Sant Clara Valley Section, Components, Packaging
and Manufacturing Technology Society Chapter
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New Class of ULow-k for Advanced Interconnects: Fundamentals and Application of Silicon Carbide Hybrid Glasses

Yusuke Matsuda
Lecturer and Ph.D. Candidate
Department of Materials Science and Engineering
Stanford University

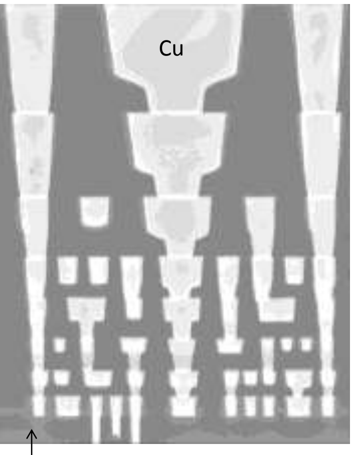
Advisor: Professor Reinhold Dauskardt

January 9th, 2013

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

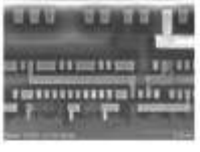


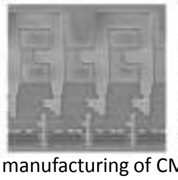
- to avoid RC delay
- to reduce power consumption

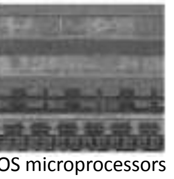
silica-based low-k dielectrics

Silica-Based Low-k Dielectrics and Challenges

SiO_2	$F\text{-}SiO_2$	SiCOH	SiCOH	p-SiCOH
k=4.3	k=3.8	k=3.0	k=2.7	k=2.4
1997	2002	2004	2006	2008

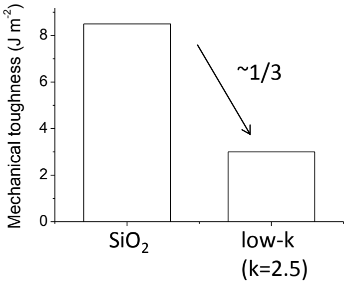


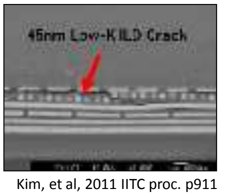




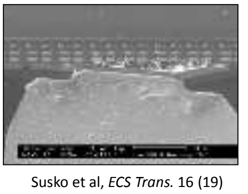
IBM volume manufacturing of CMOS microprocessors
(Dubois, et al. *Chem. Rev.* **2010,** *110,* 56–110)

mechanically weaker





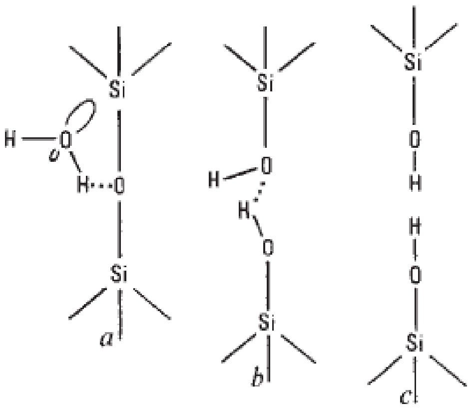
Kim, et al, 2011 IITC proc. p911



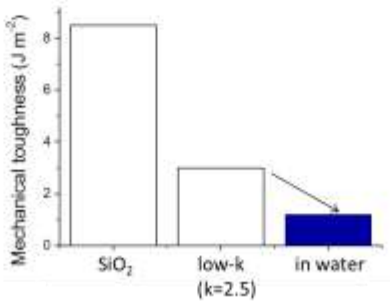
Susko et al, *ECS Trans.* 16 (19) 51-60 (2009)

Challenge: Moisture-Assisted Cracking

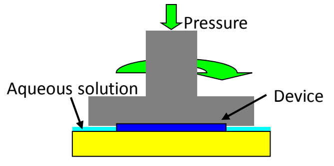
mechanochemistry between Si-O and H_2O



Michalske, Nature p511, 1982

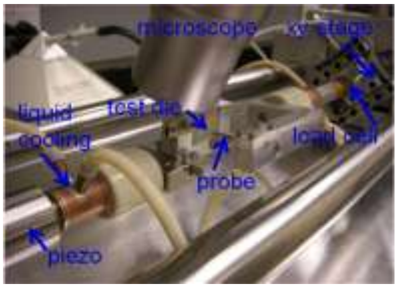


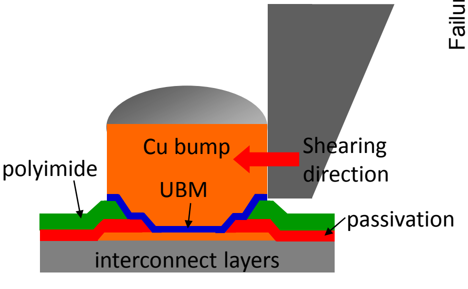
Wet processes (CMP)

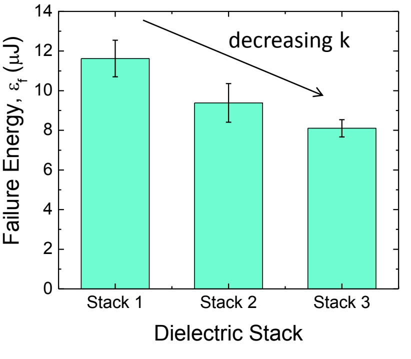


dramatically reduces fracture resistance of silica-based ULK

Impact on Chip Packaging Interaction



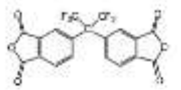




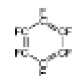
Courtesy of Alex Hsing at Dauskardt group

Solution: Non Silica-Based ULK

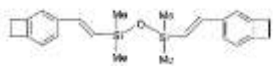
a few examples of unsuccessful attempts



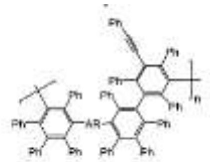
polyimid



F-DLC



DSV-BCB

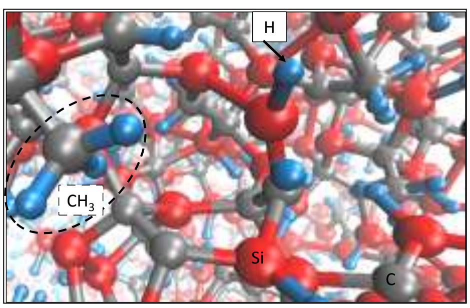


SiLK

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-H_x, C-H_x
- Nanostructures
  - nanoporosity
- Tunable multi-functionality
  - optical and electrical



significant advantages

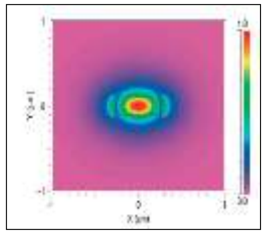
- little bond polarity
- excellent chemical/thermal stability
- no moisture-sensitive bonds

→ limited "moisture-assisted cracking"

Applications of Silicon Carbide Hybrid Glass

solar cell

semiconductor



optical waveguide
(Shoji, App. Phy. Exp. 2010)

optics

micro/nano machine
(Sandia National Lab)

water filter

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Fundamental Challenge: Mechanically Fragile

- Brittle inorganic network

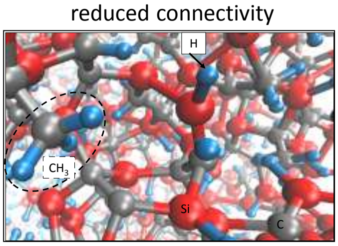
Is it possible to confer plasticity to the glasses?

fracture resistance

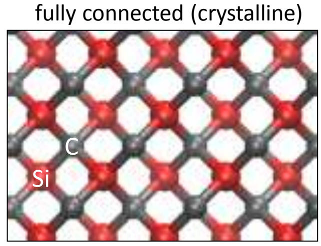
$$G_c = G_0 + \boxed{G_{plasticity}} \sim \text{negligible}$$

- Reduced network connectivity

reduced connectivity



fully connected (crystalline)



Effects of glass network connectivity on mechanical properties are unknown…

- Actual sensitivity to moisture-assisted cracking has not been reported.

