

# Understanding Stress, Chemistry and Molecular Diffusion for Optimized CMP of ULK Dielectrics

Reinhold H. Dauskardt ([dauskardt@stanford.edu](mailto:dauskardt@stanford.edu))

Department of Materials Science and Engineering

## ULK Thin-Film Materials

Taek-Soo Kim, Andrew Thiel, Yusuke Matsuda

## Polymers and Nanomaterials

Mark Oliver, Jeffery Yang, Ruiliang Jia, Ani Kamer

## Ultra-Thin Barrier Films

Ryan Birringer

## Chip Package Interactions

Alex Hsing

## Photovoltaic and Flexible Electronic Materials

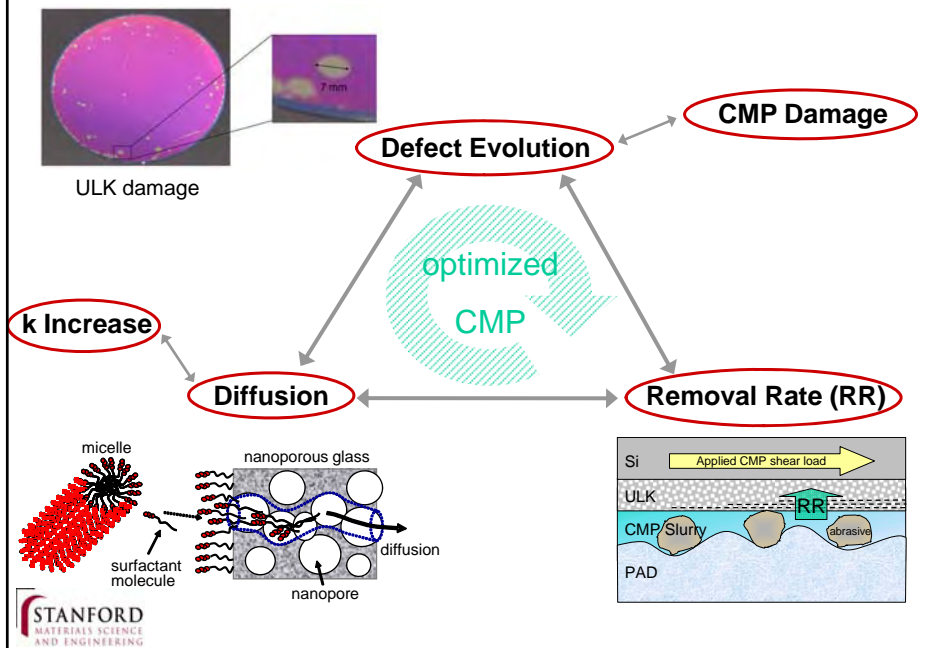
Vitali Brand, Fernando Novoa

Collaborators: T. Konno and T. Yamanaka

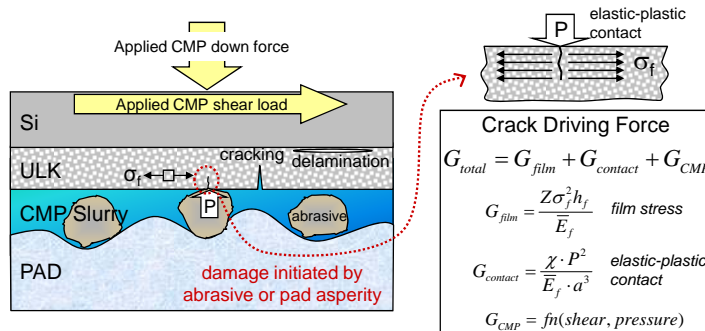
JSR Micro, Sunnyvale, CA



# Road Map for Optimized CMP of Nanomaterials



## Crack Driving Force and Subcritical Cracking



In the **absence** of chemically active environmental species, crack propagates if

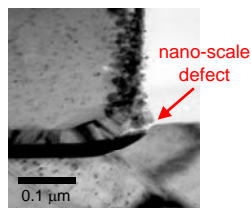
$$G_{total} \geq G_c \quad (J / m^2)$$

In the **presence** of chemically active species during CMP, crack propagates if

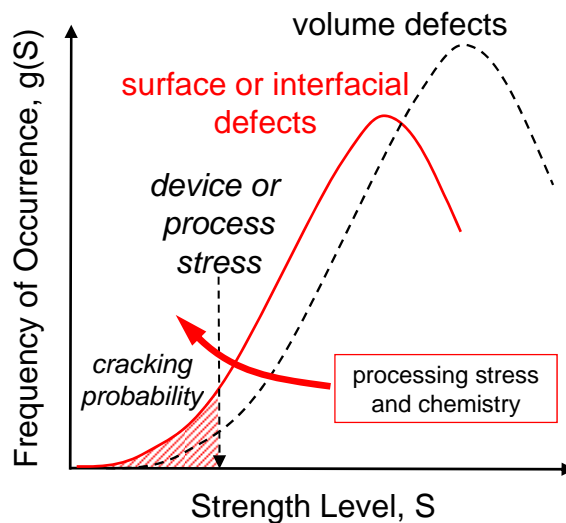
$$G_{total} < G_c \quad (J / m^2) \quad \text{CMP slurry accelerates defect evolution}$$



