Interaction of Molecular Contamination with Surfaces

Junpin Yao, Asad Iqbal, Harpreet Juneja and Farhang Shadman

Chemical and Environmental Engineering, University of Arizona

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Interaction of Molecular Contamination with High-k Dielectric Films
HfO$_2$ and ZrO$_2$ have higher IPA adsorption loading than SiO$_2$

IPA loading order: ZrO$_2$ > HfO$_2$ > SiO$_2$

Same trend was observed over a wide range of concentrations
Experimental Procedure

Step 1. Moisture challenge (conc: 56 ppb)
Step 2. IPA challenge (conc: 107 ppb)

- Presence of one contaminant can affect adsorption/desorption characteristics of other contaminants.
- Moisture hydroxylates oxide surfaces; the hydroxyl groups change the nature of the surface.
- Pre-adsorbed moisture enhances IPA adsorption on SiO$_2$, but reduces IPA adsorption on HfO$_2$ and ZrO$_2$.
- IPA is more attracted to bare HfO$_2$ and ZrO$_2$ surfaces than to hydroxylated surfaces. Presence of H$_2$O reduces their affinity for IPA.
**Interaction of IPA with Hydroxylated Surfaces**

- $\text{D}_2\text{O}$-covered surface exposed to IPA

- $\text{C}_3\text{H}_7\text{DO}$ (m/e = 46) formed when IPA is introduced on $\text{D}_2\text{O}$-covered $\text{ZrO}_2$

- $\text{C}_3\text{H}_7\text{DO}$ may be formed by surface interactions between IPA and $\text{D}_2\text{O}$

- $\text{C}_3\text{H}_7\text{DO}$ is also formed in the APIMS plasma (source) from interactions between IPA and $\text{D}_2\text{O}$

- Sample-gas ionization in the APIMS is accomplished by electron impact at atmospheric pressure

- Extensive collisions among molecules in the APIMS plasma source produce intermediate species (for example, $\text{C}_3\text{H}_7\text{DO}$)

- A technique was required to characterize and separate post-reactor interferences due to plasma effect

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**Graphical Data**

- Time, h
- APIMS response, cps

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**Chemical Formulas**

- $\text{C}_3\text{H}_7\text{DO}$

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Low Concentration Multicomponent Adsorption Model

- Oxide surface
- Vacant surface site (Metal atom)
- Chemisorbed hydroxyl group
- Surface physisorbed IPA
- Surface chemisorbed IPA

Diagram:
- $\text{H}_2\text{O}$
- $\text{CH}_3-\text{CH}-\text{CH}_3$
- $\text{OH}$
- $\text{O}$
- $\text{H}$
- $\text{X}$

Legend:
- A
- B
- C

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Conclusion

- ZrO$_2$ was shown to form the strongest metal-hydroxyl (M-OH) bond and adsorb IPA stronger than SiO$_2$ and HfO$_2$

- ZrO$_2$ should not be the material of choice from the standpoint of molecular contamination

- Isotope labeling with D$_2$O indicated chemisorption of IPA on hydroxylated surfaces via an esterification reaction
Interaction of Molecular Contamination with Low-k Dielectric Films
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, create adhesion problems, and cause reliability issues.
  - 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
Research Objectives

• Determine the fundamentals of moisture interactions and outgassing in both uniform and non-uniform porous low-k films:
  • Loading
  • Transport, incorporation and removal of moisture in all forms in the matrix
  • Mechanism of interactions of moisture and organics with wafer surfaces

• Develop experimental and process modeling techniques for minimizing the chemical and energy usage during cleaning and purging of 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 Procedure

Experimental procedure

Isothermal adsorption and desorption

Temporal profile

Exposure to 110 ppb moisture; followed by temperature-programmed desorption

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Moisture Loading and Retention Comparison

Challenge Concentration: 56 ppb; Purge Time: 10 hr

Porous low-k films have much higher sorption loading than SiO₂

Moisture removal is a very slow process
Dynamics of Moisture Removal

Purge gas purity: 1 ppb

**p-MSQ samples:**
A: 10s etch in N₂H₂, 20s ash
B: 10s etch in HeO₂, 20s ash
C: 10s etch in H₂, 20s ash

**BD IIx samples:**
A: Blanket
B: NH₃-plasma treated
C: NH₃He-plasma treated

Moisture challenge concentration: 153 ppm

Moisture Removed (%)

Moisture challenge concentration: 181 ppb

Moisture removed is a very slow process

Temperature: 380 °C

Temperature: 25 °C

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Moisture Transport Pathways in Porous Low-\(k\) Film

- Gas flow
- Desorption from matrix
- Transport in pores
- Permeation in matrix
- Exchange between matrix and pores

