New Class of ULow-k for Advanced Interconnects: Fundamentals and Application of Silicon Carbide Hybrid Glasses

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Outline

- Motivation

- Experimental Methods

- Mechanical Properties of Silicon Carbide Hybrid Glasses
  - role of glass network connectivity and plasticity
  - toughening interface by adjacent plasticity
  - moisture-assisted cracking

- Silicon Carbide Hybrid Glasses as new Low-k Dielectrics

- Summary
**Low-k Dielectrics in Microelectronic Interconnects**

- to avoid RC delay
- to reduce power consumption

- silica-based low-k dielectrics

**Silica-Based Low-k Dielectrics and Challenges**

<table>
<thead>
<tr>
<th>Material</th>
<th>k Value</th>
<th>Year</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>4.3</td>
<td>1997</td>
</tr>
<tr>
<td>F-SiO₂</td>
<td>3.8</td>
<td>2002</td>
</tr>
<tr>
<td>SiCOH</td>
<td>3.0</td>
<td>2004</td>
</tr>
<tr>
<td>SiCOH</td>
<td>2.7</td>
<td>2006</td>
</tr>
<tr>
<td>p-SiCOH</td>
<td>2.4</td>
<td>2008</td>
</tr>
</tbody>
</table>


- mechanically weaker

- SiO₂ low-k (k=2.5) ~1/3 mechanical toughness

**(45nm Low-K IILD Crack)**

Kim, et al, 2011 IITC proc. p811

Susko et al, JCS Trans. 16 (19) 51-60 (2009)
Challenge: Moisture-Assisted Cracking

Mechanochemistry between Si-O and H$_2$O

Michalske, Nature p511, 1982

dramatically reduces fracture resistance of silica-based ULK

Impact on Chip Packaging Interaction

Courtesy of Alex Hsing at Dauskardt group
Solution: Non Silica-Based ULK

a few examples of unsuccessful attempts

Can we make ULKs with silicon carbide hybrid glasses?

Silicon Carbide Hybrid Glass Films

- Hybrid structure
  - inorganic network: Si-C, C-C, Si-Si
  - terminal bonds: Si-Hₓ, C-Hₓ
- Nanostructures
  - nanoporosity
- Tunable multi-functionality
  - optical and electrical

significant advantages

- little bond polarity
- excellent chemical/thermal stability
- no moisture-sensitive bonds
  → limited “moisture-assisted cracking”
Applications of Silicon Carbide Hybrid Glass

- Solar cell
- Semiconductor
- Micro/nano machine (Sandia National Lab)
- Optical waveguide (Shoji, App. Phy. Exp. 2010)
- Water filter

Fundamental Challenge: Mechanically Fragile

- Brittle inorganic network
- Reduced network connectivity
- Actual sensitivity to moisture-assisted cracking has not been reported.

Is it possible to confer plasticity to the glasses?

\[ G_c = G_0 + G_{\text{plasticity}} \approx \text{negligible} \]
Objective

- To understand the fundamental connections between the molecular structure and mechanical properties
  - network connectivity
  - plasticity
  - moisture-assisted cracking

- To improve their mechanical properties and create new hybrid materials

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Experimental Methods

Elemental Analysis and Glass Structure
• $^{13}$C solid state NMR
• Nuclear reaction analysis/Rutherford backscattering
• FTIR, X-ray photoelectron spectroscopy

Mechanics Characterization
• Four Point Bend (FPB) and Double Cantilever Beam (DCB) geometries
• Nanoindentation, Surface Acoustic Wave (SAW)

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Hydrogenated Amorphous Silicon Carbide (a-SiC:H)

- Plasma enhanced chemical vapor deposition (PECVD)
- Hydrogenation up to 60 at.%
  - connectivity
  - \( k: 2.8 \text{ to } 7.2 \)
- A wide variety of chemical compositions
  - Stoichiometric (Si/C ~ 1)
  - Non-stoichiometric (C/Si > 1)
- Nanoporosity by second organic phases