## Reliability and Implications for Processing Yield



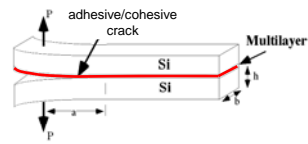
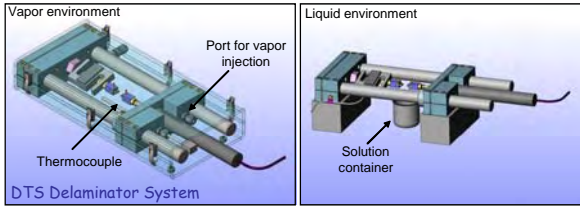
damage initiation



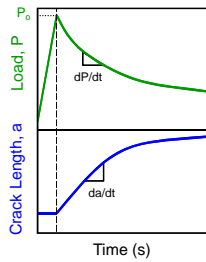
Depends on defect size and fracture energy,  $G_c$



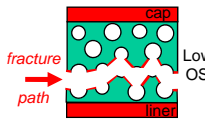
# Automated Crack Velocity Testing



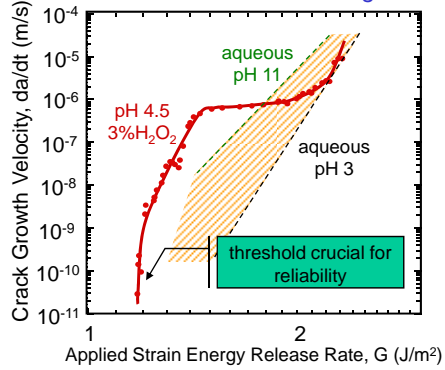
## Load Relaxation Crack Growth Technique



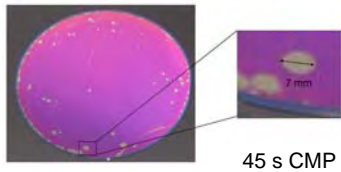
compliance analysis



## Accelerated Cracking

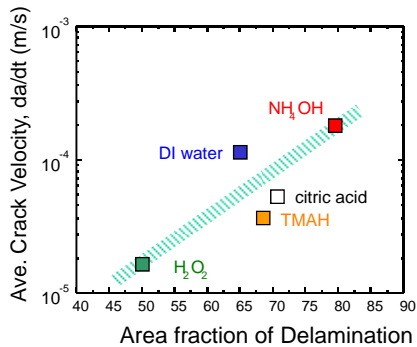
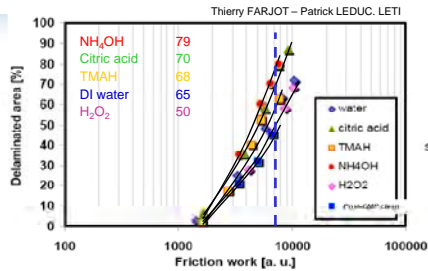
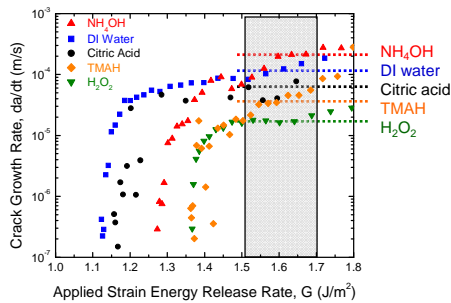


# Relevance to CMP Damage



45 s CMP

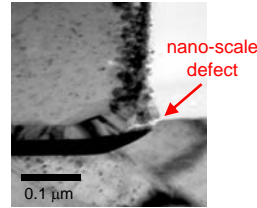
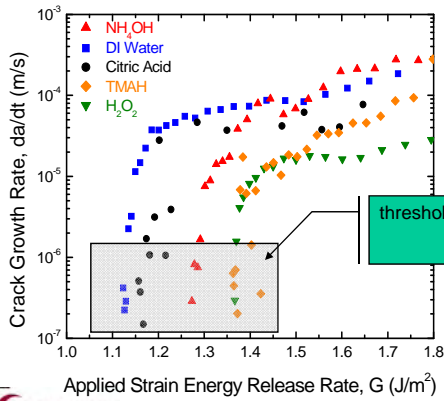
Characterize crack growth rate to predict damage...



