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

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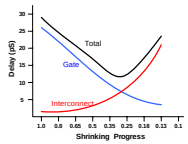
Device Shrinkage and Interconnect Delay

Increased line resistance and capacitive coupling

Interconnect delay dominates overall circuit delay



Al / SiO_2 → Cu / Low K materials (organic, silica based materials) / Nano porous low K materials

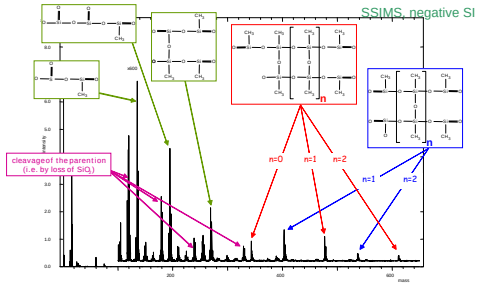
SiO_2 (K = 4.0) Al (ρ ~ 3.0 μΩ cm)

Low k (k ~ 2.0) Cu (ρ - 1.7 μΩ cm)

Nanoporous PMSSQ

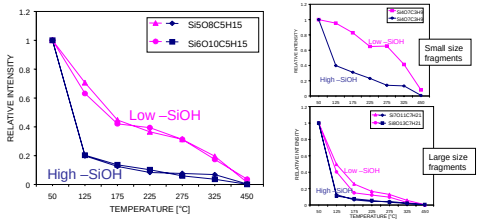
Low polarizability matrix (K ~ 2.7)
Nano porous low K (K ≤ 2.0)
Low water uptake (<1%), thermal stability, mechanical strength.

PMSSQ Finger Print Analysis



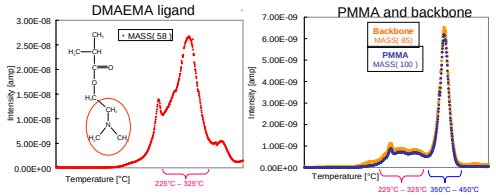
- Peak assignments are well matched to experimental results.
- Peaks are regularly spaced by a monomer unit.
- Fragmentation pattern depends on chemical structure and is sensitive to cross linking.

High –SiOH vs. Low –SiOH



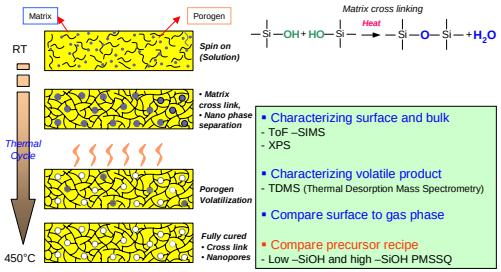
- High – SiOH PMSSQ crosslinks faster than low – SiOH PMSSQ.
- Reaction rate depends on the concentration and proximity of SiOH end groups.

Porogen : Gas phase analysis



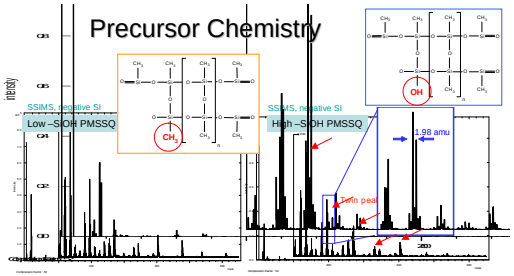
- Mass spectrometer detected fragment of DMAEMA (mass 58) and PMMA parent ion (mass 100).
- The decomposition temperature range for DMAEMA is 225°C ~ 325°C ,and PMMA 350°C ~ 450°C.
- Good agreement with ToF –SIMS result.

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

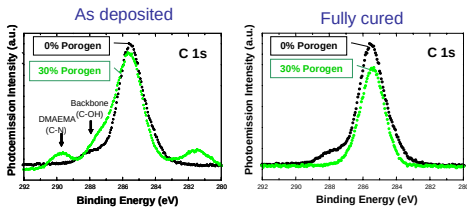
Precursor Chemistry



- 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.
- $[SiOH]_{high} \sim 2 * [SiOH]_{low}$

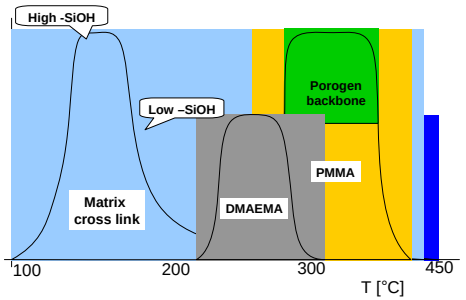
Porogen : Surface Analysis (XPS)

High –SiOH

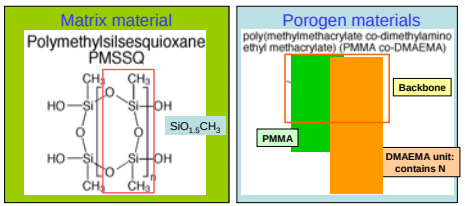


- Porogen related components : Backbone and DMAEMA
- Porogen materials completely volatilized at T = 450°C

Thermal Behavior of Nanoporous PMSSQ

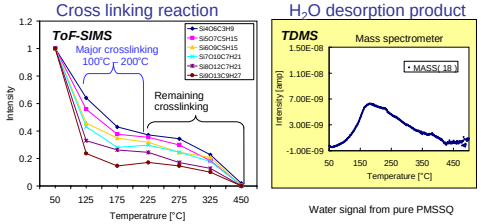


Nanoporous PMSSQ Materials



PMSSQ	Methyl group → *Non-polar, hydrophobic and space-occupying* Hydroxyl group → *Cross linking of matrix*
PMMA-co-DMAEMA	Tertiary amino group → *Hydrogen bonding with OH in Matrix* *Miscibility between matrix and porogen*

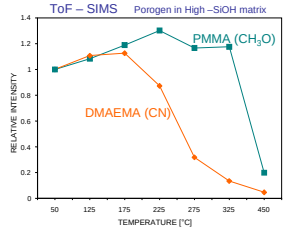
Polymerization of High –SiOH PMSSQ



Water signal from pure PMSSQ

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

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.

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)