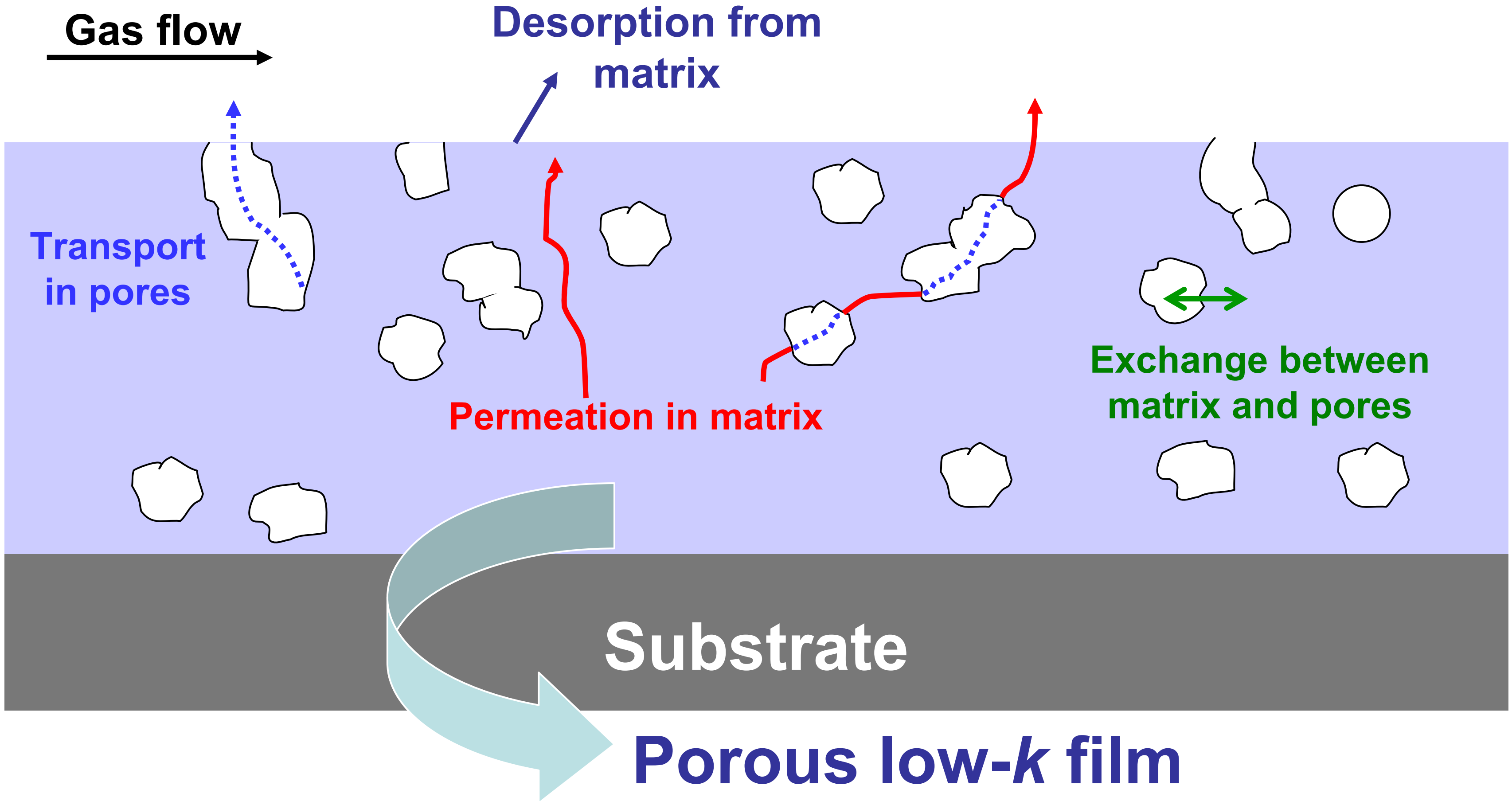
Moisture Retention after Isothermal Purge

Challenge Concentration: 56 ppb; Purge time: 10 hrs
P-MSQ F: JSR LKD 5109. Standard JSR cure, partial etch and partial ash.



- **~55 % of adsorbed moisture removed from SiO_2 at 150ºC**
- **~28 % of absorbed moisture removed from p-MSQ F at 250ºC**

Moisture Transport Pathways in A Porous Low-*k* Film



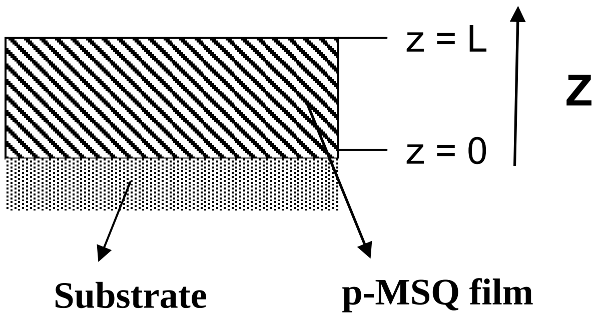
Model Development for Uniform Film

Transport of moisture in matrix:

$$\frac{\partial C_S}{\partial t} = D_S \frac{\partial^2 C_S}{\partial z^2} - \frac{\varepsilon}{1-\varepsilon} k_m S_p \left(\frac{C_S}{S} - C_g\right)$$

Transport of moisture in pore:

$$\frac{\partial C_g}{\partial t} = D_g \frac{\partial^2 C_S}{\partial z^2} + k_m S_p \left(\frac{C_S}{S} - C_g\right)$$



C_S / C_g: Moisture concentration in matrix / pore;

D_S / D_g: Moisture diffusivity in matrix / pore;

ε: Film porosity;

S_p: Specific surface area;

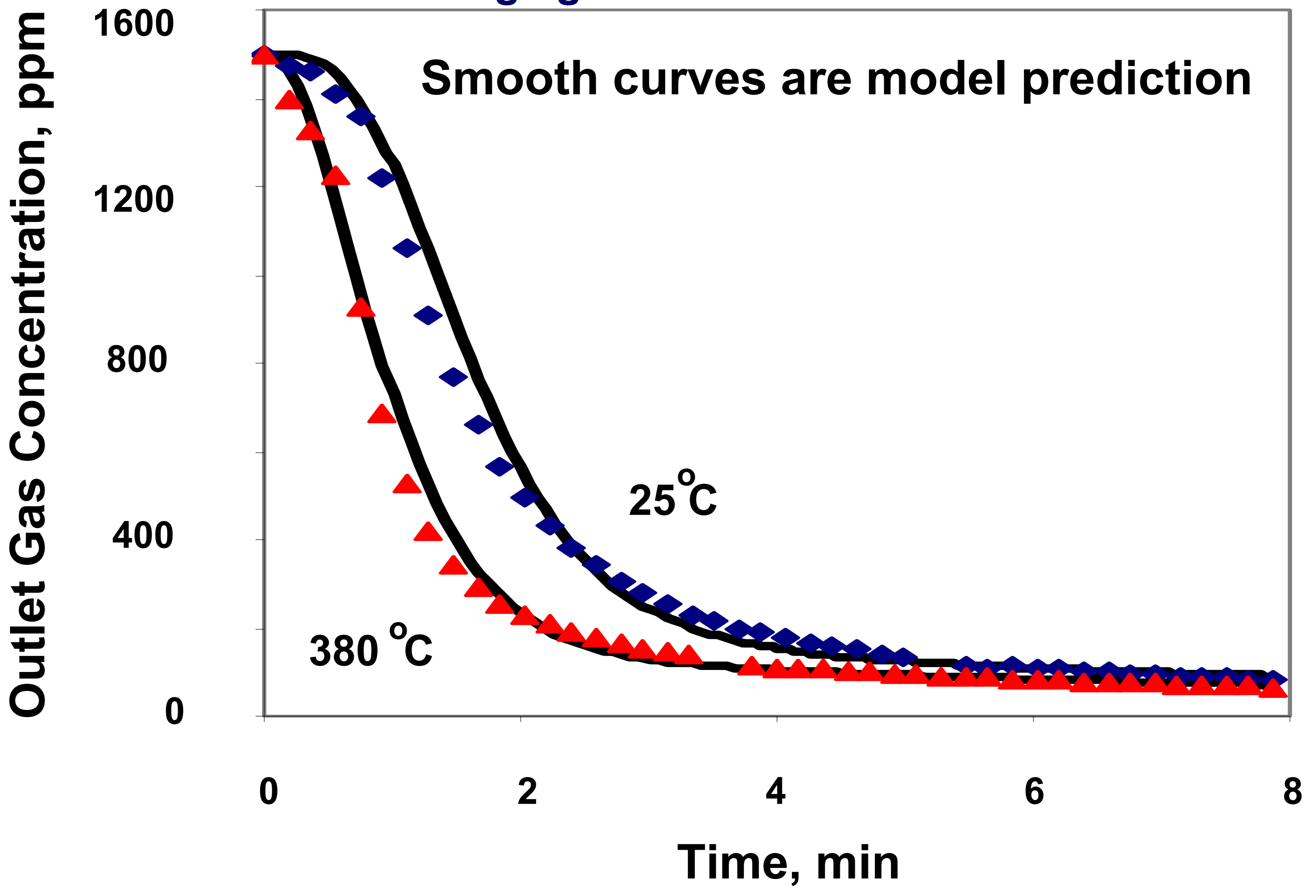
S: Moisture solubility in matrix;

k_m: Mass transport coefficient between pore and matrix

Experimental Data and Model Validation at Different Temperatures

p-MSQ E; Challenge conc.: 1500 ppm; Purge gas purity: 1 ppb;