Mechanical Properties and Glass Network Connectivity

Fracture properties (brittle materials)

Elastic properties

“"The deepest and most interesting unsolved problem in solid state theory is probably the theory of the nature of glass and the glass transition”

P. W. Anderson (Novel-Prize Laureate), 1995
Mean Field Approach for Connectivity

average network bond number (per atom)

\[ <r'> = \frac{\sum N_i x_i - 2 x_H}{1 - x_H} \]

simply count number of network bonds

\[ N_i: \text{number of bonds in element } i \]
\[ N_{Si}: 4, \ N_C: 3 \text{ or } 4, \ N_H = 1 \]
\[ x_i: \text{atomic fraction of element } i \]

- Rutherford backscattering
- \(^{13}\text{C} \text{NMR}\rightarrow \text{sp}^2 \text{ and sp}^3 \text{ C}\)

Effects of Connectivity on Elastic Properties

- Rigidility percolation
- \(<r'>\sim 2.4\)

- Bulk SiC
- Stoichiometric films (Si/C~1)
- Non-stoichiometric films (Si/C>5)

\[ \frac{N}{m^2} = \text{stiffness} \]

Young's modulus, E (GPa)

Average network bond number, <r'>

Fitting SiO2
Effects of Connectivity on Fracture Energy

\[ G_c = \frac{\text{energy}}{\text{area}} = \frac{\text{bonds}}{\text{area}} \times \frac{\text{energy}}{\text{bond}} \]

Average network bond number, \( <r'> \)

Matsuda, Kim, Stebbins, Dauskardt, et al., in review
Effects of Connectivity on Fracture Energy

![Graph showing the effects of connectivity on fracture energy.](image)

**Matsuda, Kim, Stebbins, Dauskardt, et al., in review**

Plasticity in Non-Stoichiometric a-SiC:H

![Graph showing plasticity in non-stoichiometric a-SiC:H.](image)

**Matsuda, Dauskardt, et al., Acta Materialia, 2012**

Origin of plasticity

![Chemical reactions and diagrams showing the origin of plasticity.](image)

**Matsuda, Kim, Stebbins, Dauskardt, et al., in review**
Tunable Plasticity Contribution to $G_c$

Chemical/Thermal stability ~ 400 °C

Plasticity contribution is tunable!

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Toughening Interface by Adjacent Plasticity

\[ G_C = G_0 + G_{\text{plasticity}} \]

- **a-SiC:H with plasticity**
  - plastic zone, \( G_{\text{plasticity}} \)
  - fragile materials
- **brittle film**
- **weak interface** \( G_0 \)
- **silicon substrate**

Limitations of Metal and Polymers for Toughening

- **limited metal plasticity** at the nanoscale
  - low dislocation mobility
  - small grain size (Hall-Petch)

- **limitations of polymer**
  - thermal stability
  - too soft
Toughening Interface by Adjacent Plasticity

\[ G_C = G_0 + G_{\text{plasticity}} \]

**Limited Film Thickness**
- < 250 nm
- 25 - 1000 nm

- Excellent thermal & chemical stability
- a-SiC:H with plasticity
- Fragile dielectrics
- Brittle film (25 nm)
- Silicon substrate

Effects of a-SiC:H Film Thickness

\[ G_C = G_0 + G_{\text{plasticity}} \]

Matsuda, Ryu, Dauskardt et al., To be submitted to Small
Effects of Separation Thickness

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Moisture-Assisted Cracking

Organosilicate low-k

Crack growth velocity, $v$ (m s$^{-1}$)

Applied Strain Energy Release Rate, $G$ (J m$^{-2}$)

$G_c$

$G_{th}$

$30\%$ RH

$85\%$ RH

$\Delta G_{th}$

Guyer, Dauskardt (unpublished results)
Moisture-Assisted Cracking in a-SiC:H Films