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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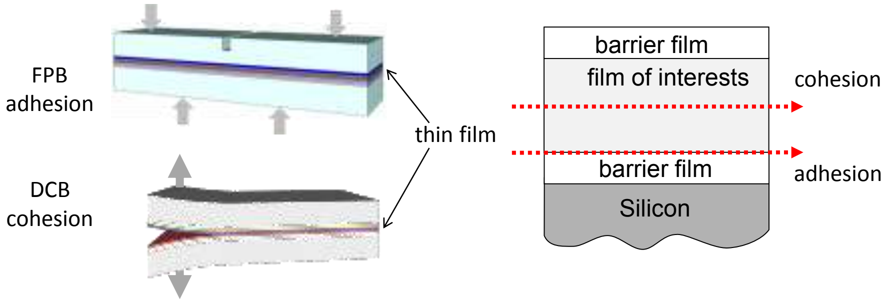
Experimental Methods

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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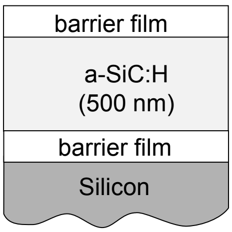
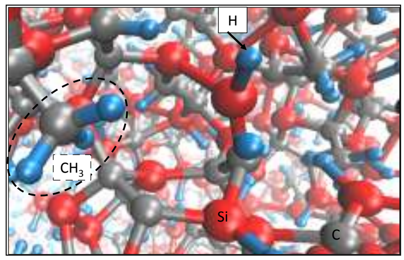
Hydrogenated Amorphous Silicon Carbide (a-SiC:H)

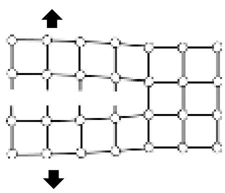
- Plasma enhanced chemical vapor deposition (PECVD)
- Hydrogenation up to 60 at.%
  - connectivity
  - k: 2.8-7.2
- A wide variety of chemical compositions
  - Stoichiometric (Si/C ~ 1)
  - Non-stoichiometric (C/Si > 1)
- Nanoporosity by second organic phases





Mechanical Properties and Glass Network Connectivity

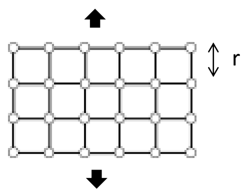
Fracture properties (brittle materials)



$$G_c\left[\frac{energy}{area}\right] = \boxed{\frac{bonds}{area}}\,\frac{energy}{bond}$$

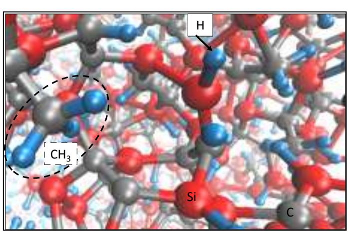
connectivity

Elastic properties



$$E\left[\frac{N}{m^2}\right] = stiffness\left[\frac{N}{m}\right]\boxed{\frac{1}{r}}$$

connectivity



"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

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Mean Field Approach for Connectivity

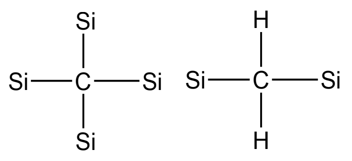
average network bond number (per atom)

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

simply count number of network bonds

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

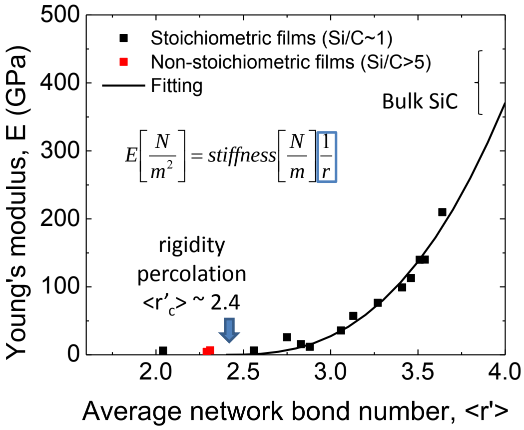
- Rutherford backscattering
- ^{13}C NMR → sp^2 and sp^3 C



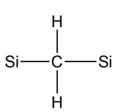
max <r'>=4
crystalline SiC

<r'>=2
a-SiC:H

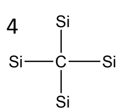
Effects of Connectivity on Elastic Properties