# Relevance to CMP Damage

- Low crack growth rates critical for growth of nano-scale defects
- Dominated by threshold behavior in v-G curves

Synergistic effects of CMP slurry chemistry and stress on defect evolution/crack growth



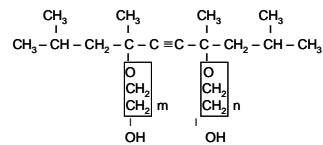
Crack growth rates  $< 10^{-10}$  m/s (below threshold) necessary to achieve reliable integration



# Surfactant Effects on Defect Growth and Diffusion

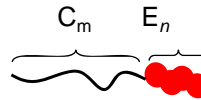
Dimeric (Gemini) surfactant

Low foaming (defoaming) and rapid surface wetting



Linear (bridged) surfactant

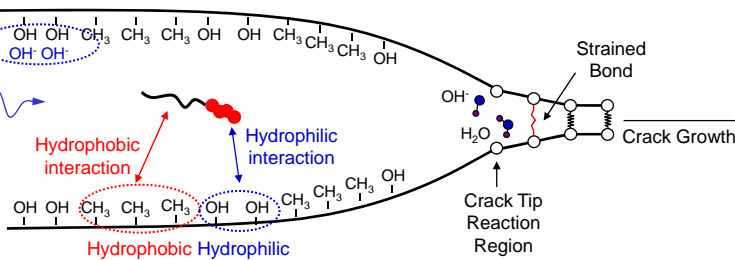
Polyoxyethylene Alkyl Ethers



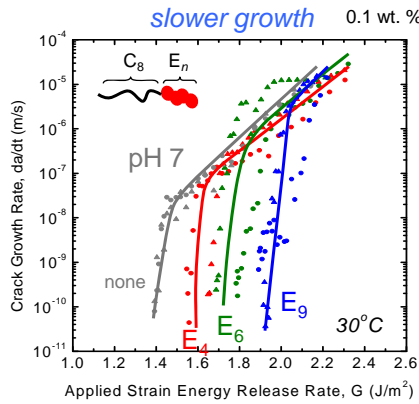
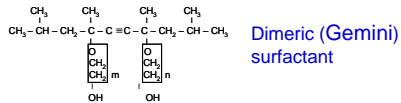
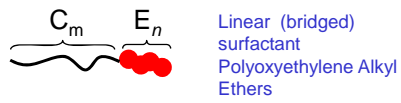
Effects of surfactant molecules on the defect evolution/crack growth are unknown!

Competition for adsorption sites at high pH

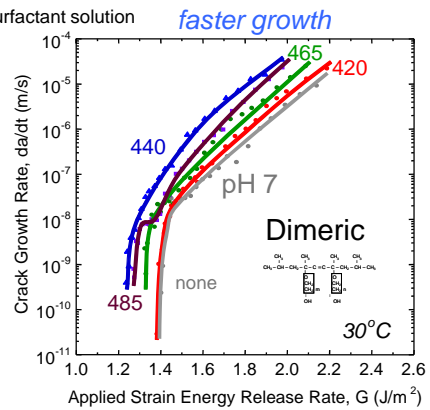
Surfactant containing solution



# Surfactant Effects on Defect Growth and Diffusion



*Dimeric surfactant accelerates crack growth*  
 *$C_mE_n$  surfactants suppressed crack growth!*

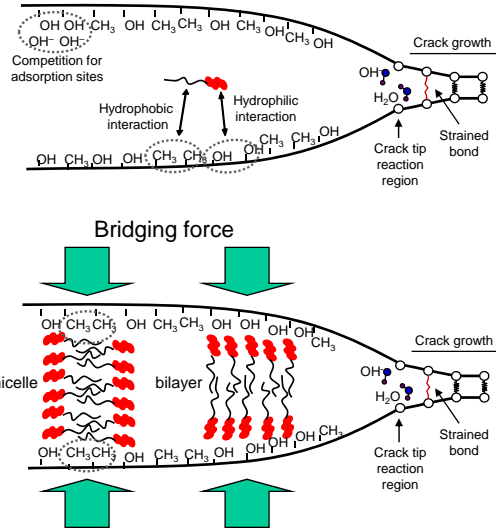
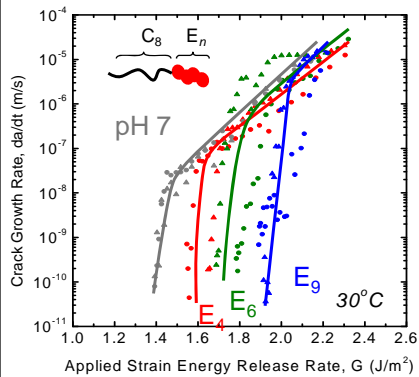


*Dimeric surfactant decreases diffusion*  
 *$C_mE_n$  surfactants accelerate diffusion!*