Silicon carbide hybrid glasses

- $\Delta G_{th} \approx 0$

Crack Growth Velocity, $v$ (ms$^{-1}$)

Applied Strain Energy Release Rate, $G$ (J m$^{-2}$)

$E: 11.5$GPa
$k: 4.0$
$\text{Temp: 25}^\circ\text{C}$


Much less sensitivity, but still exhibit crack growth below $G_c$

formation of Si-O-Si bonds
$\text{Si} - \text{H} + \text{H}_2\text{O} \rightarrow \text{SiOH} + \text{H}_2$
$\text{Si} - \text{OH} + \text{Si} - \text{OH} \rightarrow \text{Si} - \text{O} - \text{Si} + \text{H}_2\text{O}$

removing Si-H, groups can result in total insensitivity

Absorbance (a.u.)


Moisture-Assisted Cracking in a-SiC:H Films

Silicon carbide hybrid glasses

\[
\Delta G_{th} \sim 0
\]

Crack Growth Velocity, \( v \) (ms\(^{-1}\))

Applied Strain Energy Release Rate, \( G \) (J m\(^{-2}\))

E: 11.5GPa
k: 4.0
Temp: 25\(^\circ\)C
90%RH

Moisture-Assisted Cracking in a-SiC:H Films

\[ \Delta G_{th} = N_{Si-O-Si} kT \ln \left( \frac{P_{H_2O}^{\text{high humidity}}}{P_{H_2O}^{\text{low humidity}}} \right) \]

Model Prediction: \( \Delta G_{th} \)

<table>
<thead>
<tr>
<th>Humidity range</th>
<th>( \Delta G_{th} ) [J/m²]</th>
</tr>
</thead>
<tbody>
<tr>
<td>20 – 70% RH</td>
<td>0.005</td>
</tr>
<tr>
<td>1-90% RH</td>
<td>0.019</td>
</tr>
<tr>
<td>0.1-90% RH</td>
<td>0.028</td>
</tr>
</tbody>
</table>

\( \Delta G_{th} \approx 0 \) predictions consistent with measurements
How Sensitivity to Moisture-Assisted Cracking Change with Si-O-Si Bond Density?

Oxidized a-SiC:H films

Matsuda, King, Dauskardt, to appear in Thin Solid Films

Technological motivation
O-doping for tailoring electrical/optical properties

Moisture Sensitivity and Si-O-Si Bond Density

Increasing sensitivity

Matsuda, King, Oliver, Dauskardt, in review
Moisture Sensitivity and Si-O-Si Bond Density

\[ \Delta G_{\text{th}} = 0.0225 \exp(0.1038 \rho_{\text{Si-O-Si}}) \]

Matsuda, King, Oliver, Dauskardt, in review

Moisture Sensitivity and Si-O-Si Bond Density

\[ \Delta G_{\text{th}} = N_{\text{Si-O-Si}} \Delta T \ln \left( \frac{P_{\text{H}_2O, \text{high humidity}}}{P_{\text{H}_2O, \text{low humidity}}} \right) \]

Matsuda, King, Oliver, Dauskardt, in review

...disproportionate number of Si-O-Si bonds ruptured in moisture-assisted cracking...

Matsuda, King, Oliver, Dauskardt, in review
Moisture Sensitivity and Si-O-Si Bond Density

\[
N_{Si-O-Si} = \rho^{2/3}_{Si-O-Si}
\]

...disproportionate number of Si-O-Si bonds ruptured in moisture-assisted cracking...

Matsuda, King, Oliver, Dauskardt, in review

Atomistic Crack Path Meandering in MD

generate molecular structure

bond length & angles: crystalline SiC
oxygen: \(~17\) at.%

mathematically count ruptured bonds

max-flow min-cut theorem
(Ford, 1956), Oliver (2010)

Matsuda, Oliver, King, Dauskardt, in review
Atomistic Crack Path Meandering in MD

generate molecular structure

mathematically count ruptured bonds

max-flow min-cut theorem (Ford, 1956), Oliver (2010)

develop bonds

change bond strength

Si-O

Si-C

reduce bond strength

Si-O

Si-C

moist environment

reducing Si-O bond strength

Matsuda, Oliver, King, Dauskardt, in review
Key Findings

- Plasticity can be conferred to silicon carbide hybrid glasses by incorporating sp$^3$ C chains.
  - Plasticity is tunable.
  - Plasticity improves adhesion at adjacent interfaces.