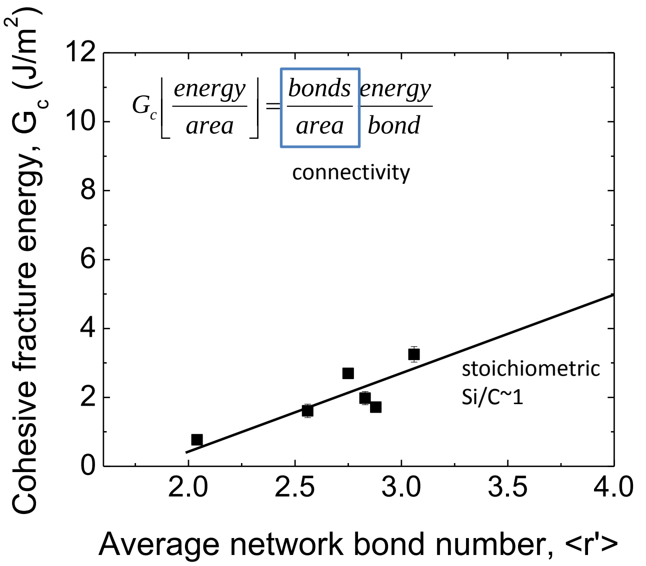
<r'> = 2



<r'> = 4

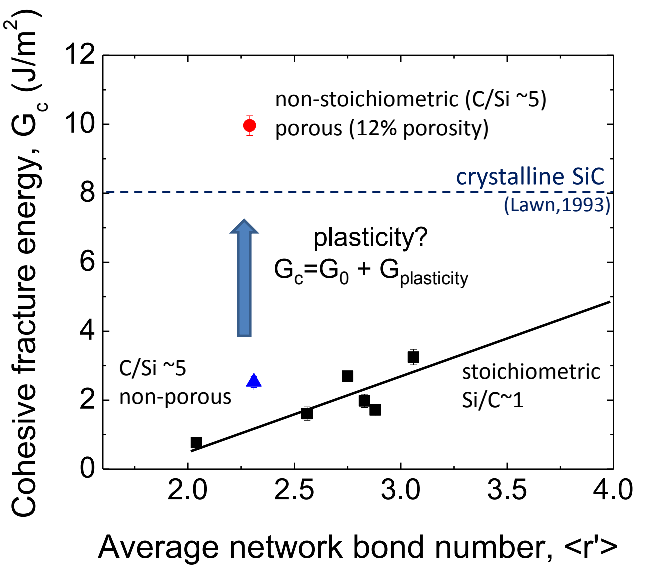


Effects of Connectivity on Fracture Energy



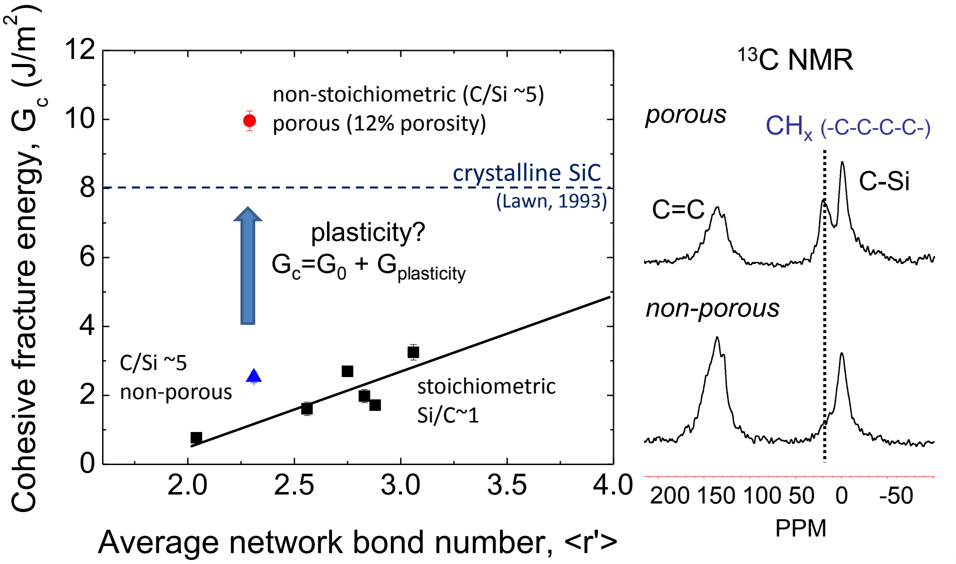
Matsuda, Kim, Stebbins, Dauskardt, et al., in review

Effects of Connectivity on Fracture Energy



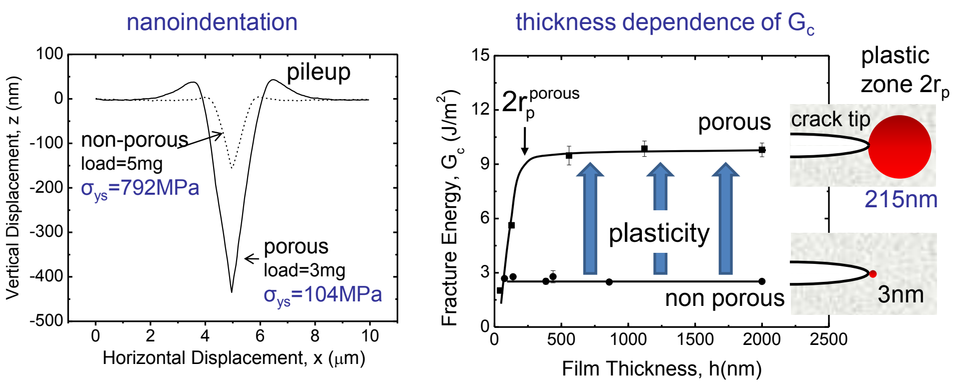
Matsuda, Kim, Stebbins, Dauskardt, et al., in review

Effects of Connectivity on Fracture Energy



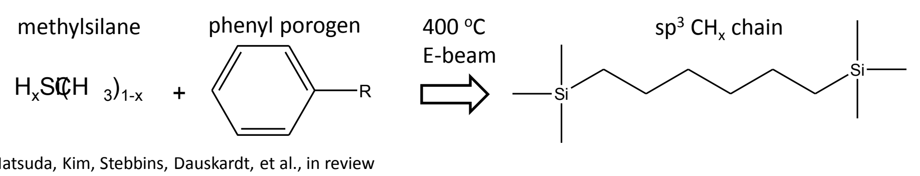
Matsuda, Kim, Stebbins, Dauskardt, et al., in review

Plasticity in Non-Stoichiometric a-SiC:H



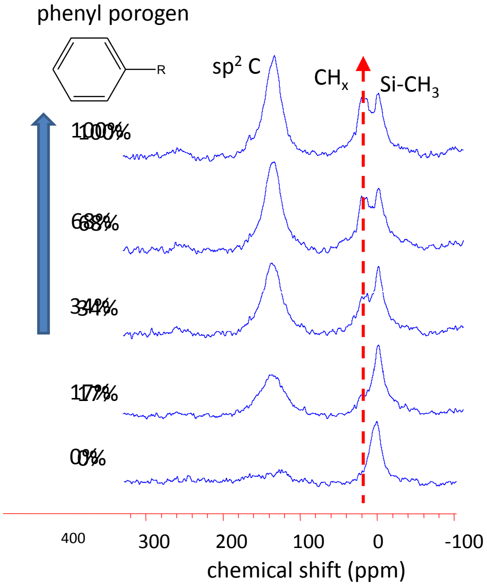
Matsuda, Dauskardt, et al., Acta Materialia, 2012

Origin of plasticity



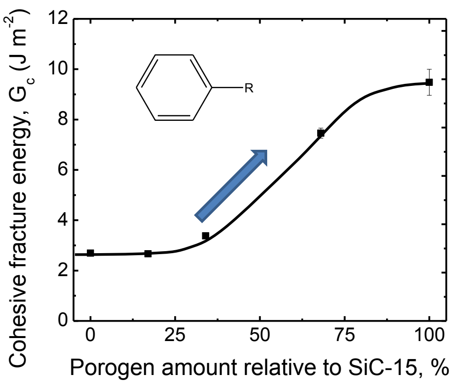
Matsuda, Kim, Stebbins, Dauskardt, et al., in review

Tunable Plasticity Contribution to G_c



Plasticity contribution is tunable!