Substrate

Porous low-\(k\) film

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Transport of moisture in matrix:

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

Transport of moisture in pore:

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

- $C_S / C_g$: Moisture concentration in matrix / pore;
- $D_S / D_g$: Moisture diffusivity in matrix / pore;
- $\varepsilon$: Film porosity;
- $S_p$: Specific surface area;
- $S$: Moisture solubility in matrix;
- $k_m$: Interphase transport coefficient between pore and matrix;
Validation of Model

Sample: p-MSQ A, partial etch for 10s in N$_2$H$_2$ and 20s ash;
Moisture challenge concentration: 1500 ppm; Temperature: 25 °C

Two smooth curves are model predictions

Estimated parameters:
- $D_s$: $1 \times 10^{-15}$ to $1 \times 10^{-12}$ cm$^2$/s
- $D_g$: $1 \times 10^{-10}$ to $1 \times 10^{-8}$ cm$^2$/s
- $S$: $1 \times 10^3$ to $1 \times 10^5$ cm$^3$(gas)/cm$^3$(solid)

Good agreement between the model and the experimental data
Cell Design
Purge Dynamics of IPA in Empty Cell

The cell is well purged, no accumulation

Peak Area: 2950 – 3000 Wave number
Outgassing Dynamics of IPA using FTIR

FTIR Spectra for IPA Exposure

Unexposed sample

Purge time ~27 hr

12 hr liquid IPA exposure

BD IIx, NH₃He-plasma treated, k~2.6
Outgassing Dynamics of IPA using FTIR

Desorption

BD IIx, NH₃He-plasma treated, k~2.6

Peak Area: 2950 – 3000 Wave number

IPA removal is a slow process
IPA Outgassing Comparison

Initially the samples were saturated with liquid IPA; Purge gas: UHP N₂; FTIR peak at 2950-3000 cm⁻¹ (-CH₃ stretching)
Conclusion

- FTIR looks a promising technique to study dynamics of impurity interaction with thin films.
- A novel cell was designed to study outgassing dynamics.
- IPA removal depend on the low-k type and the processing conditions.
- Etching and ashing affects IPA interaction.

Future Work

- Extend this study for moisture interaction with low-k films.
- Study the effect of multicomponent on outgassing dynamics.
Interaction of Molecular Contamination with EPSS Surface
1. Moisture removal is a slow process in gas-distribution system.

Sample: EP SS tubing, 0.5 in OD, 70 cm length
Background

2. Surface adsorption and desorption, back diffusion, dead legs, and pressure fluctuation can cause fluctuation of moisture concentration in gas distribution system.
Research Objective

To develop a model that allows us to optimize the purge process for moisture contaminated gas distribution system, in other words, with shortest time and lowest chemical and energy cost.
Experimental Setup

- Atmospheric Pressure Ionization Mass Spectrometer (APIMS) – ppb levels
Experimental Procedure

Temporal profile of moisture absorption/desorption

Outlet Gas Moisture Conc., ppb

Time, h

Absorption at 25 ºC; Desorption at 25 ºC; Challenge Conc.: 56 ppb
Model Development for Mass Transport in Cylindrical Tubing

Moisture sorption on tubing wall:

\[ \frac{\partial C_s}{\partial t} = k_{ads} C_g (S_0 - C_s) - k_{des} C_s \]

Governing equation for gas phase:

\[ \frac{\partial C_g}{\partial t} = D_L \frac{\partial^2 C_g}{\partial z^2} - u \frac{\partial C_g}{\partial z} + \frac{A_S}{V} (k_{des} C_s - k_{ads} C_g (S_0 - C_s)) \]

- \( C_s \): Moisture concentration on wall, mol/cm\(^2\);
- \( C_g \): Moisture concentration in gas, mol/cm\(^3\);
- \( k_{ads} \): Adsorption rate constant, cm\(^3\)/mol/s
- \( k_{des} \): Desorption rate constant, 1/s
- \( S_0 \): Site density of surface sorption, # of sites/cm\(^2\);
- \( D_L \): Dispersion coefficient, cm\(^2\)/s
- \( u \): Velocity, m/s; \( A_S \): Surface area of wall, m\(^2\); \( V \): Volume of tubing, m\(^3\)
Model Validation at Different Concentrations

Purge gas flow rate: 350 sccm; Temperature: 25 ºC;
Purge gas purity: 1 ppb,

Smooth curves are model prediction

$k_{ads}$: $3.359 \times 10^9$ cm$^3$/mol/s;
$k_{des}$: $4 \times 10^{-4}$ 1/s;
$S_0$: $6.29 \times 10^{13}$ # of sites/cm$^2$;
$D_L$: 1.82 cm$^2$/s
Effect of Purge Flow Rate