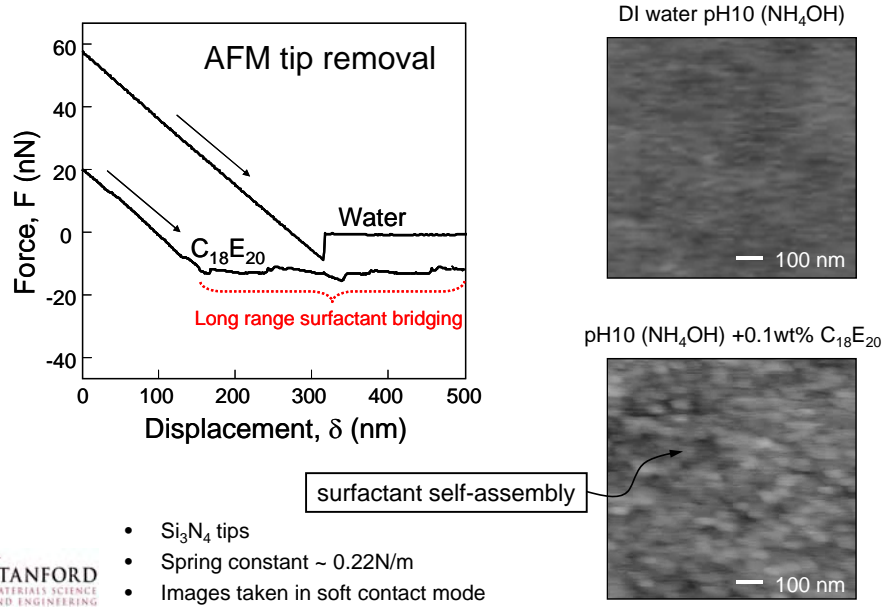
## Micellar Bridging in Aqueous Solution

$$G_{tip} = G_{applied} - G_{bridging}$$

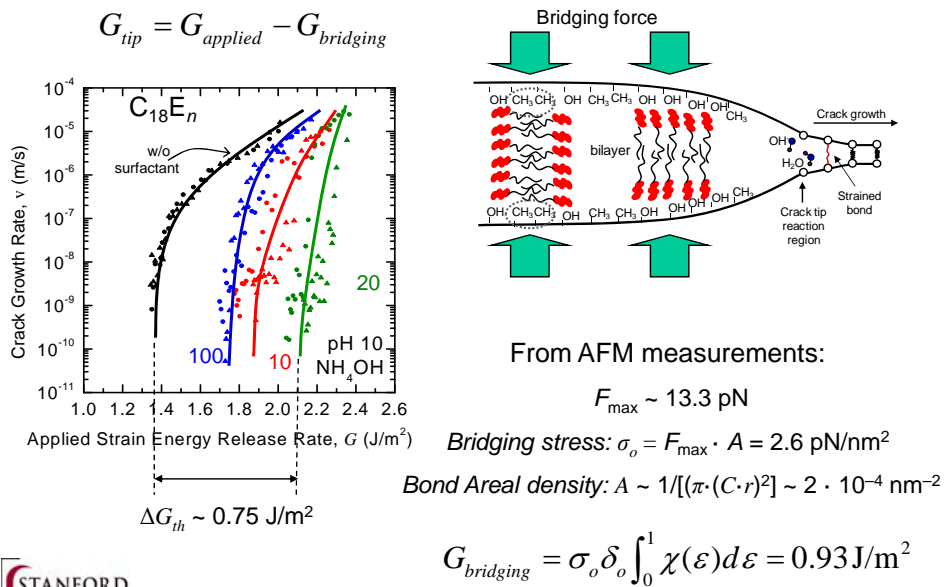
Micellar bridging reduces crack tip driving force



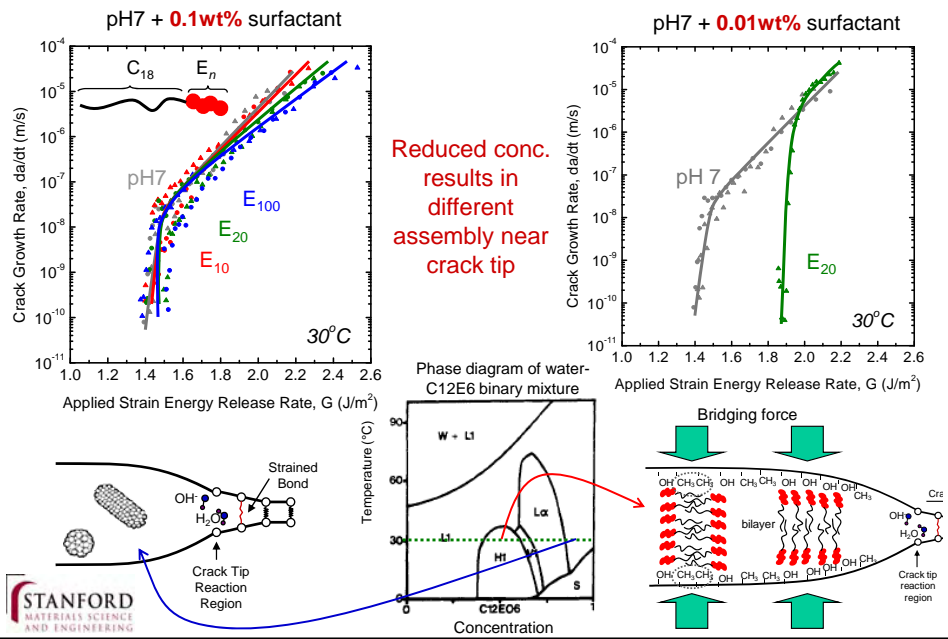
# Probing Molecular Interactions with AFM