Chemical/Thermal stability ~ 400 °C



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

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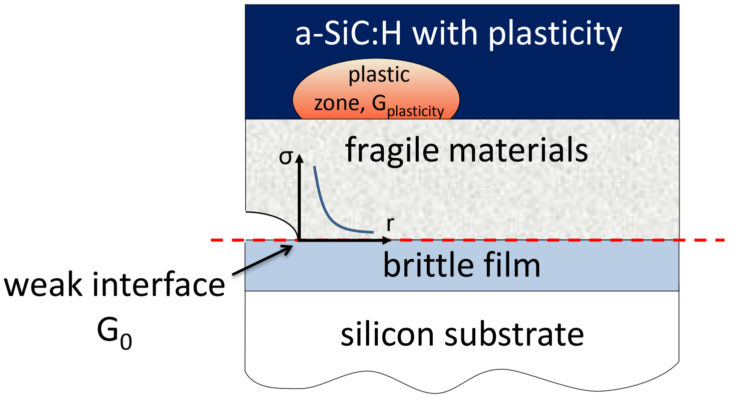
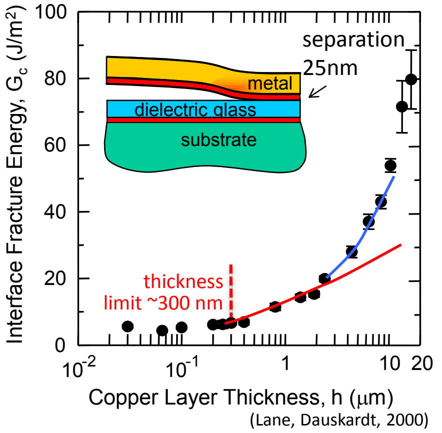
Toughening Interface by Adjacent Plasticity

$$G_C = G_0 + G_{plasticity}$$

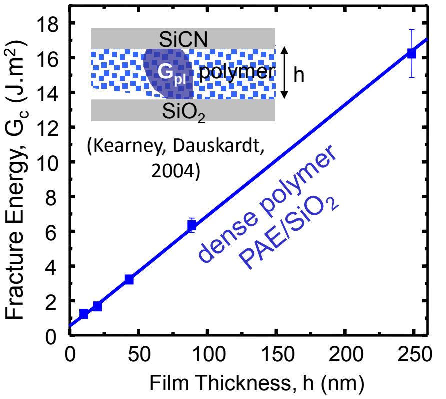


Limitations of Metal and Polymers for Toughening



(Lane, Dauskardt, 2000)

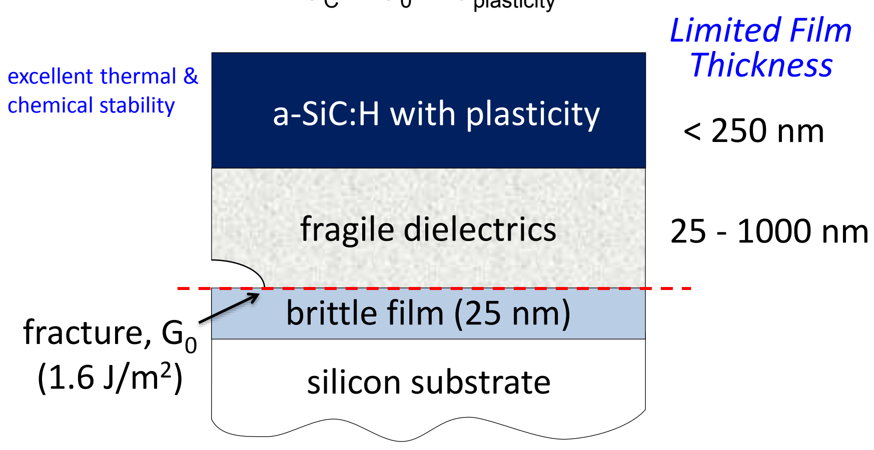
limited metal plasticity at the nanoscale
- low dislocation mobility
- small grain size (Hall-Petch)



limitations of polymer
- thermal stability
- too soft

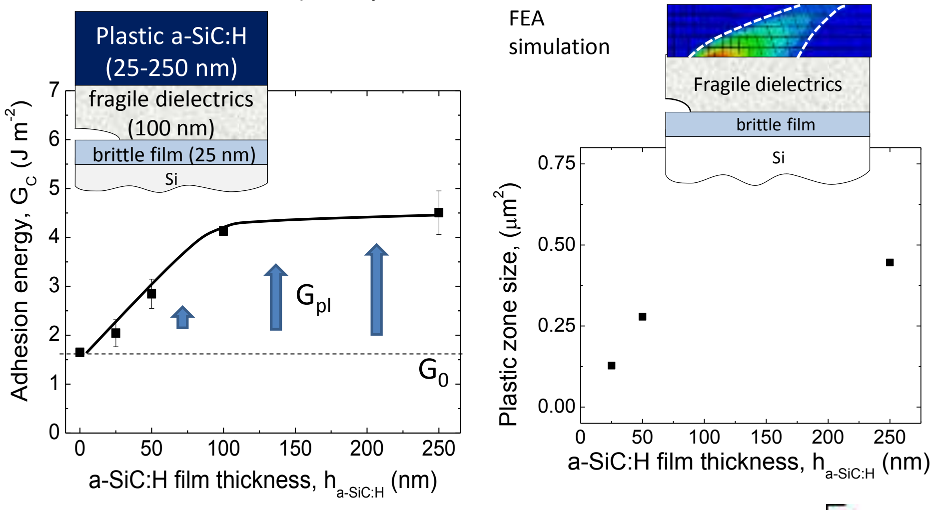
Toughening Interface by Adjacent Plasticity

$G_C = G_0 + G_{plasticity}$



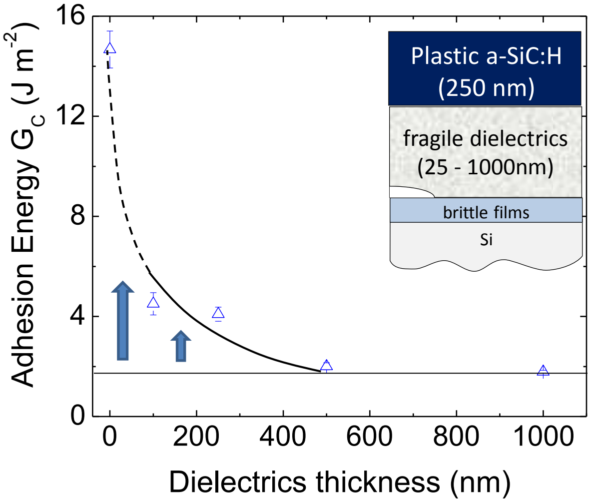
Effects of a-SiC:H Film Thickness

$G_c = G_0 + G_{plasticity}$



Matsuda, Ryu, Dauskardt et al., To be submitted to Small

Effects of Separation Thickness



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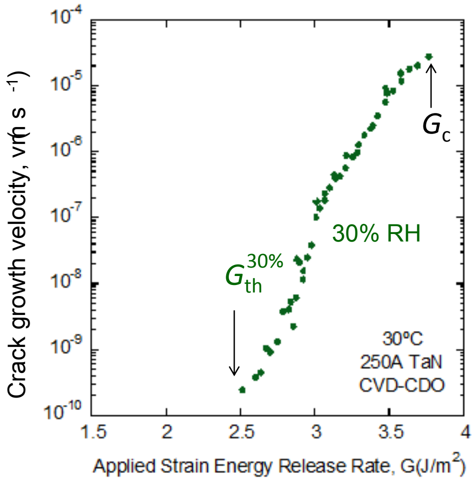
Moisture-Assisted Cracking