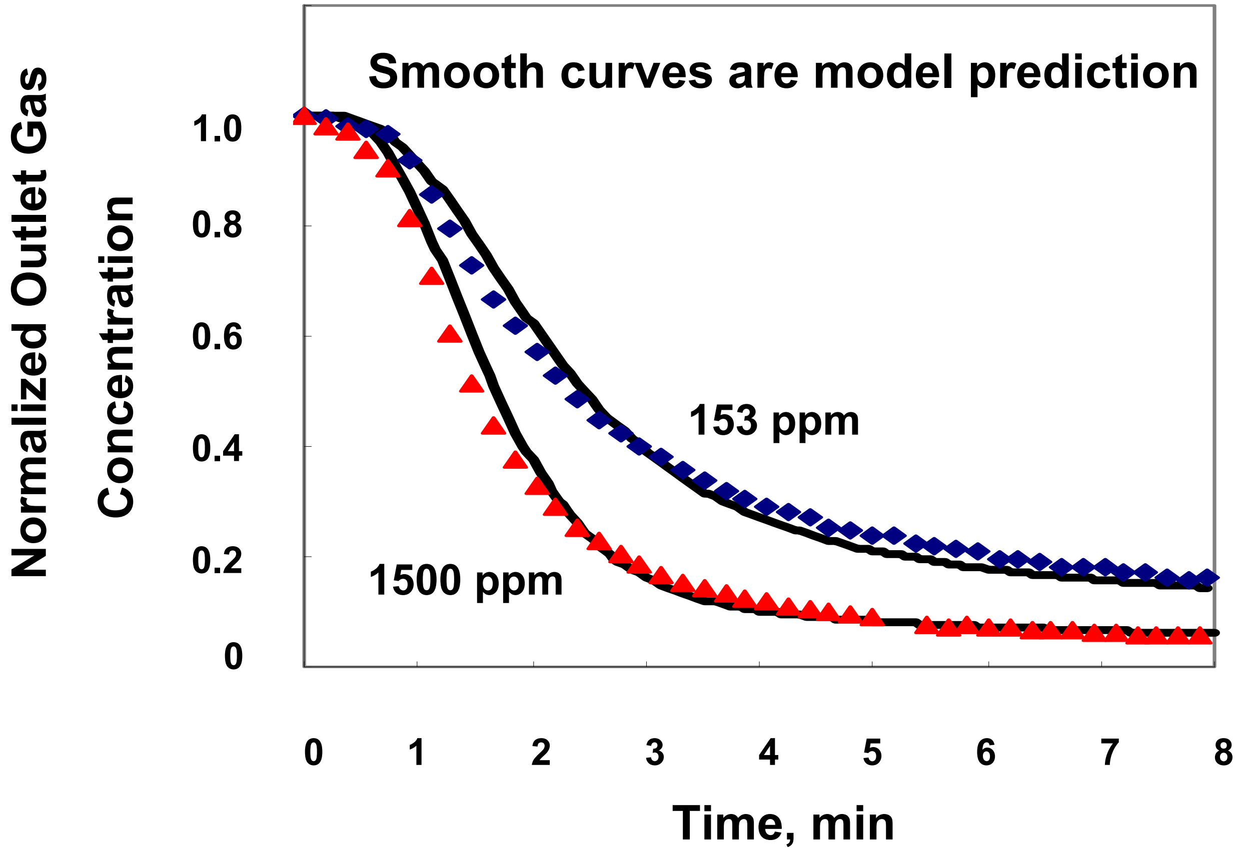
Purge gas flow rate: 350 sccm



Experimental Data and Model Validation at Different Concentrations

p-MSQ E; Temperature: 25 ºC; Purge gas purity: 1 ppb;

Purge gas flow rate: 350 sccm



Estimated Parameters

p-MSQ Film: E (blanket low-k film)

Temp. ºC	D_S cm²/sec	D_g cm²/sec	$\mathcal{E}$	S*
25	7.0e-15	3e-10	0.3	1.3e5
200	1.0e-13	2.8e-9	0.3	5.2e4
380	3.5e-13	8e-9	0.3	3.4e4

D_S / D_g: Moisture diffusivity in matrix / pore;

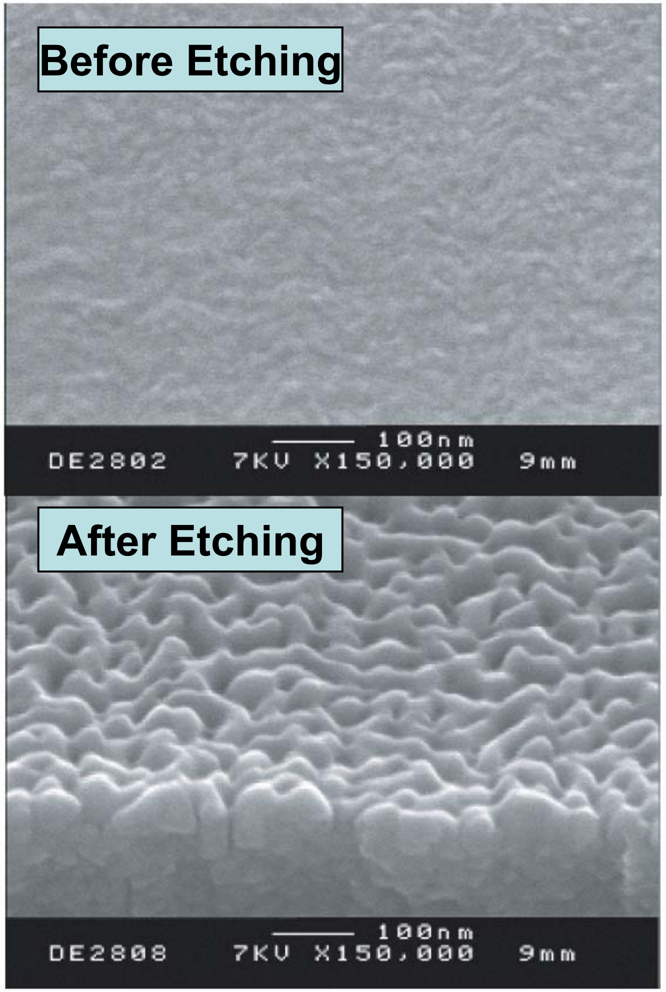
ε: Film porosity;

S: Moisture solubility in matrix;

Moisture removal is a slow and activated process.

Effects of Etch on Low-*k* Film

Spin on p-MSQ (JSR LKD 5109^{TM}, k = 2.2)

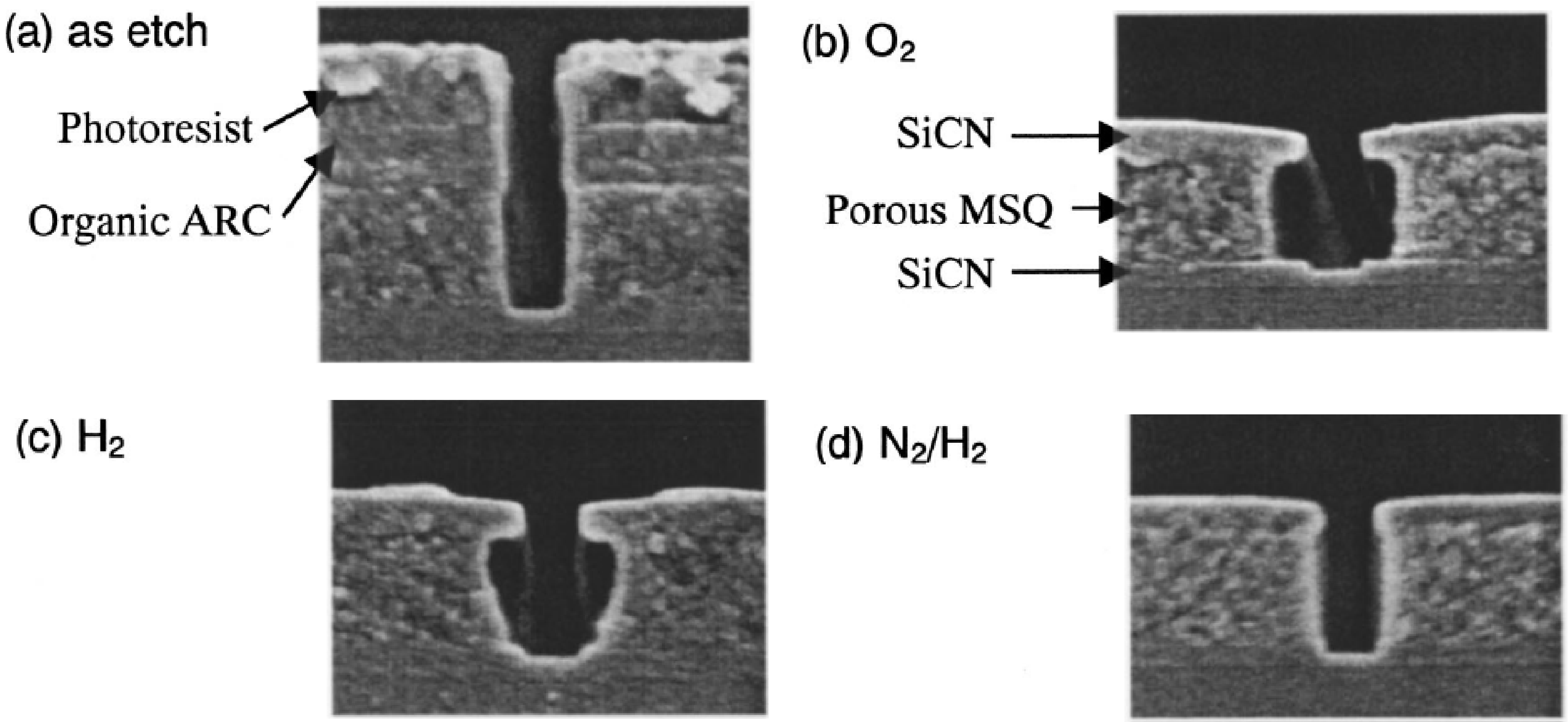


P-MSQ before and after 1 minute etching in C_2F_6/H_2 (25%–75%) mixture 800 W, 40 sccm, 10 mtorr, −100 V.