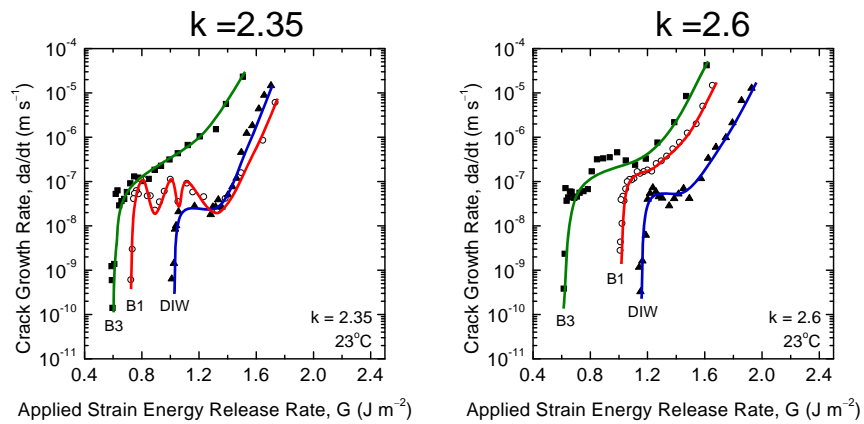
# Molecular Bridging Contribution



## $C_m E_n$ Concentration Effects on Crack Growth

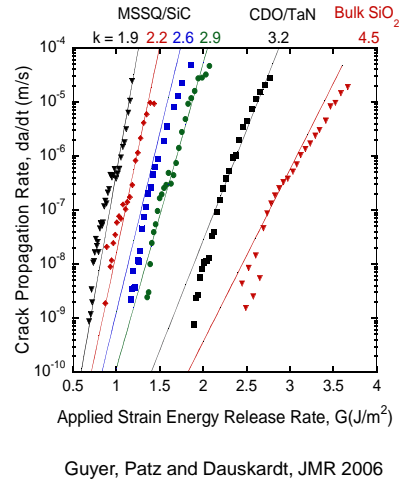
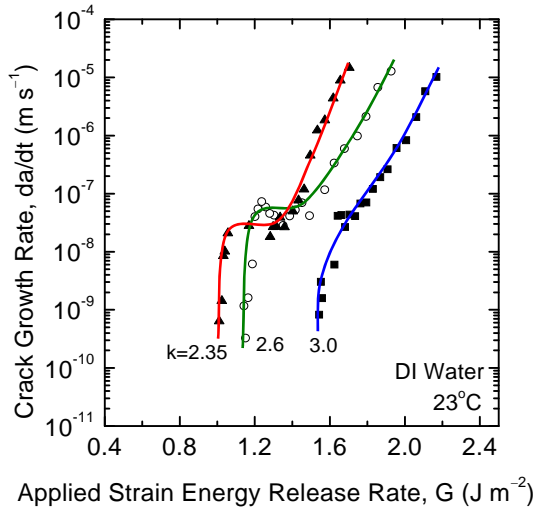


## Crack Growth in Commercial Slurries

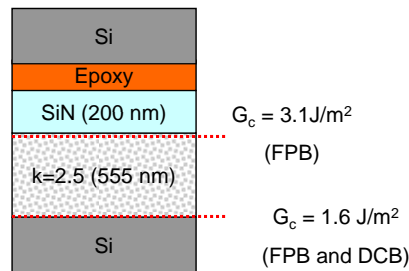
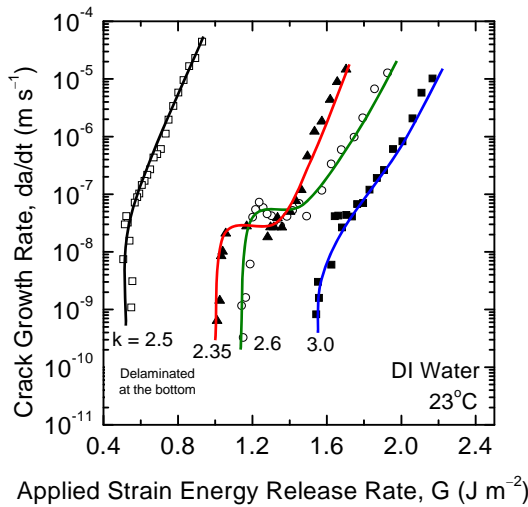