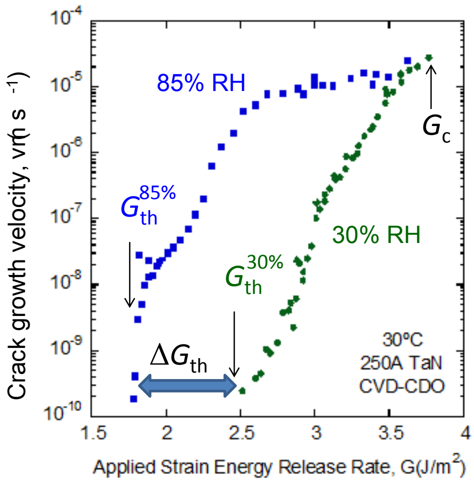
Organosilicate low-k



Guyer, Dauskardt (unpublished results)

Moisture-Assisted Cracking

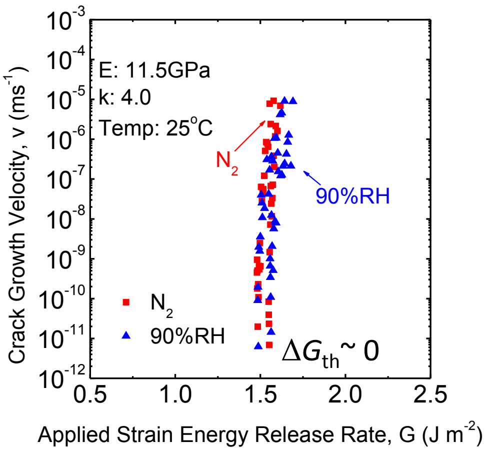
Organosilicate low-k



Guyer, Dauskardt (unpublished results)

Moisture-Assisted Cracking in a-SiC:H Films

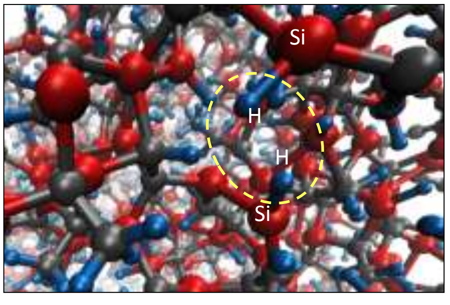
Silicon carbide hybrid glasses



Much less sensitivity, but still exhibit crack growth below G_c

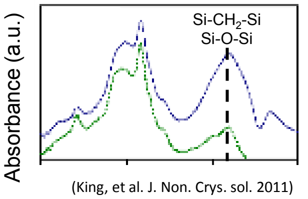
Matsuda, Dauskardt, et al., Acta Materialia, 2012

Moisture-Assisted Cracking in a-SiC:H Films

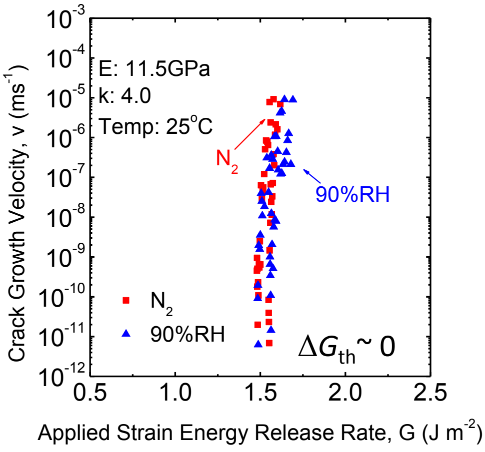


formation of Si-O-Si bonds

$$\mathrm{Si-H + H_2O \rightarrow SiOH + H_2}$$
$$\mathrm{Si-OH + Si-OH \rightarrow Si-O-Si + H_2O}$$



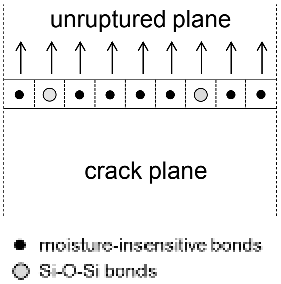
(King, et al. J. Non. Crys. sol. 2011)



removing Si-H_x groups can result in total insensitivity

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

Moisture-Assisted Cracking in a-SiC:H Films

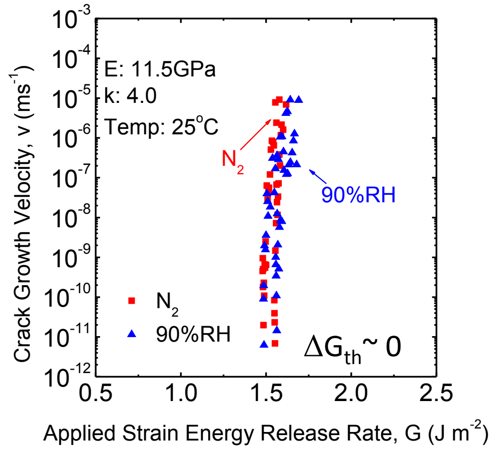


separation of strain energy G

$$G = G^{Si\text{-}C} + G^{Si\text{-}O}$$

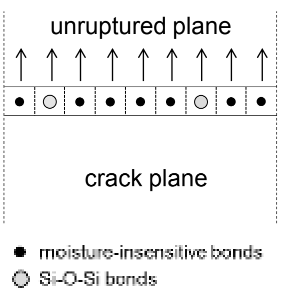
insensitive *moisture sensitive*

Silicon carbide hybrid glasses



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

Moisture-Assisted Cracking in a-SiC:H Films

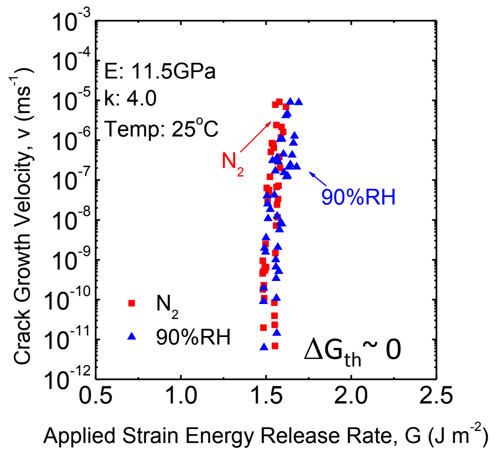


threshold, G_{th}

$$G_{th} = G_c^{Si\text{-}C} + 2\gamma^{Si\text{-}O}$$

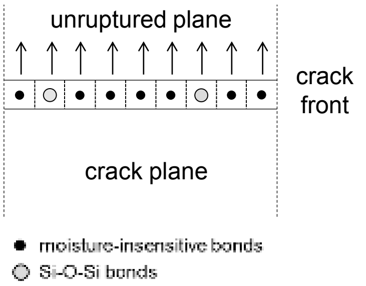
insensitive *moisture sensitive*

Silicon carbide hybrid glasses



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

Moisture-Assisted Cracking in a-SiC:H Films

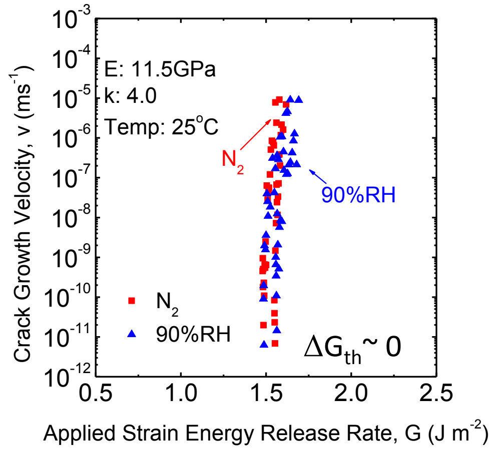


$$\Delta G_{th} = N_{Si-O-Si} kT \ln \left(\frac{P_{H_2O}^{\text{high humidity}}}{P_{H_2O}^{\text{low humidity}}} \right)$$