Source: Eur. Phys. J. Appl. Phys. 28, 2004, p336

Effects of Plasma Ash on Low-k Film

Spin on p-MSQ

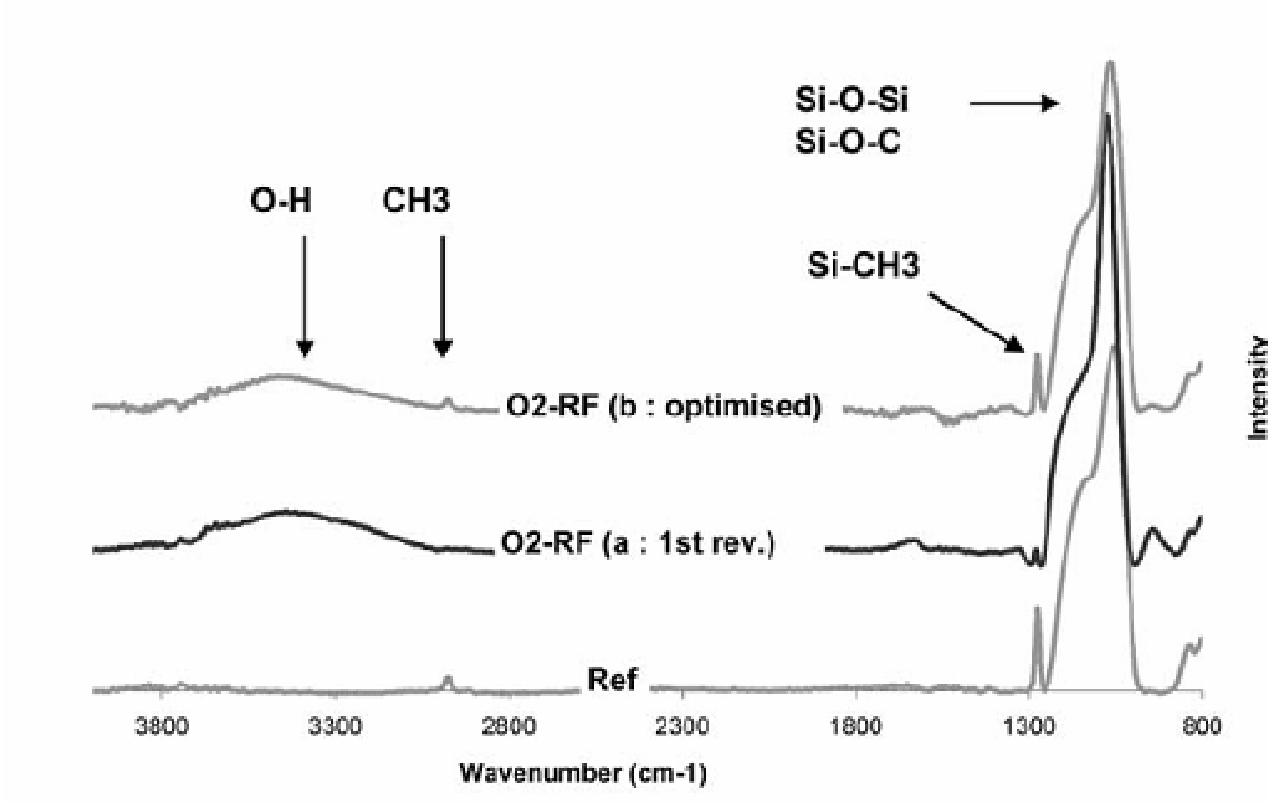


Cross-sectional SEM images of single damascene profiles after: (a) trench etch, (b) O_2 ash, (c) H_2 ash, and (d) N_2 /H_2 ash.

Source: J. Vac. Sci. Technol. B. Vol. 22, No. 2, 2004, p552

Effects of O_2 Plasma Ash on Low-*k* Film

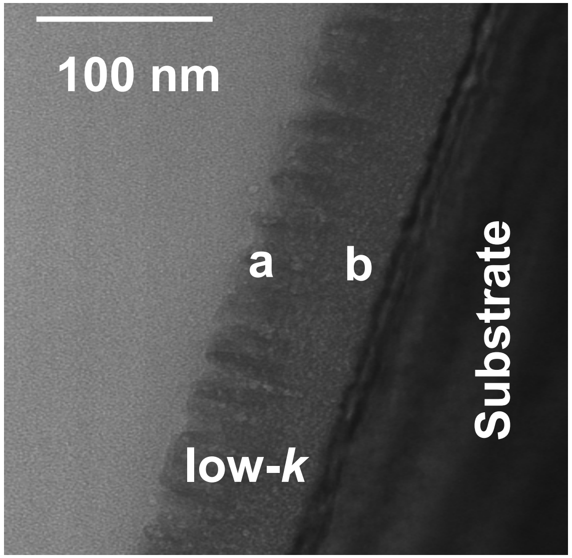
O_2-based RF-bias process; spin on p-MSQ



FTIR spectra after O_2 plasma ash.

Source: Microelectronic Engineering 73-74 (2004) p352

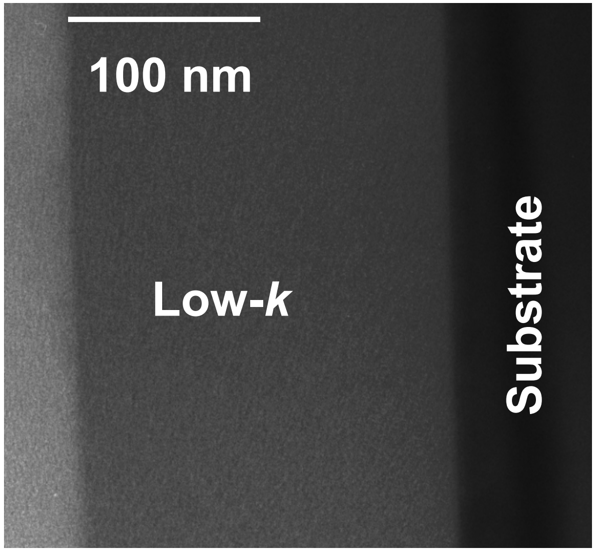
TEM Images of Film A and Film E



a – Damaged low-*k* layer, 50 nm

b – Bulk low-*k* layer, 50 nm

Low-*k* thickness ~ 100 nm

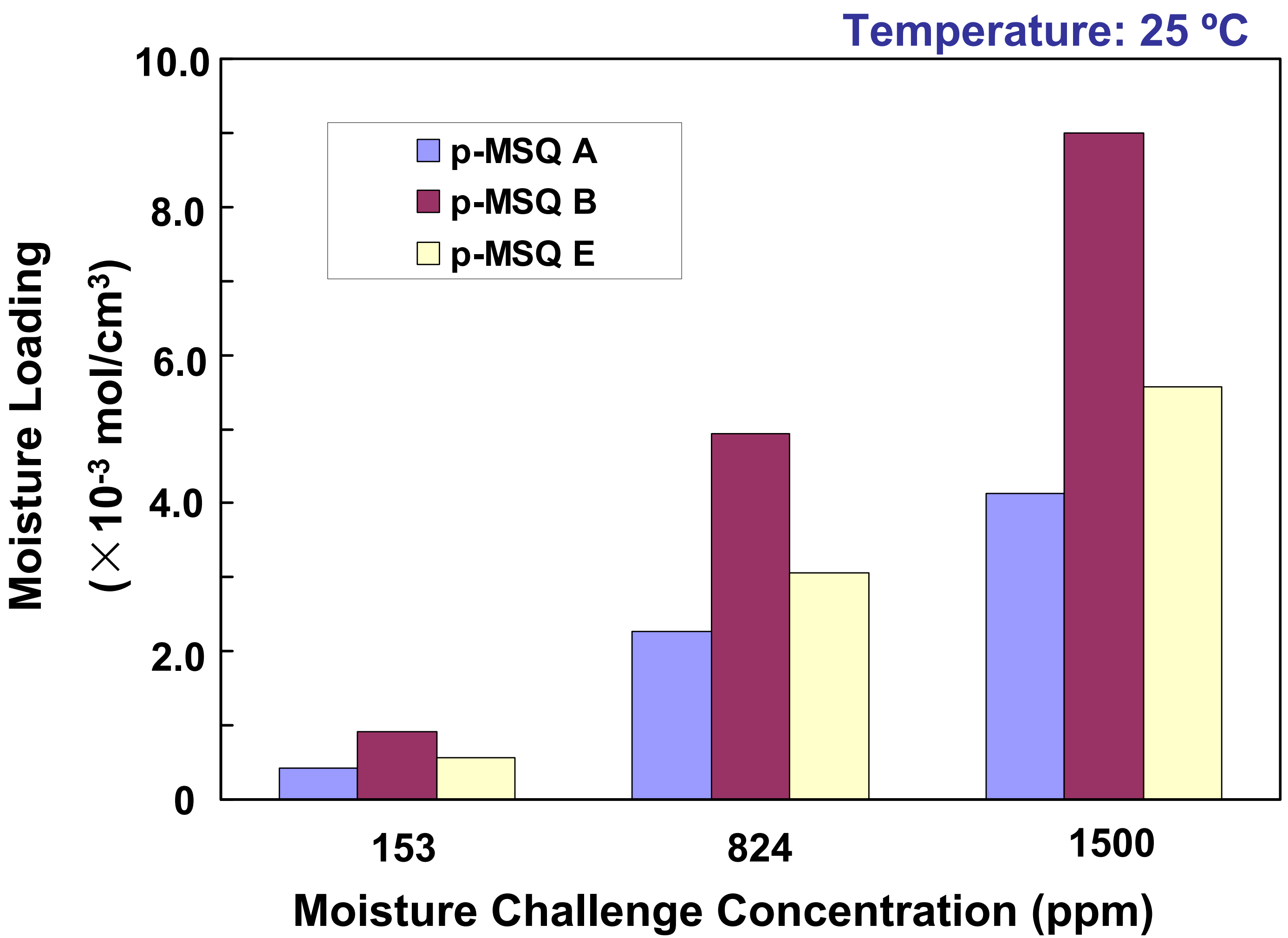


Low-*k* thickness ~ 200 nm

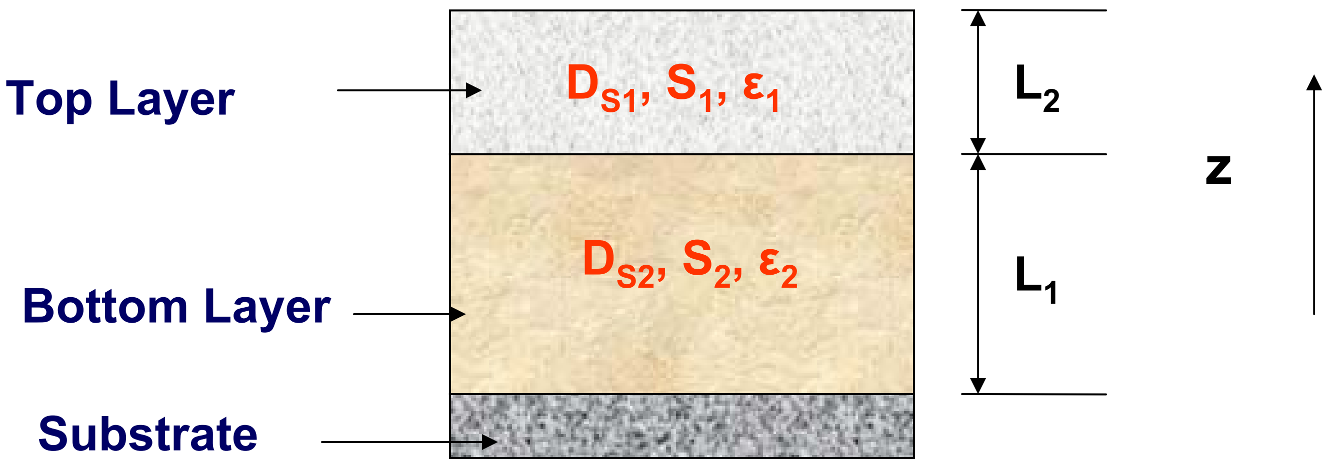
p-MSQ A -- Partial etch, N_2H_2 ash

p-MSQ E -- blanket and cure only

Moisture Loading Comparison



Schematic of A Processed Low-*k* Film



Properties and depth of the two layers depend on conditions, chemistry and time of the etch/ash processes.