	BMS-B1	BMS-B3
pH	10.5	9-11
Oxidizing agent	0.4 wt% H <sub>2</sub> O <sub>2</sub>	1.0 wt% H <sub>2</sub> O <sub>2</sub>
Inhibitor	BTA	BTA
Surfactant	O	O
Chelate	O	O
Abrasive (silica)	12.5 - 15 wt%	1 - 30 wt%

## Effect of Low-k Film Density/Dielectric Constant



## Effect of Low-k Film Density/Dielectric Constant

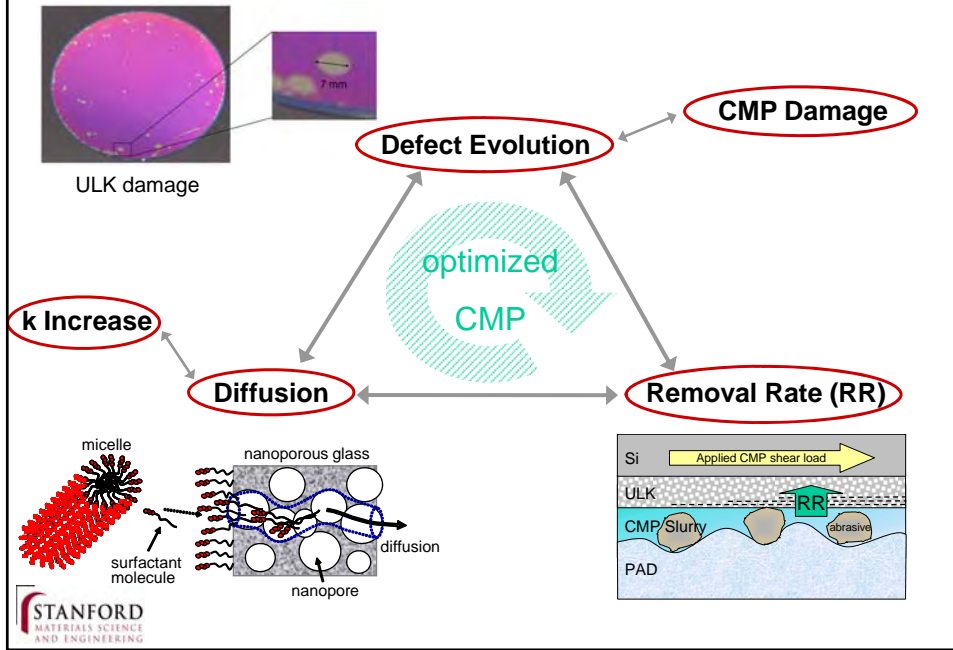


- Failure near the bottom interface
- Lower bond density
- Fast diffusion path
- Further accelerated environment assisted crack growth

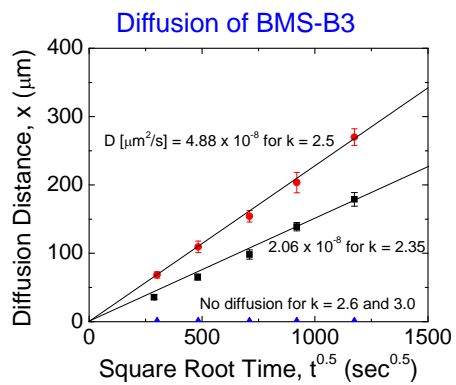
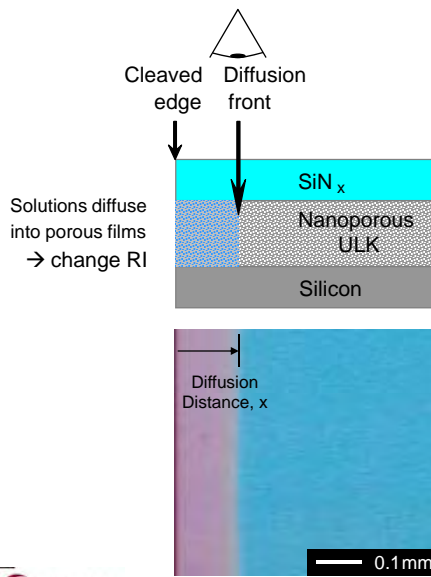