Si-O-Si ruptured bonds

vapor pressure

Silicon carbide hybrid glasses



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

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Model Prediction: ΔG_{th}

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

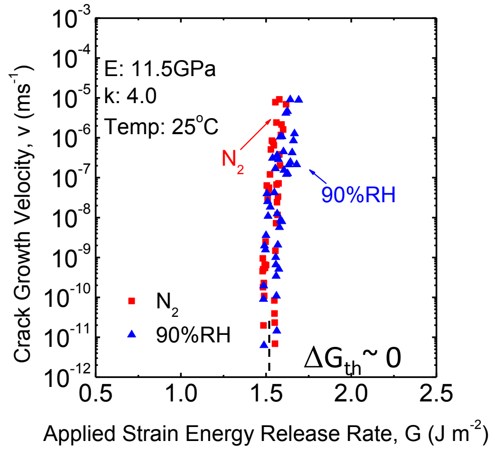
~10^{18} bonds/m^2

predictions

Humidity range	ΔG_{th} [J/m^2]
20 – 70% RH	0.005
1-90% RH	0.019
0.1-90% RH	0.028

consistent with measurements

Silicon carbide hybrid glasses



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

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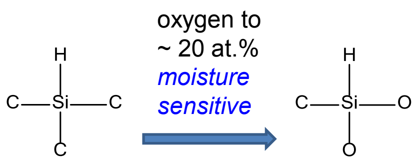
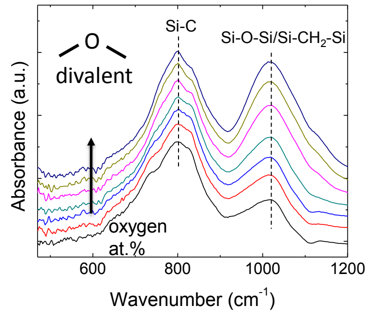
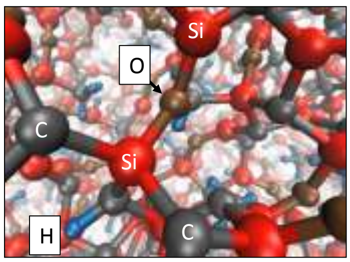
How Sensitivity to Moisture-Assisted Cracking Change with Si-O-Si Bond Density?





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

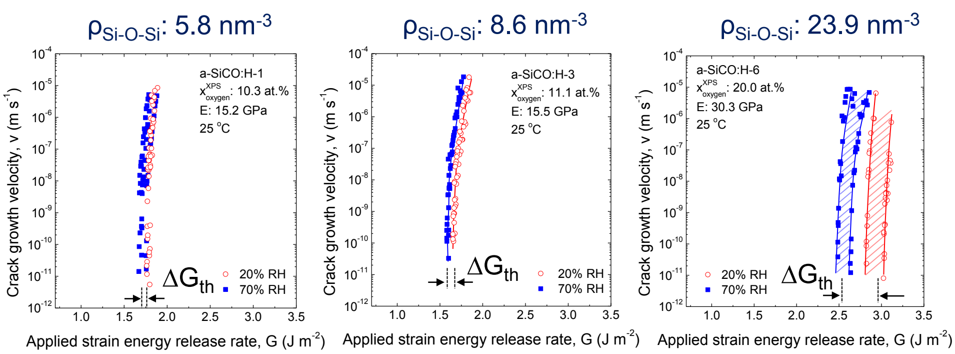
Oxidized a-SiC:H films



Technological motivation

O-doping for tailoring electrical/optical properties

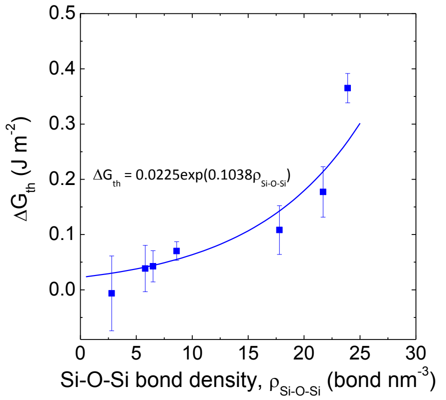
Moisture Sensitivity and Si-O-Si Bond Density