Model Development for Non-Uniform Film

Transport of moisture in matrix:

$$\frac{\partial C_S}{\partial t} = \frac{1}{1-\varepsilon}\frac{\partial}{\partial z}[(1-\varepsilon)D_S\frac{\partial C_S}{\partial z}] - \frac{\varepsilon}{1-\varepsilon}k_m S_p(\frac{C_S}{S} - C_g)$$

Transport of moisture in pore:

$$\frac{\partial C_g}{\partial t} = \frac{1}{\varepsilon}\frac{\partial}{\partial z}[\varepsilon D_g\frac{\partial C_S}{\partial z}] + k_m S_p(\frac{C_S}{S} - C_g)$$

C_S / C_g: Moisture concentration in matrix / pore;

D_S / D_g: Moisture diffusivity in matrix / pore;

ε: Film porosity;

S_p: Specific surface area;

S: Moisture solubility in matrix;

k_m: Mass transport coefficient between pore and matrix

Estimated Parameters

p-MSQ Film: A (etched and ashed with N_2H_2)

Temp. °C	D_{S1} cm²/sec	D_{S2} cm²/sec	D_g cm²/sec	ε_1	ε_2	S_1*	S_2*
25	2.0e-14	7.0e-15	3e-10	0.6	0.3	1.1e5	1.3e5
200	2.0e-13	1.0e-13	2.8e-9	0.6	0.3	6.0e4	5.2e4
380	5.9e-13	3.5e-13	8e-9	0.6	0.3	4.5e4	3.4e4

* Unit: cm^3 (gas)/cm^3(solid)

1: Top layer / damaged layer;

2: Bottom / unaffected bulk layer;

D_S / D_g: Moisture diffusivity in matrix / pore;

ε: Film porosity;

S: Moisture solubility in matrix;

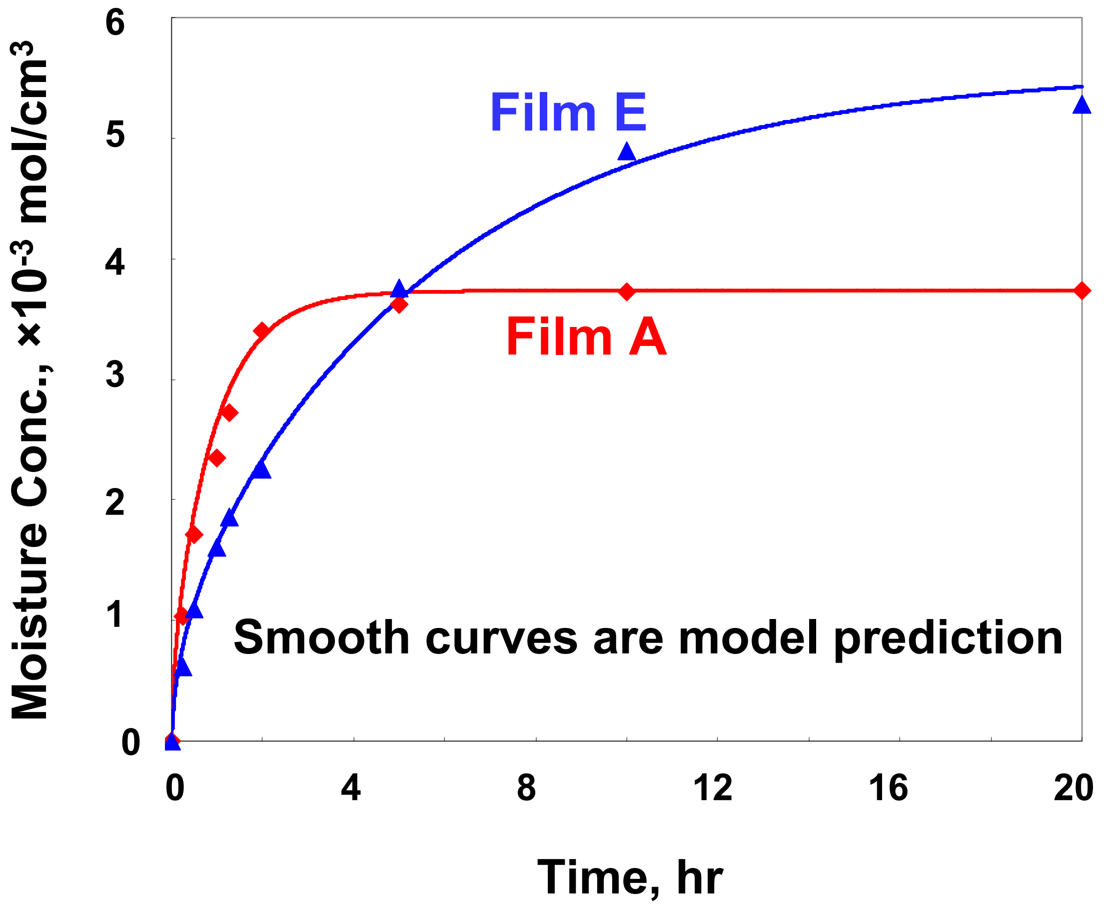
1. The damaged layer has higher moisture diffusivity.

2. These two layers have close moisture solubility.

Moisture Uptake in p-MSQ Film A and Film E

Challenge conc.: 1500 ppm; Temperature: 25 ºC;

Challenge gas flow rate: 350 sccm



Film A: etched / ashed low–*k* film; thickness:100 nm

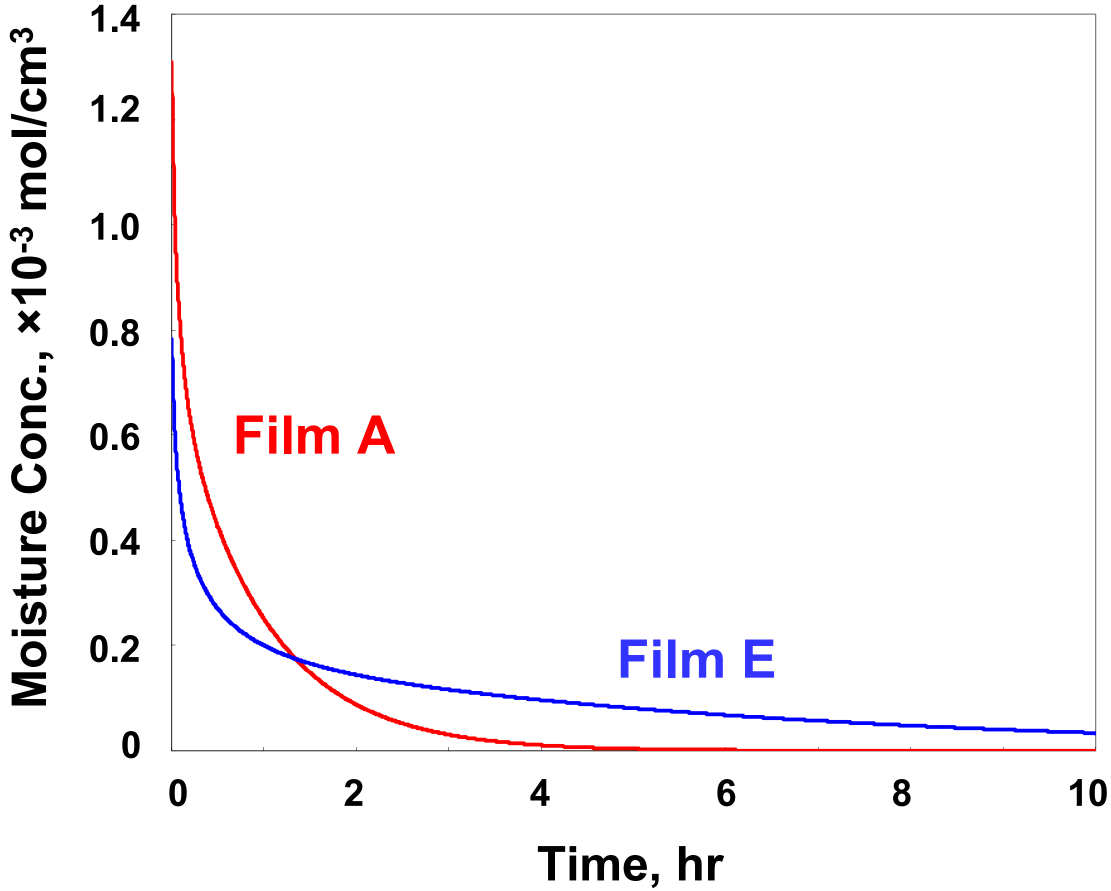
Film E: blanket low–*k* film; thickness:200 nm

Assumed initially two films were completely cleaned

Moisture Retention in p-MSQ Film A and Film E

Challenge conc.: 1500 ppm; Exposure time: 15 min; Temperature: 25 ºC;