# Road Map for Optimized CMP of Nanomaterials



# Diffusion of Solutions into ULK Films



Fick's law:  $x = \sqrt{Dt}$

## Diffusion of CMP Slurry: Effect of H<sub>2</sub>O<sub>2</sub> Addition

### With H<sub>2</sub>O<sub>2</sub> (1 wt.%)

- Uniform Fickian diffusion
- No buckling



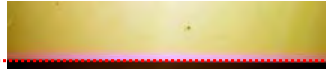
23  
5



14  
0



64



23.  
5



300 μm

Cleaved edge

### Without H<sub>2</sub>O<sub>2</sub>

- Severe buckling

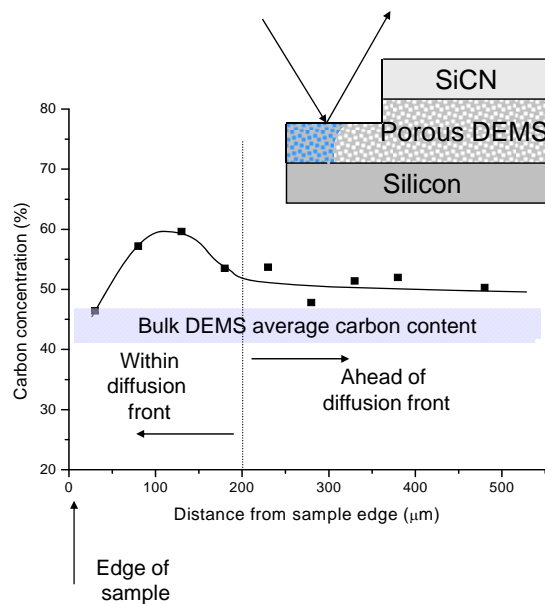


69

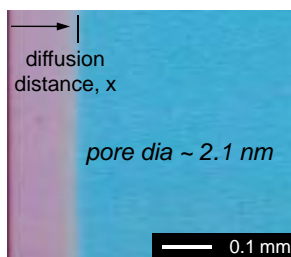
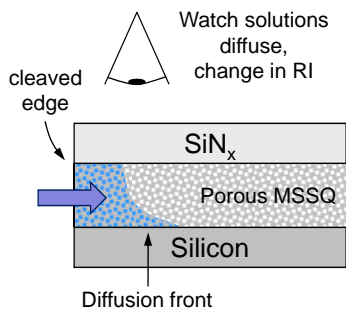
300 μm

## Analyzing Diffusion Front with XPS

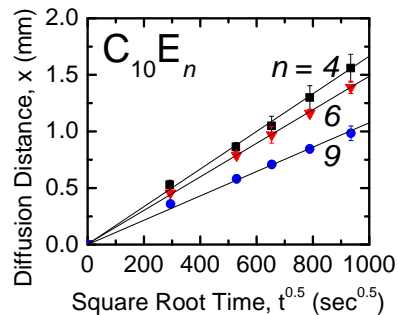
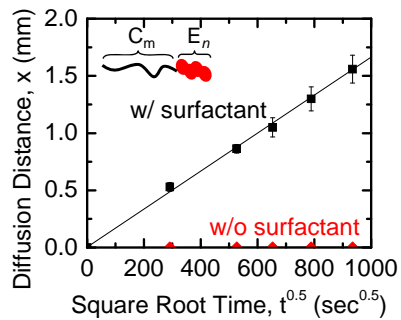
- Carbon content is used to track extent of slurry infiltration
- Chemical analysis shows a clear carbon maximum in the middle of the diffusion front
- Due to complexity of slurry the exact diffusing species cannot be determined using XPS



# Diffusion of Solutions into Nanoporous Films

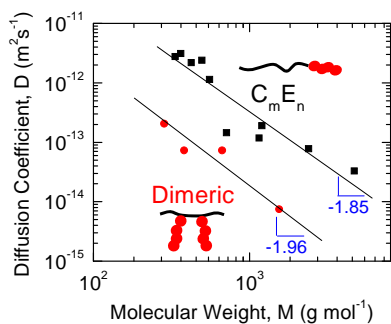


STANFORD  
MATERIALS SCIENCE  
AND ENGINEERING

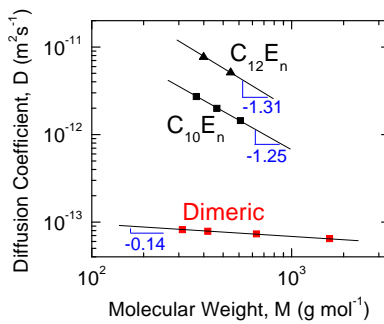


# Surfactant Solution Diffusion

0.1wt% solution

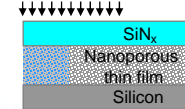


100 wt% surfactant



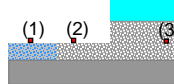
Ar ion etching

(2 mm x 2 mm)

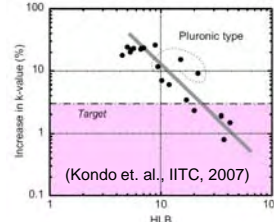


XPS scan

(0.1 mm x 0.1 mm)