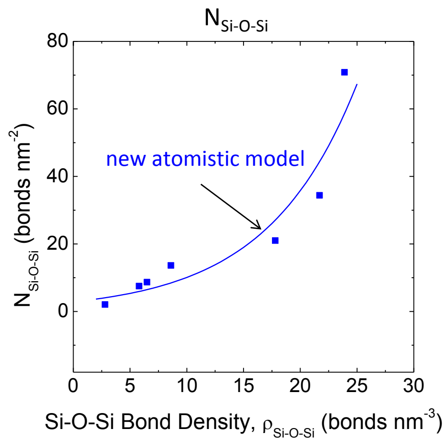


increasing sensitivity

Matsuda, King, Oliver, Dauskardt, in review

Moisture Sensitivity and Si-O-Si Bond Density



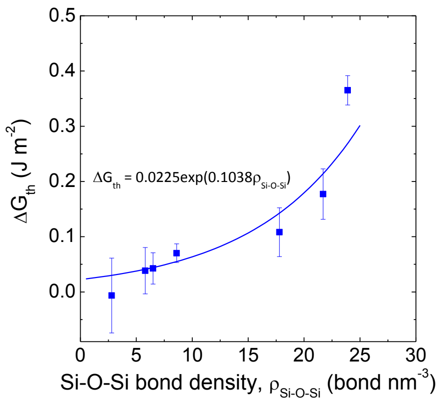


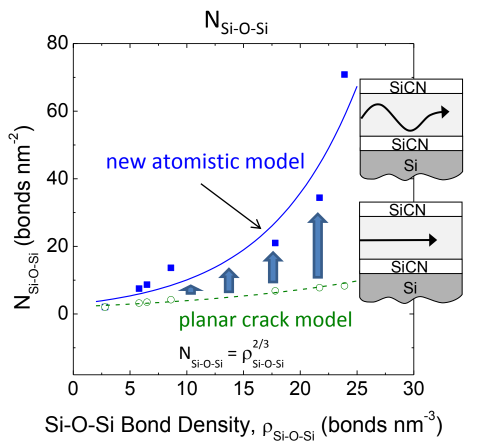
new atomistic model

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

Matsuda, King, Oliver, Dauskardt, in review

Moisture Sensitivity and Si-O-Si Bond Density





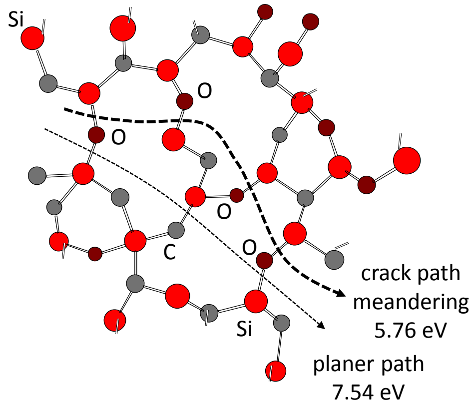
new atomistic model

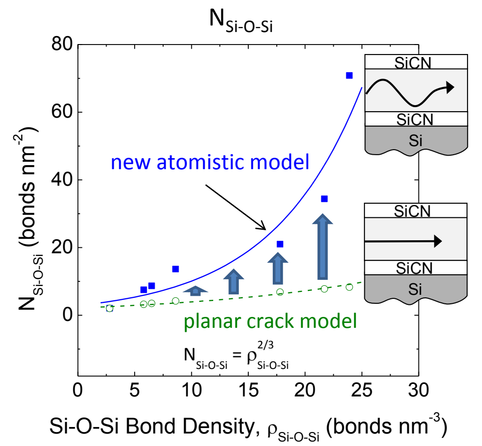
$$\Delta G_{th} = \boxed{N_{Si-O-Si}}\, kT \ln\left(\frac{P_{H_2O}^{\text{highhumidity}}}{P_{H_2O}^{\text{lowhumidity}}}\right)$$

…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





bond energies (Wiederhorn 1980)

- Si-C: 4.66eV
- Si-O (moist) : 1.44 eV

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

Matsuda, King, Oliver, Dauskardt, in review

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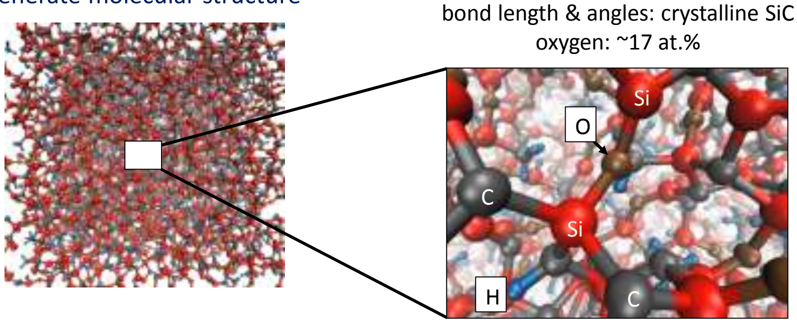
Atomistic Crack Path Meandering in MD

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

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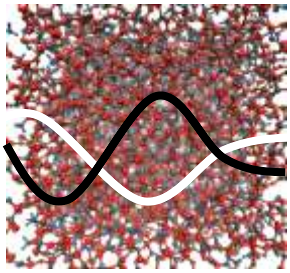
Atomistic Crack Path Meandering in MD

generate molecular structure



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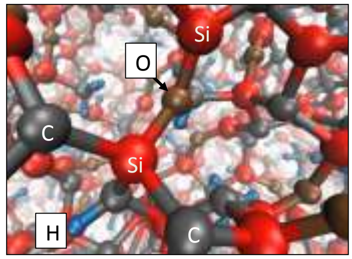
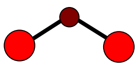


mathematically count ruptured bonds

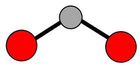
max-flow min-cut theorem
(Ford, 1956), Oliver (2010)

change bond strength

Si-O



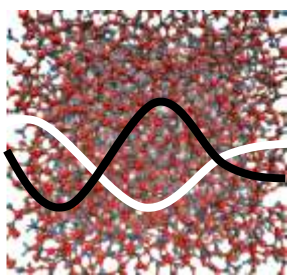
Si-C



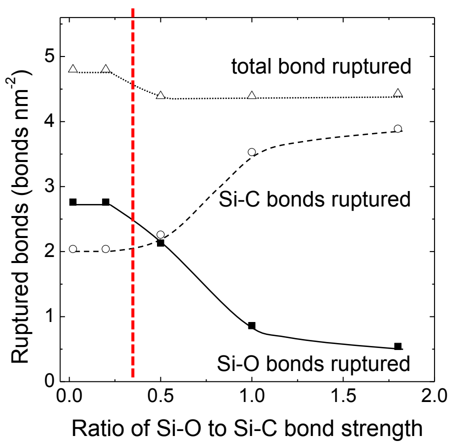
Matsuda, Oliver, King, Dauskardt, in review

Atomistic Crack Path Meandering in MD

generate molecular structure



moist environment



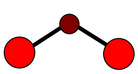
reducing Si-O bond strength

mathematically count ruptured bonds

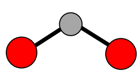
max-flow min-cut theorem
(Ford, 1956), Oliver (2010)

change bond strength

Si-O



Si-C



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 $Si\text{-}H_x$ bonds can lead to a complete insensitivity.

STANFORD MATERIALS SCIENCE AND ENGINEERING

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

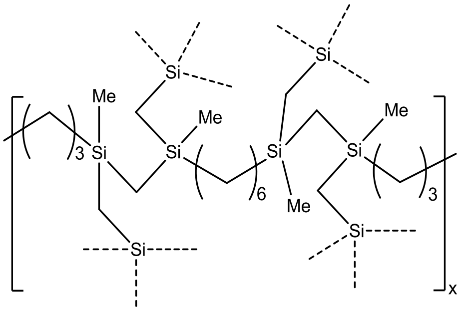
STANFORD MATERIALS SCIENCE AND ENGINEERING

Silicon Carbide Based Low-k Dielectrics

Leveraging from fundamental research to develop new low-k

- Moisture-insensitivity
  no Si-O and Si-H_x bonds
  → total insensitivity
- sp^3 CH_x 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

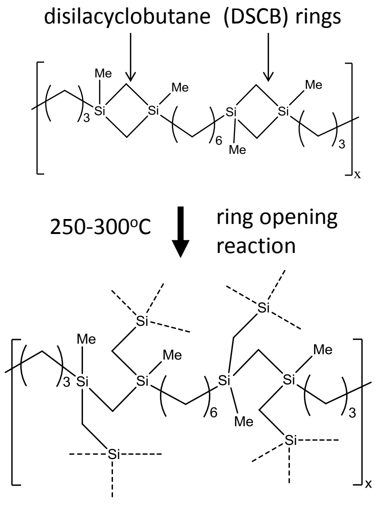


- sp^3 C chains
- no Si-O bonds
- no Si-H_x bonds
- k=as low as 2.3
  without additional porosity
- thermal/chemical stability
- hydrophobic (>110°)
- a low-leakage current
  < 2 x 10^{-9} Amp/cm^2 at 1MV/cm
- high breakdown voltage > 5MV/cm
- good adhesion with Cu and SiO_2

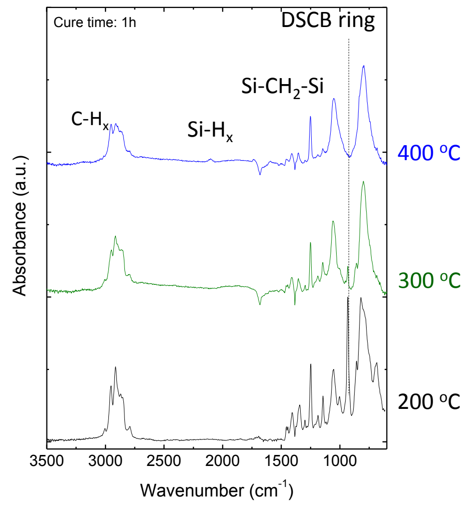
Matsuda, Interrante, Dauskardt, Dubois, et al., ACS Applied Materials & Interfaces
Interrante, Ramanath, et al. Phys Chem Lett 2010, 1, 336
Interrante, Ramanath, Acs Appl Mater Inter 2010, 2, 1275.
Interrante et al., Dalton Trans., **39**, 9193, 2010

