Processing and Characterization of PMSSQ Based Materials for Nanoporous Low-K Dielectrics

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Device Shrinkage and Interconnect Delay

Increased line resistance and capacitive coupling

Interconnect delay dominates overall circuit delay

Al / SiO₂ → Cu / Low K

SiO₂ (K = 4.0)  Low k (k ~ 2.0)
Al (ρ ~ 3.0 μΩ cm)  Cu (ρ ~ 1.7 μΩ cm)

Low K materials (organic, silica based materials)
Nanoporous low K materials

Nanoporos PMSSQ

Low polarizability matrix (K ~ 2.7)
Nanoporous low K (K ≤ 2.0)
Low water uptake (<1%), thermal stability, mechanical strength.
Strategy for Nanoporous Low – K

- Characterizing surface and bulk
  - ToF –SIMS
  - XPS

- Characterizing volatile product
  - TDMS (Thermal Desorption Mass Spectrometry)

- Compare surface to gas phase

- Compare precursor recipe
  - Low –SiOH and high –SiOH PMSSQ

- Spin on (Solution)
  - Matrix cross link, Nano phase separation

- Porogen Volatilization
  - Fully cured Cross link Nanopores

Matrix

Porogen

RT

Thermal Cycle

450°C C

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Thermal Reaction Goal

Matrix cross link

Porogen release

T, t

Max 450°C
Nanoporous PMSSQ Materials

Matrix material
Polymethylsilsesquioxane (PMSSQ)

- Methyl group: Non-polar, hydrophobic, and space-occupying
- Hydroxyl group: Cross linking of matrix

Porogen materials
poly(methylmethacrylate co-dimethylamino ethyl methacrylate) (PMMA co-DMAEMA)

- Tertiary amino group: Hydrogen bonding with OH in matrix
- Miscibility between matrix and porogen

<table>
<thead>
<tr>
<th>Material</th>
<th>Group</th>
<th>Property</th>
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<tbody>
<tr>
<td>PMSSQ</td>
<td>Methyl group</td>
<td>Non-polar, hydrophobic and space-occupying</td>
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Low – K film Processing

low-k matrix resin (PMSSQ)
porogen (PMMA co-DMAEMA)
solvents

$Rpm = 3000$
$Time = 20 \text{ sec}$
$Thickness \sim 1 \mu m$

450 °C, 2Hrs

Material fingerprint and molecular structure
Degree of polymerization
Thermal behavior of porogen material
Interaction between matrix and porogen
Matrix precursor chemistry effect

ToF –SIMS
Static-SIMS (Ga+ @ 11-25 keV)
Surface Spectroscopy, Surface Imaging
Pseudo-Dynamic SIMS (sputtering by Cs+)
Depth Profiling

XPS
TDMS

Designing nanoporous low–K materials for electrical performance

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PMSSQ Finger Print Analysis

SSIMS, negative SI

- Peak assignments are well matched to experimental results.
- Peaks are regularly spaced by a monomer unit.
- Fragmentation pattern depends on chemical structure and is sensitive to cross linking.

Cleavage of the parent ion (i.e. by loss of SiO\textsubscript{2})
Precursor Chemistry

- Mass spectrum of high –SiOH PMSSQ has a twin peak near the key species with mass difference 1.98 amu by replacing CH$_3$ group with OH group.

- \([\text{SiOH}]_{\text{high}} \sim 2 * [\text{SiOH}]_{\text{low}}\)

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Polymerization of High –SiOH PMSSQ

- Major crosslinking ~ 100°C – 200°C, completed at 450°C.
- Dehydration occurs as OH groups crosslink.

Major crosslinking: 100°C – 200°C

ToF-SIMS

Remaining crosslinking

H₂O desorption product

TDMS

Mass spectrometer

Water signal from pure PMSSQ
High –SiOH vs. Low –SiOH

- High – SiOH PMSSQ crosslinks faster than low – SiOH PMSSQ.
- Reaction rate depends on the concentration and proximity of SiOH end groups.
Porogen : Surface Analysis (XPS)

- Porogen related components: Backbone and DMAEMA
- Porogen materials completely volatilized at $T = 450^\circ C$

High $-\text{SiOH}$

As deposited

Fully cured

- Porogen related components: Backbone and DMAEMA
- Porogen materials completely volatilized at $T = 450^\circ C$
Porogen : Surface Analysis

- DMAEMA ligand: Cleavage and evolution 225°C - 325°C (90%)
  Remaining material desorbs by > 325 °C
- PMMA ligand: No apparent transformation until > 325 °C
- Backbone: Behavior follows that of PMMA ligand
- No porogen agglomeration observed in high –SiOH matrix.

\[
\text{ToF – SIMS} \quad \text{Porogen in High –SiOH matrix}
\]

- DMAEMA (CN)
- PMMA (CH$_3$O)
Porogen: Gas phase analysis

- Mass spectrometer detected fragment of DMAEMA (mass 58) and PMMA parent ion (mass 100).
- The decomposition temperature range for DMAEMA is 225°C ~ 325°C, and PMMA 350°C ~ 450°C.
- Good agreement with ToF–SIMS result.
Thermal Behavior of Nanoporous PMSSQ

- High -SiOH
- Low -SiOH
- Matrix cross link
- DMAEMA
- Porogen backbone
- PMMA

T [°C]
Conclusion

- ToF–SIMS, XPS, and TDMS were used to analyze the thermal behavior of porogen-containing PMSSQ

- **Polymerization kinetics of PMSSQ Matrix**
  Polymerization of PMSSQ was observed mainly at 100°C – 200°C, and water was detected as a byproduct by mass spectrometry

  Rate of polymerization depends on the concentration of OH functional groups: high –SiOH PMSSQ shows faster polymerization

- **Porogen behavior upon thermal processing**
  Porogen materials decompose at higher temperatures than PMSSQ polymerization temperatures ( > 225°C)

  DMAEMA and PMMA thermally decompose at different temperatures (225°C – 300°C, PMMA and backbone > 325°C)
Particles Containing Porogen Materials
(AVS 02 Denver)

imaging ToF-SIMS, negative SI

225 °C < curing < 450 °C

Porogen particles are observed only in low –SiOH PMSSQ film.
Slow cross linking process of low –SiOH PMSSQ allows diffusion of porogen material.
Low concentration of –OH with less hydrogen bonding with DMAEMA does not hinder phase separation.

agglomerate density depends on curing T
agglomerate composition (PMMA/DMAEMA ligand/backbone) depends on curing T