Challenge conc.: 181 ppb; Temperature: 25 °C; Purge gas purity: 1 ppb; Length: 0.9 m

Percentage of Moisture Removal

<table>
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<th>Time, min</th>
<th>0</th>
<th>40</th>
<th>80</th>
<th>120</th>
<th>160</th>
<th>200</th>
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<tbody>
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<td>50</td>
<td>80</td>
</tr>
</tbody>
</table>

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Effect of Purge Gas Purity

Challenge conc.: 181 ppb; Temperature: 25 ºC; Flow rate: 350 sccm; Length: 0.9m

Percentage of Moisture Removal vs. Time, min
Effect of Purge Gas Temperature

Challenge conc.: 181 ppb; Temperature: 25 ºC;
Flow rate: 350 sccm; Purge gas purity: 1 ppb

\[ E_{\text{ads}}: \sim 19 \text{ kJ/mol}; \quad E_{\text{des}}: \sim 47 \text{ kJ/mol} \]

* Reference data
Model Application: Extension of Transfer Line

Challenge conc.: 181 ppb; Temperature: 25 ºC;
Flow rate: 350 sccm; Purge gas purity: 1 ppb
Moisture Distribution along the Tubing at Different Purge Times

Challenge conc.: 181 ppb; Temperature: 25 ºC; Flow rate: 350 sccm; Purge gas purity: 1 ppb

Surface Moisture Concentration

\[ \times 10^{-11} \text{ mol/cm}^2 \]

Length, m

1 – 0 min;
2 – 10 min;
3 – 20 min;
4 – 30 min;
5 – 60 min;
6 – 180 min;
Model Application: Back Diffusion at Laterals

**Governing equation for bulk gas:**

\[
U = 2U_{avg} \left[ 1 - \left( \frac{r}{R} \right)^2 \right] \]

\[
2u_{avg} \left[ 1 - \left( \frac{r}{R} \right)^2 \right] \frac{\partial C_g}{\partial z} + D_g \frac{\partial^2 C_g}{\partial z^2} + \frac{D_k}{r} \frac{\partial}{\partial r} \left( \frac{r \partial C_g}{\partial r} \right) = 0 \]

The boundary conditions used for Eq. 2 are:

1. \( C_g = C_{g_0} \) at \( z = 0, \ 0 \leq r \leq R \) \[3\]
2. \( C_g = C_{g_0} \) at \( z = L, \ 0 \leq r \leq R \) \[4\]
3. \( \frac{\partial C_g}{\partial r} = 0 \) at \( r = 0, \ 0 \leq z \leq L \) \[5\]
4. \(-D_g \frac{\partial C_g}{\partial r} = k_a C_g - k_d C_g \) at \( r = R, \ 0 \leq z \leq L \) \[6\]

**Governing equation for surface diffusion:**

\[
k_a C_g \big|_{r=R} - k_d C_s + D_s \frac{\partial^2 C_g}{\partial z^2} = 0 \]

\[
C_s = \frac{k_a}{k_d} C_g \quad \text{at} \quad z = 0 \]

\[
C_s = \frac{k_a}{k_d} C_{g_0} \quad \text{at} \quad z = L \]
Back Diffusion at Laterals-Simplified model

Governing equation:

\[ D_L \frac{\partial^2 C_g}{\partial z^2} - u \frac{\partial C_g}{\partial z} = 0 \]

BC:

\[
\begin{align*}
z = 0, & \quad C_g = C_{g0} \\
Z = L, & \quad C_g = 1 \text{ ppb}
\end{align*}
\]

\( C_g \): Moisture concentration in gas, mol/cm\(^3\);
\( D_L \): Dispersion coefficient, cm\(^2\)/s;
\( u \): Velocity, m/s;
\( C_{g0} \): Ambient moisture concentration

Back diffusion direction

Gas flow direction

1 ppb

1: Bulk Convection
2. Bulk diffusion
Back Diffusion at Laterals

----Contd.

Moisture profile along the lateral (Length: 2 m)

1: Bulk Convection
2. Bulk diffusion

Length, m

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Conclusion

1. The combination of experiments and modeling we have developed helps in optimizing the dry-down time and lower the purge-gas and energy consumption during system start-up or recovery.

2. This technique can be used to minimize the back diffusion problem.
Future Work

1. Extend the application of the model

   Single tubing $\rightarrow$ one lateral $\rightarrow$ More laterals $\rightarrow$ Complex gas delivery system

2. Effects of dead legs and pressure fluctuation
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