Purge gas conc.: 1 ppb; Challenge gas flow rate: 350 sccm



Film A: etched / ashed low–*k* film; thickness: 100 nm

Film E: blanket low–*k* film; thickness: 200 nm

Practical Applications of Model

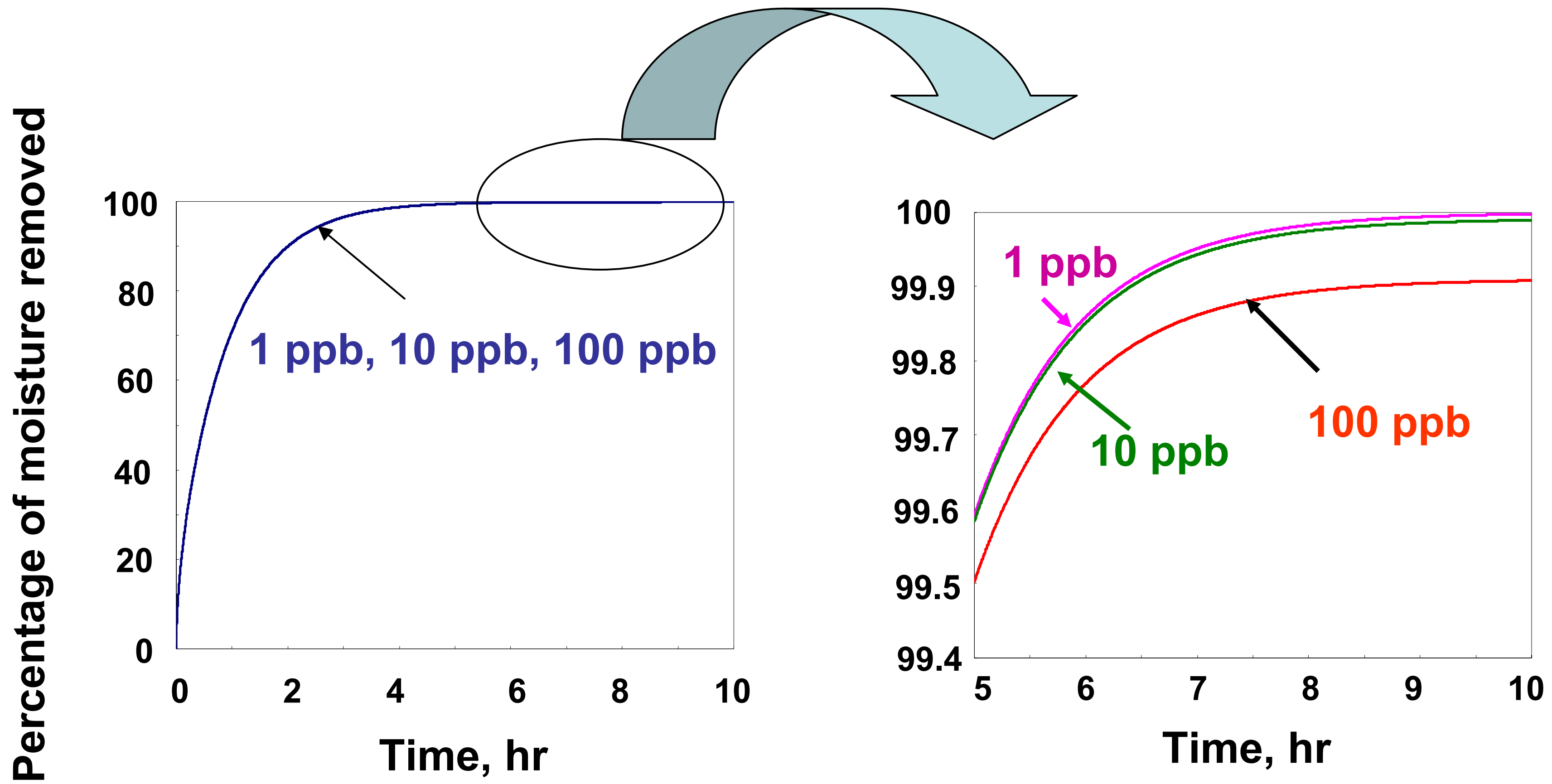
It is a practical tool for:

- evaluating the effect of purge temperature and purge gas purity.

- evaluating the effect of cap layer on contaminants outgassing and retention.

Effect of Purge Gas Purity

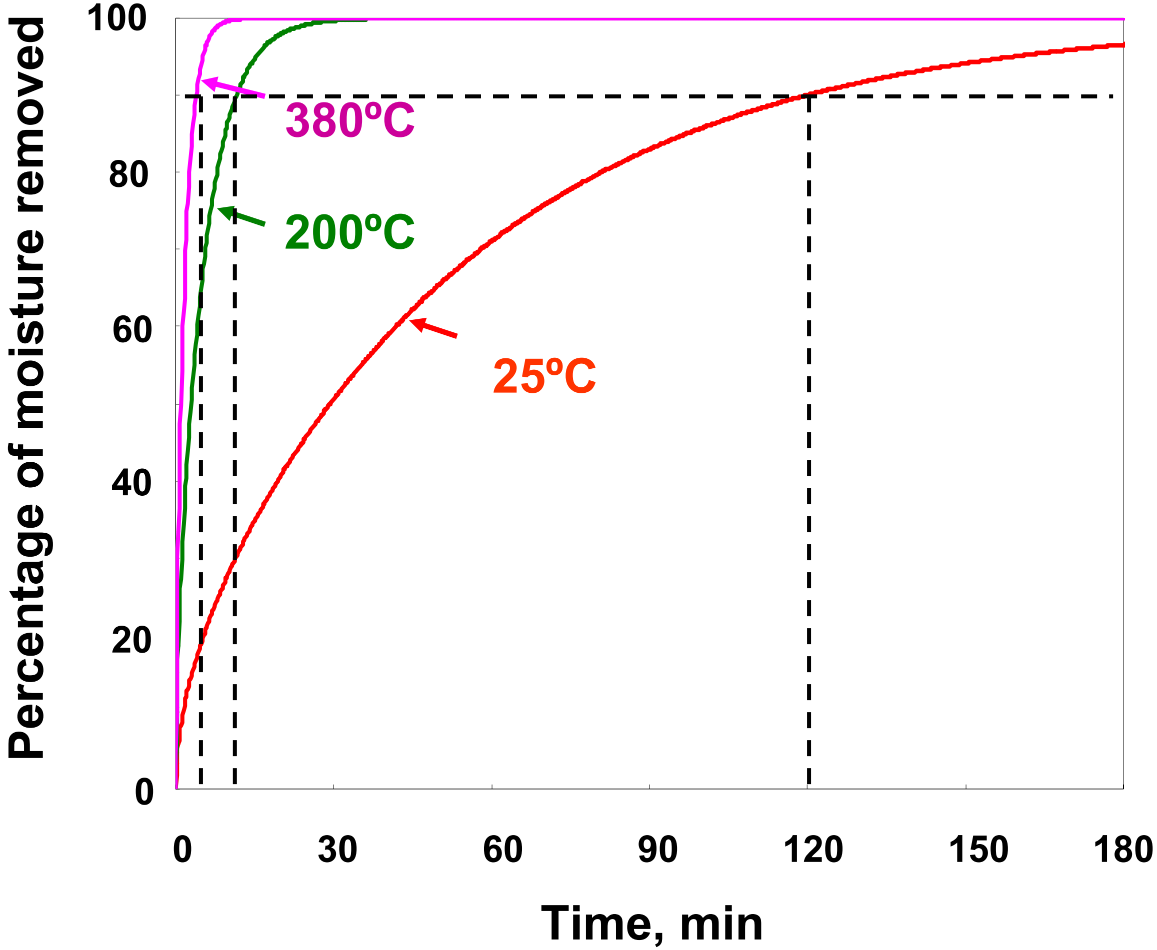
p-MSQ Film A; Challenge conc.: 100 ppm; Temperature: 25 °C



Purge purity enhances drying primarily at the late stages of desorption

Effect of Purge Temperature

p-MSQ Film A; Challenge conc.: 1500 ppm; Purge gas purity: 1ppb



There is an optimum extent of heating for enhancing the desorption

Moisture Uptake in Capped and Uncapped p-MSQ Films

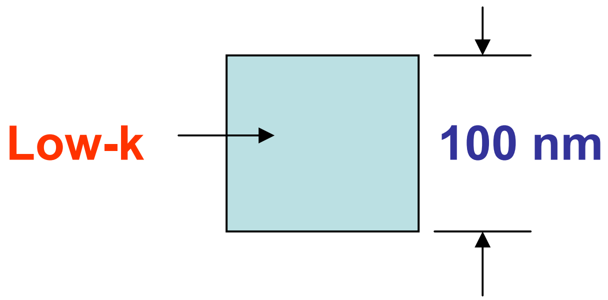
(I) Uncapped p-MSQ film:

Film thickness: 100 nm

Porosity: 0.3

$D_S = 7.0 \times 10^{-15}\ cm^2/sec$

$S = 1.3 \times 10^5\ cm^3\ (gas)/cm^3(solid)$



(II). Capped p-MSQ films:

Thickness of low-k layer: 100 nm

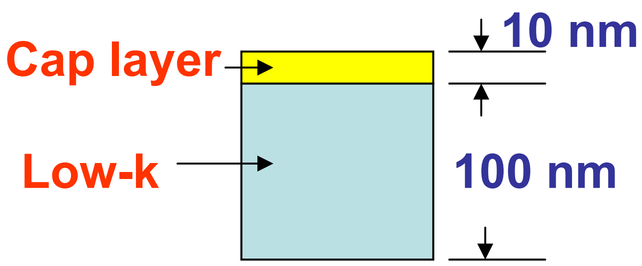
Thickness of cap layer: 10 nm

Porosity of low-k layer: 0.3

Porosity of cap layer: ~0

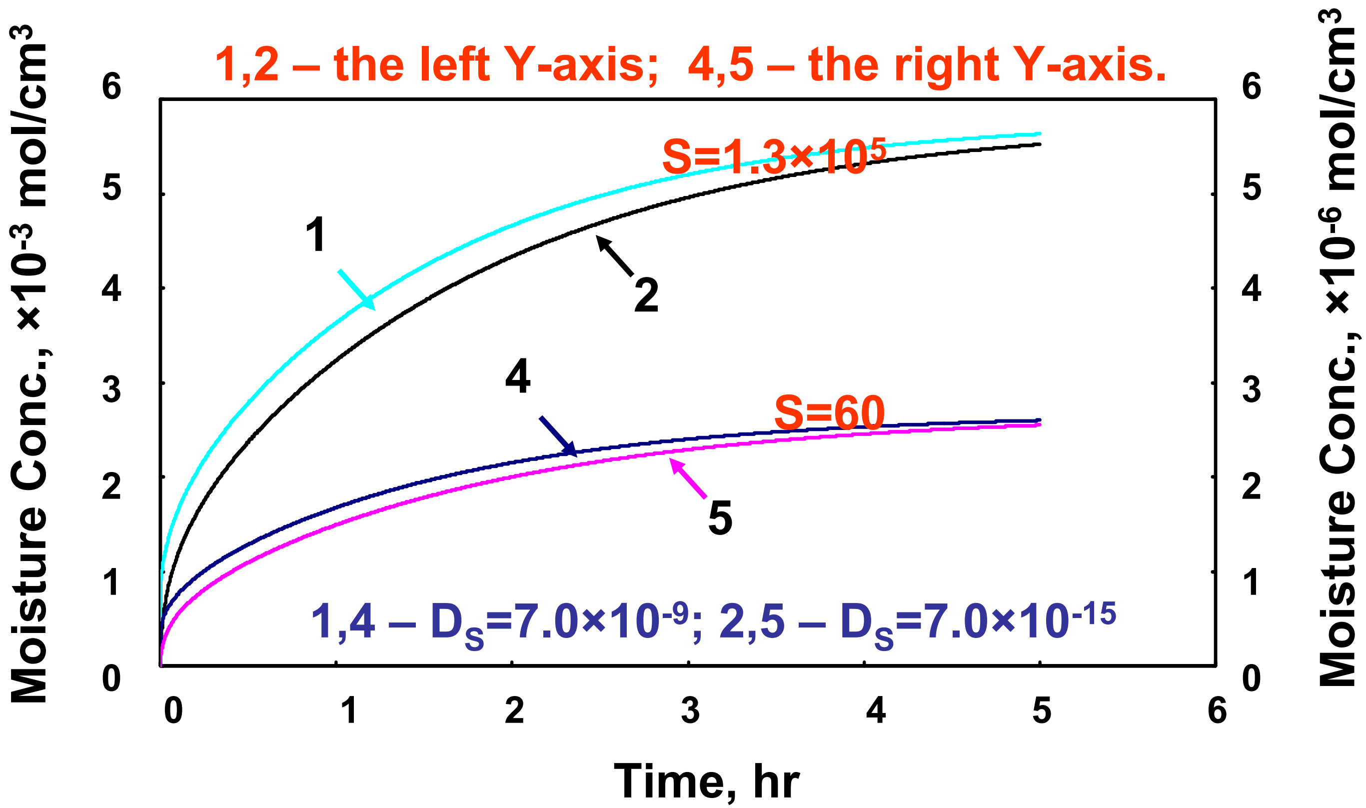
$D_S = 7.0 \times 10^{-9} - 7.0 \times 10^{-15} cm^2/sec$

$S = 60 - 1.3 \times 10^5 cm^3(gas)/cm^3(solid)$



Moisture Uptake in Capped p-MSQ Films

Challenge conc.: 1500 ppm; Temperature: 25 ºC

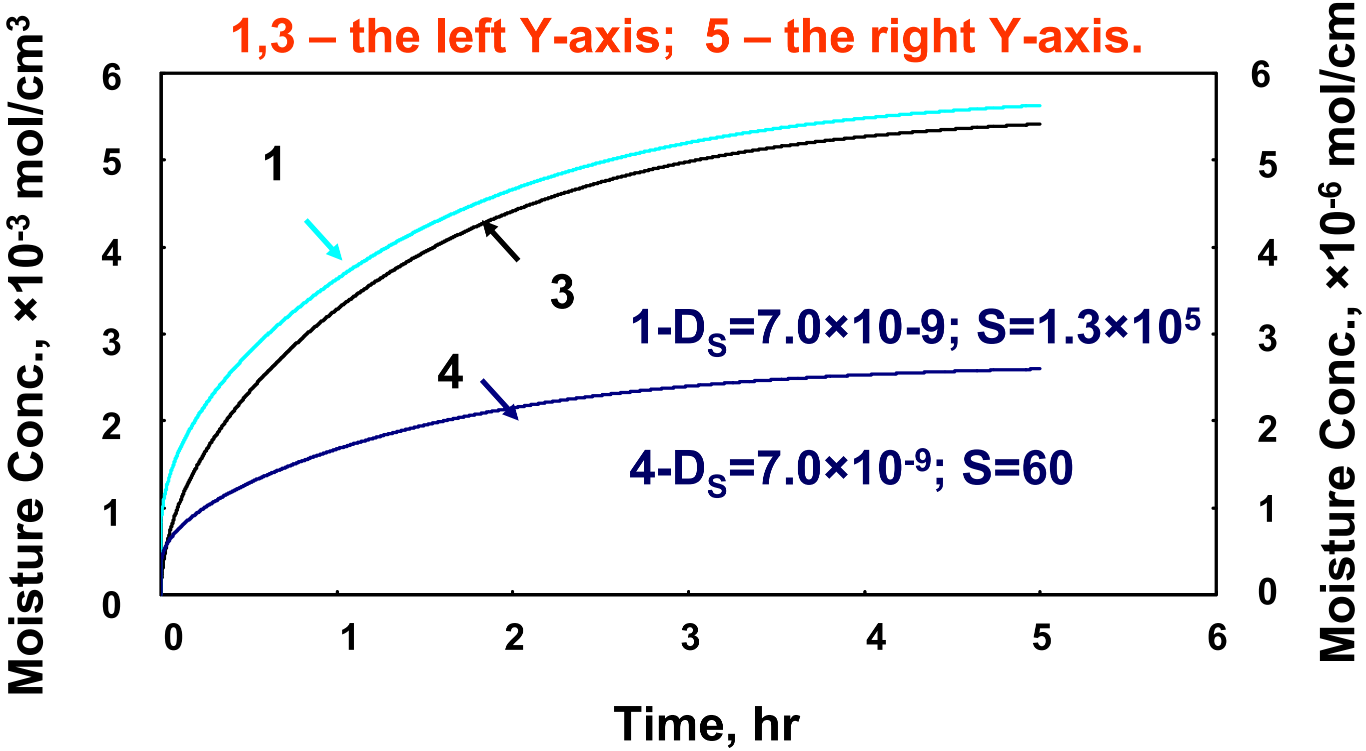


S: cm^3(gas)/cm^3(solid);

D_S: cm^2/s

Moisture Uptake in Capped and Uncapped p-MSQ Films

Challenge conc.: 1500 ppm; Temperature: 25 ºC

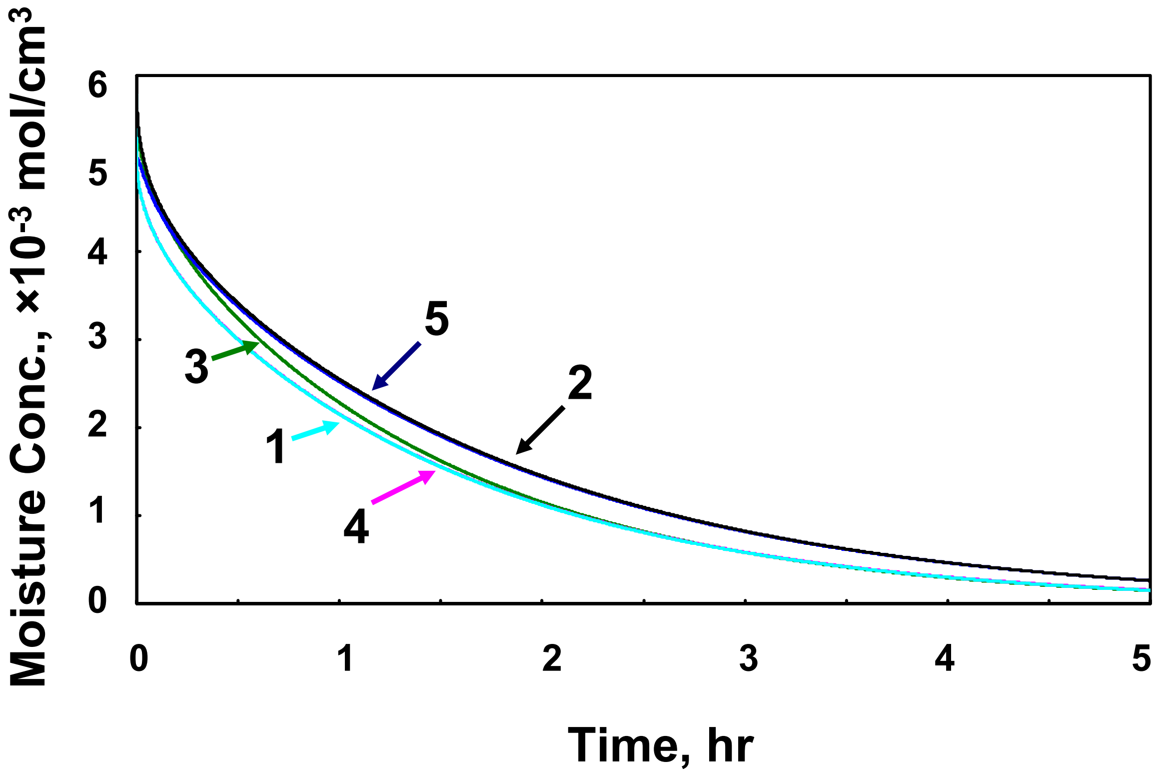


S: cm^3(gas)/cm^3(solid);

D_S: cm^2/s

Moisture Retention in Capped and Uncapped p-MSQ Films

Temperature: 25 ^oC; Purge gas conc.: 1 ppb; Initially all the films were equilibrated with 1500 ppm of moisture



Conclusions

- **Moisture removal is a slow and activated process**
- **Etching and ashing processes change the properties of a low-*k* film and its interactions with moisture. A reducing plasma environment during ashing process accelerates the interaction between moisture and the low-k film by increasing moisture diffusivity and porosity of the low-k film.**
- **Solubility of the cap layer is more important than diffusivity in preventing moisture intrusion into low-k film even for a wide range of diffusivity.**

High-k Gate Dielectrics

High-k Gate Dielectrics

- SiO_2 (k ~ 3.9) was the material of choice so far.
- Currently, promising candidates are HfO_2, ZrO_2, TiO_2, $ZrSiO_4$, HfSiON and HfSiO.
- Other high-k that have been studied include Al_2O_3, Ta_2O_5, TiO_3, Y_2O_3 etc.