Silicon Carbide Based Low-Dielectrics

solution process



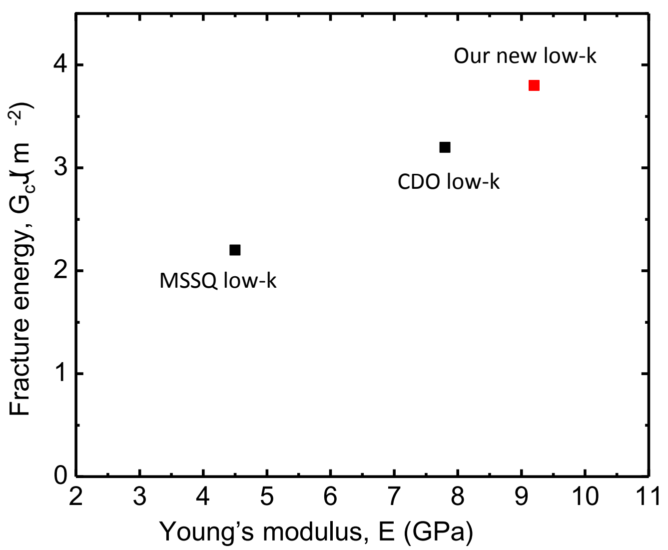
FTIR



good thermal stability ~ 400 °C

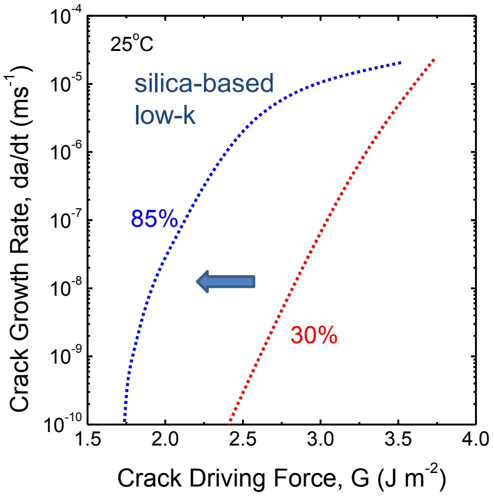
Matsuda, Interrante, Dauskardt, Dubois, et al., ACS Applied Materials & Interfaces

Excellent Mechanical Properties



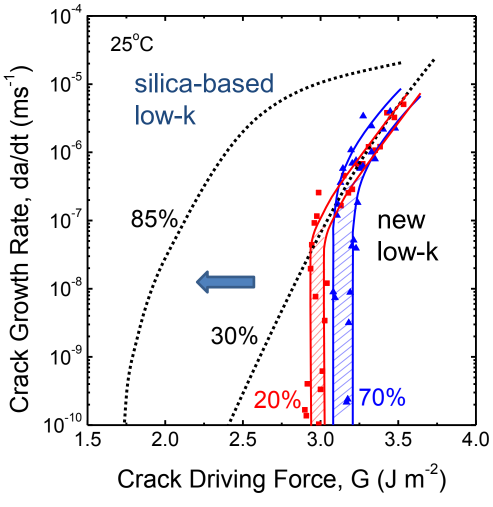
Matsuda, Interrante, Dauskardt, Dubois, et al., ACS Applied Materials & Interfaces

Sensitivity to Moisture-Assisted Cracking



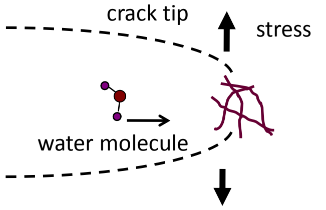
Matsuda, Interrante, Dauskardt, Dubois, et al., ACS Applied Materials & Interfaces

Sensitivity to Moisture-Assisted Cracking



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 sp^3 C-C chains

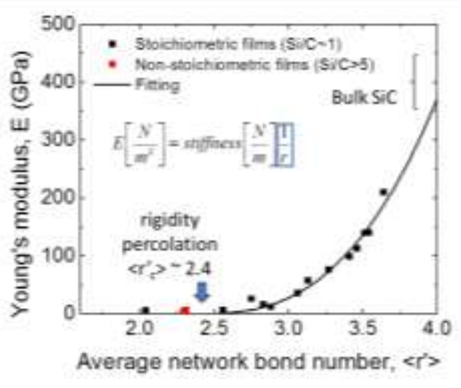


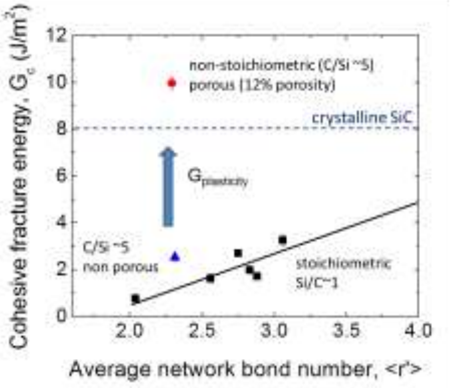
chain slip and disentanglement

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

Summary

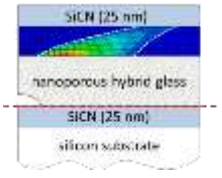
- Important roles of connectivity and plasticity in mechanical properties of silicon carbide hybrid glasses



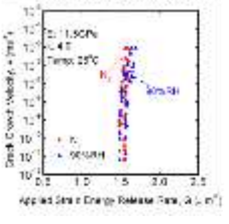


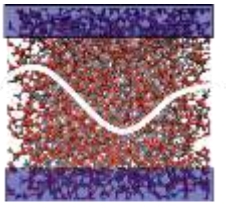
Summary

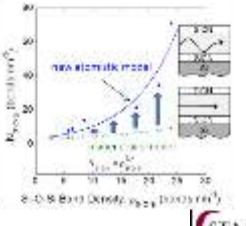
- Toughening interface using adjacent plasticity



- Moisture-assisted cracking in silicon carbide hybrid glasses

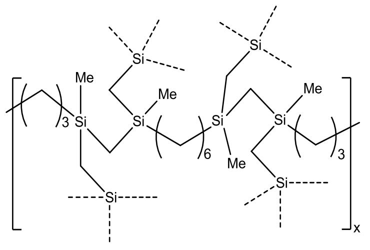


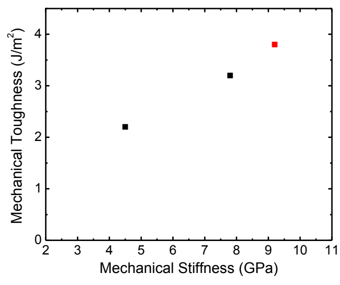




Summary

- New material development leveraging from fundamental research.





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  - Prof. Jonathan Stebbins, Dr. Namjun Kim, Ill Ryu (Stanford)
  - Prof. Leonard Interrante (Rensselaer Polytechnic Institute)
- Dauskardt group:
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