- Silicon carbide hybrid glasses still exhibit low sensitivity to moisture-assisted cracking.
  - Trace Si-O-Si bonds were responsible for this little sensitivity.
  - Eliminating Si-H$_x$ bonds can lead to a complete insensitivity.

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Silicon Carbide Based Low-k Dielectrics

Leveraging from fundamental research to develop new low-k

- Moisture-insensitivity
  - no Si-O and Si-Hₓ bonds
  - total insensitivity
- sp³ CHₓ chains
  - toughness
- Mechanically stiffer
- Thermally and chemically stable
  - process compatible (up to 400°C)
- Little bond polarity
  - lower dielectric constant using less porosity

Silicon Carbide Based Low-Dielectrics

- sp³ C chains
- no Si-O bonds
- no Si-Hₓ bonds
- k=as low as 2.3
  - without additional porosity
- thermal/chemical stability
- hydrophobic (>110°)
- a low-leakage current
  - < 2 x 10⁻⁹ Amp/cm² at 1MV/cm
- high breakdown voltage > 5MV/cm
- good adhesion with Cu and SiO₂

Matsuda, Interrante, Dauskardt, Dubois, et al., ACS Applied Materials & Interfaces
Interrante, Ramanath, Acs Appl Mater Inter 2010, 2, 1275.
Interrante et al., Dalton Trans., 39, 9193, 2010
Silicon Carbide Based Low-Dielectrics

solution process

disilacyclobutane (DSCB) rings

250-300°C ring opening reaction

FTIR

Cure time: 1h

DSCB ring

good thermal stability ~ 400 °C

Matsuda, Interrante, Dauskardt, Dubois, et al., ACS Applied Materials & Interfaces

Excellent Mechanical Properties

Matsuda, Interrante, Dauskardt, Dubois, et al., ACS Applied Materials & Interfaces
Sensitivity to Moisture-Assisted Cracking

![Graph showing crack growth rate and driving force for silica-based low-k and silicon carbide low-k materials at 25°C.]

**Silica-based low-k**
- high sensitivity to moisture-assisted cracking

**Silicon carbide low-k**
- insensitivity to moisture-assisted cracking
- crack growth is due to viscoelastic relaxation of sp³ C-C chains

Matsuda, Interrante, Dauskardt, Dubois, et al., ACS Applied Materials & Interfaces

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New low-k materials are highlighted with arrows indicating 85%, 30%, and 20% water molecule presence at crack tips, showing improved crack growth rates compared to silica-based low-k materials.

Matsuda, Interrante, Dauskardt, Dubois, et al., ACS Applied Materials & Interfaces
Summary

- Important roles of connectivity and plasticity in mechanical properties of silicon carbide hybrid glasses

- Toughening interface using adjacent plasticity

- Moisture-assisted cracking in silicon carbide hybrid glasses
Summary

- New material development leveraging from fundamental research.

Advisor: Prof. Reinhold H. Dauskardt

Collaborators:
- Drs. Sean King, Jessica Xu, Jeff Bielefeld (Intel)
- Drs. Geraud Dubois, Theo Frot, Willi Volksen (IBM Almaden)
- Prof. Jonathan Stebbins, Dr. Namjun Kim, Ill Ryu (Stanford)
- Prof. Leonard Interrante (Rensselaer Polytechnic Institute)

Dauskardt group:
- Mark Oliver (Dow Electronic Materials), Taek-Soo Kim (KAIST), Jeff Yang, Tissa Mirfakhrai, Scott Issacson

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