Test Samples

- **Silicon wafers:**

- 8 inch p-type

- 10–80 Ω cm

- Czochralski grown

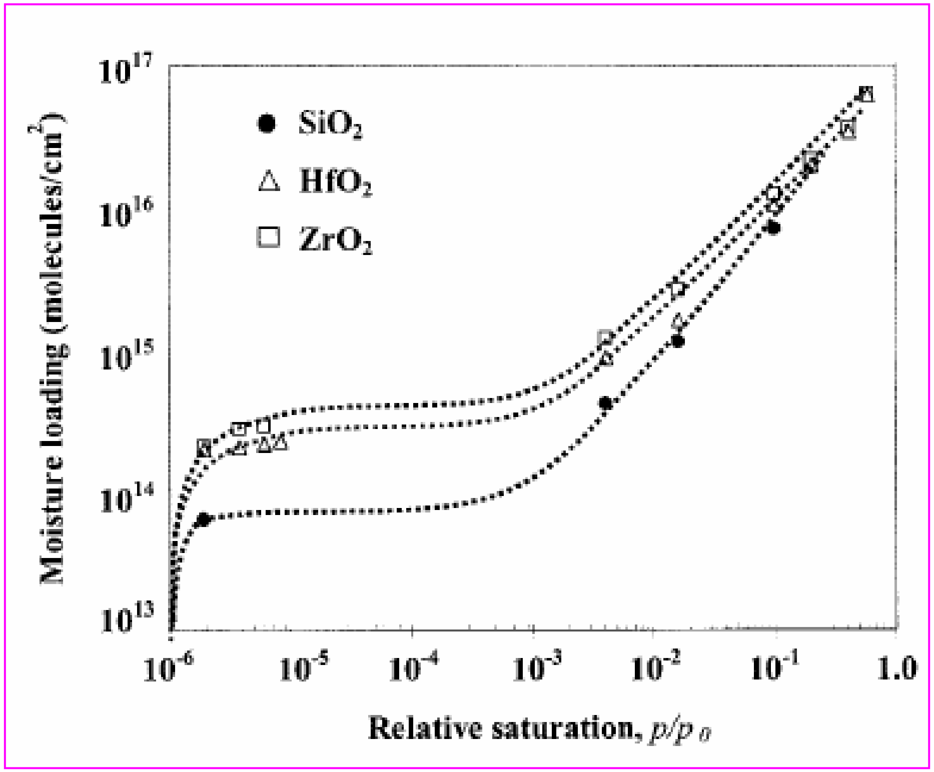
- double-side polished

- (100) oriented

- 50 Å thick ZrO_2 or HfO_2 film

- ALCVD process

Effect of Moisture Challenge Concentration on Loading



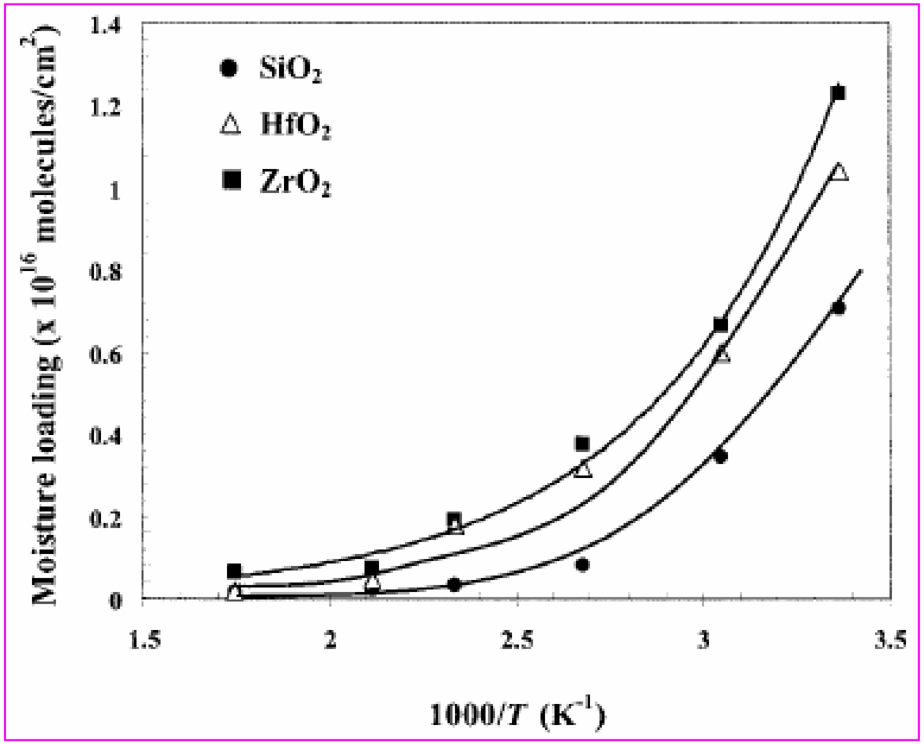
T = 24^{0}C

* Raghu, P.; Yim, C.; Shadman, F. Susceptibility of SiO_2, ZrO_2, and HfO_2 dielectrics to moisture contamination. *AIChE Journal*. 2004, 50 (8), 1881-1888.

- **Loading: ZrO_2 > HfO_2 > SiO_2**

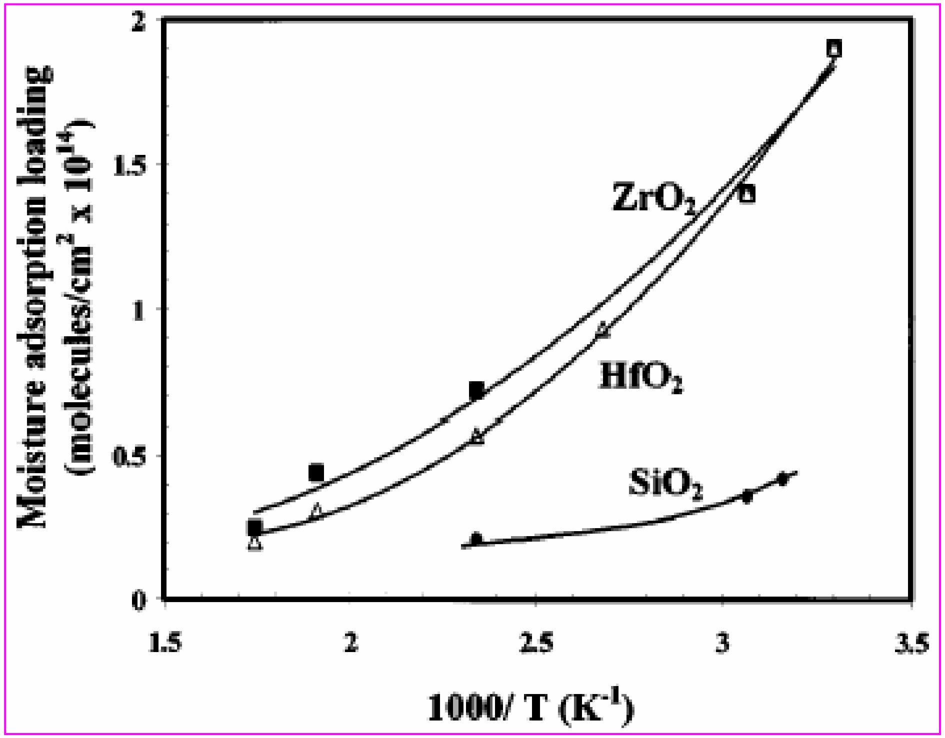
Effect of Temperature on Loading

Challenge Conc. = 0.3%



* Raghu, P.; Yim, C.; Shadman, F. Susceptibility of SiO_2, ZrO_2, and HfO_2 dielectrics to moisture contamination. *AIChE Journal*. 2004, 50 (8), 1881-1888.

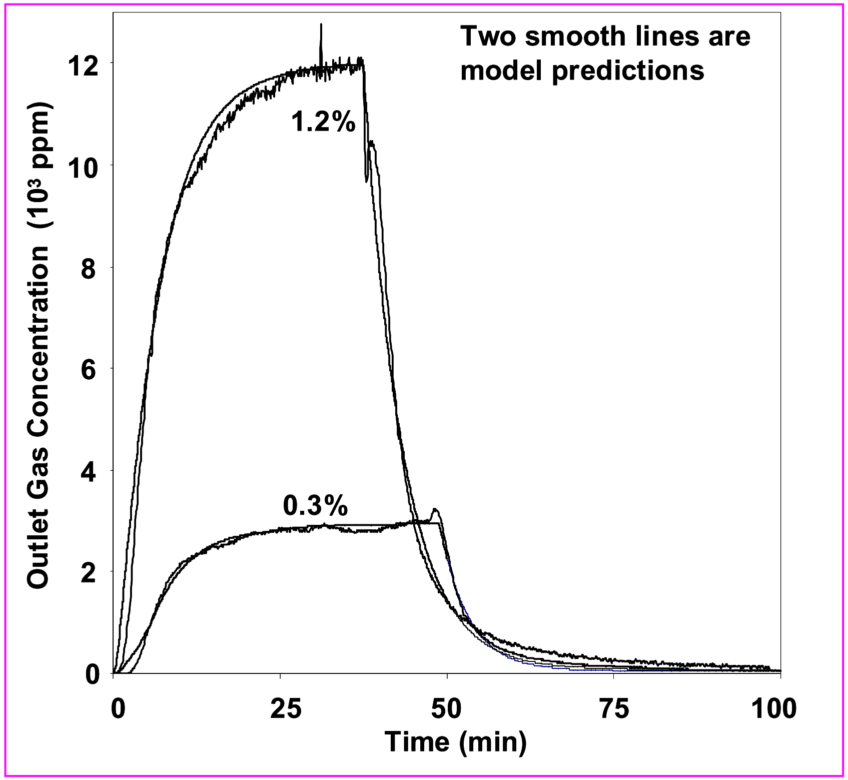
Challenge Conc. = 56 ppb



*Raghu, P.; Rana, N.; Yim, C.; Shero, E.; Shadman, F. Adsorption of moisture and organic contaminants on hafnium oxide, zirconium oxide, and silicon oxide gate dielectrics. *J. Electrochem. Soc*. 2003, 150 (10), F186-F193.

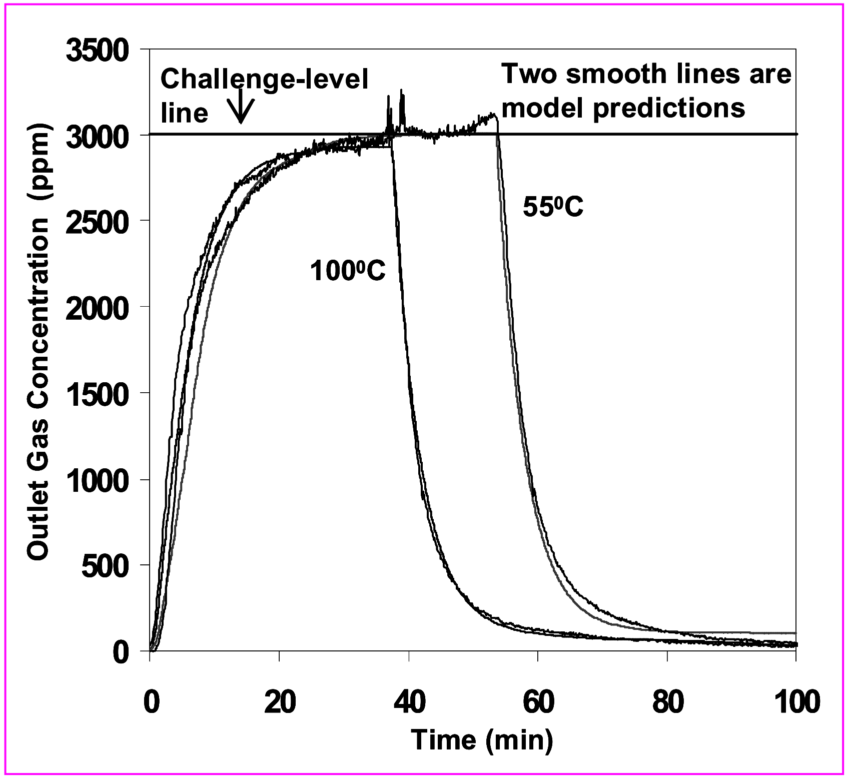
- **Loading: ZrO_2 > HfO_2 > SiO_2**

Effect of Moisture Challenge Concentration on HfO_2 Surface



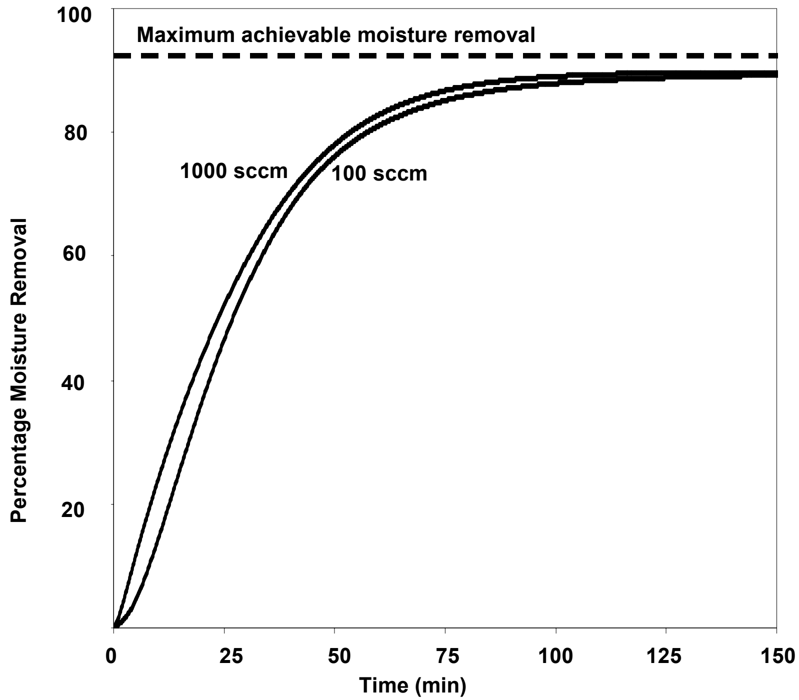
- **Loading increases as the moisture challenge concentration increases.**

Effect of Temperature on ZrO_2 Surface.



- Equilibrium is reached more rapidly for 100 ^{0}C.
- Moisture loading is higher at 55 ^{0}C.

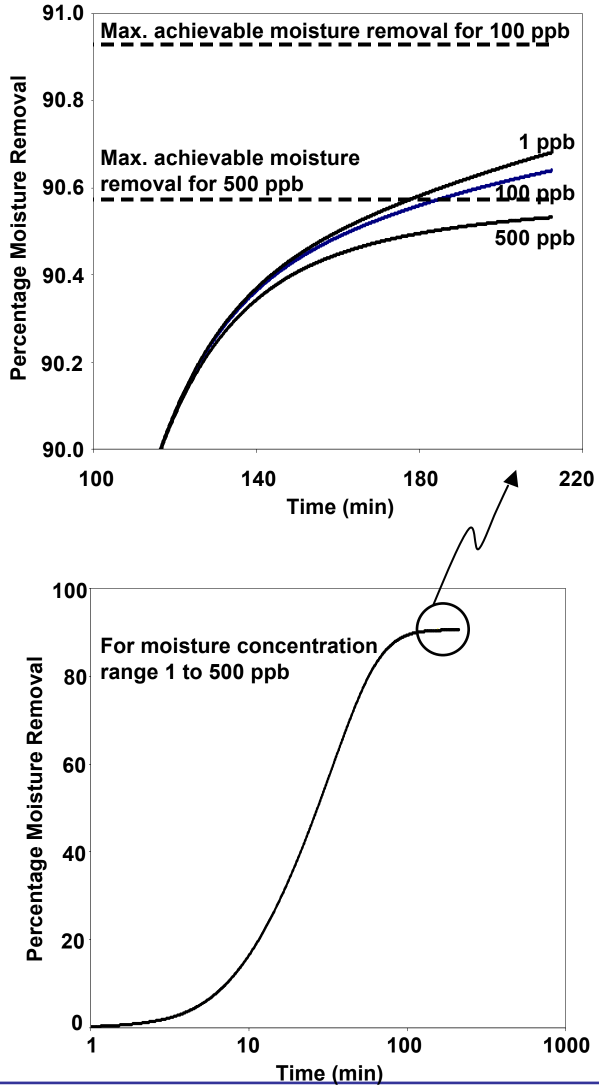
Effect of Purge Flow Rate on Removal of Moisture



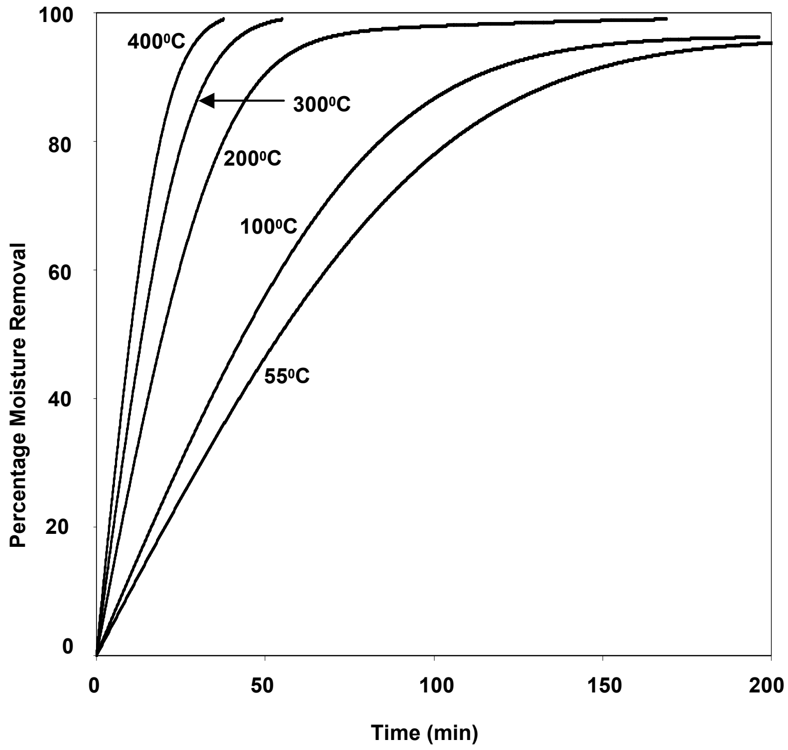
- **Increase in flow rate has a noticeable effect only at the beginning of the purge.**

Effect of Purge Gas Moisture Concentration on Removal of Moisture

- Effect of purge gas moisture concentration is only significant towards the end of purge process.



Effect of Temperature on Removal of Moisture



- **Increasing temperature enhances moisture removal rate.**

Application of the Model to Compare Alternate Purge Schedules.

Process no.	Processing time for 90% cleanup (min)	Volume (lit)	Purity (ppb)	Operation cost* (cents)
1	115.67	23.13	1	69
2	26.53	13.27	1	39
3	30.48	3.50 4.10	1000 1	22

Process 1: 200 sccm flow rate; purge gas purity: 1 ppb moisture; 100°C.
Process 2: 500 sccm flow rate; purge gas purity: 1 ppb moisture; 400°C.
Process 3: 5 minutes: 500 sccm flow rate; purge gas purity: 1000 ppb moisture; 100°C.
5 minutes: 200 sccm flow rate; purge gas purity: 1000 ppb moisture; 200°C.
Remaining: 200 sccm flow rate; purge gas purity: 1 ppb moisture; 400°C.

* Includes cost of maintaining furnace temperature and generating purge gas. Does not include the cost of operating instrumentation. Cost of electricity = 10 cents/kWh. Total exposed surface area of wafers = 3140 cm^2.

- Process 1: Isothermal removal of moisture from the film.
- Process 2: High flow rate, purest purge gas, high temperature.
- Process 3: Optimized process.

Conclusions

- **Moisture is a prominent problem for high-k dielectric films.**
- **Loading increases as the moisture challenge concentration increase, and the order is ZrO_2 > HfO_2 > SiO_2.**
- **Moisture loading is higher at lower temperature.**
- **Application of the model to optimize process conditions for efficient cleanup of dielectric films is illustrated.**

Acknowledgement

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Texas Instruments	
Dr. Ting Tsui	For providing samples
Intel	For providing Si wafers
ASM America	Deposition of ZrO_2 and HfO_2 films
NSF/SRC ERC for Environmentally Benign Semiconductor Manufacturing	For partial support