Increase in k-value after direct CMP

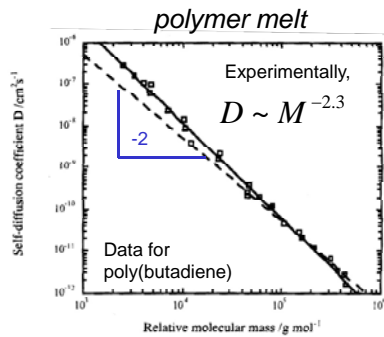


STANFORD  
MATERIALS SCIENCE  
AND ENGINEERING

# Mechanism Likely Related to Polymer Reptation

$$D \sim M^{-\alpha}$$

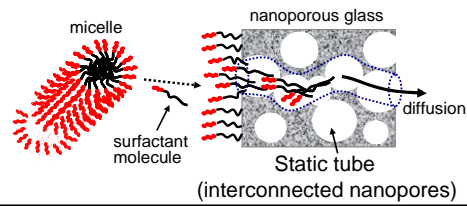
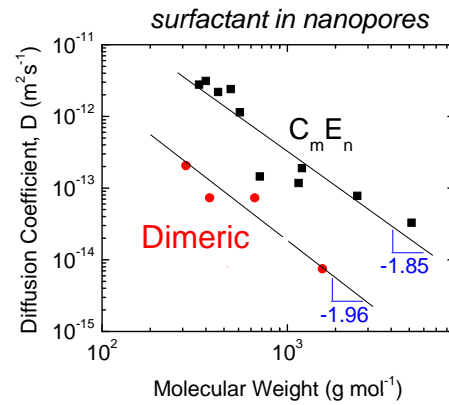
$\alpha = 2$  polymer reptation theory



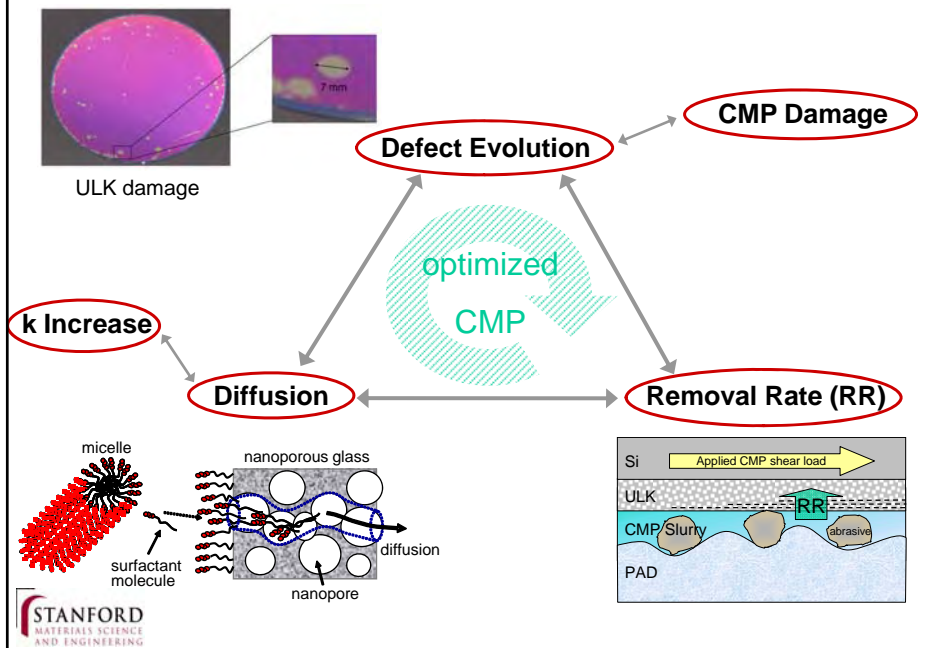
Jones, *Soft Condensed Matter*



Dynamic tube  
(polymer entanglement)



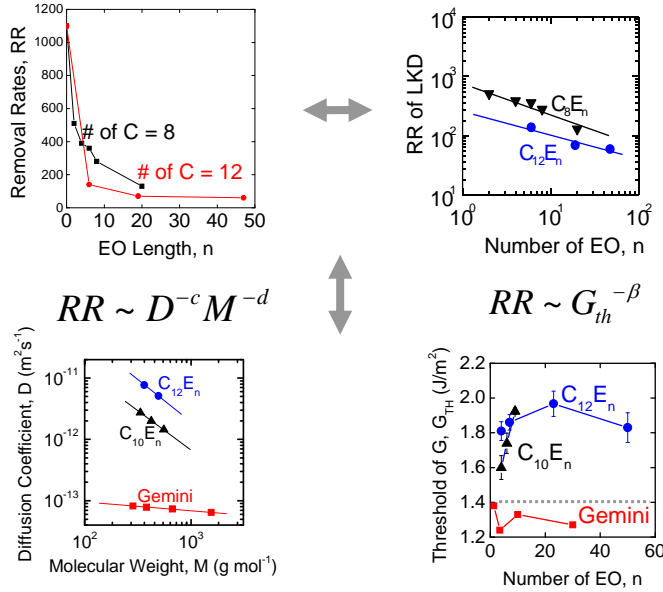
# Road Map for Optimized CMP of Nanomaterials



STANFORD  
MATERIALS SCIENCE  
AND ENGINEERING

# Correlations with CMP Removal

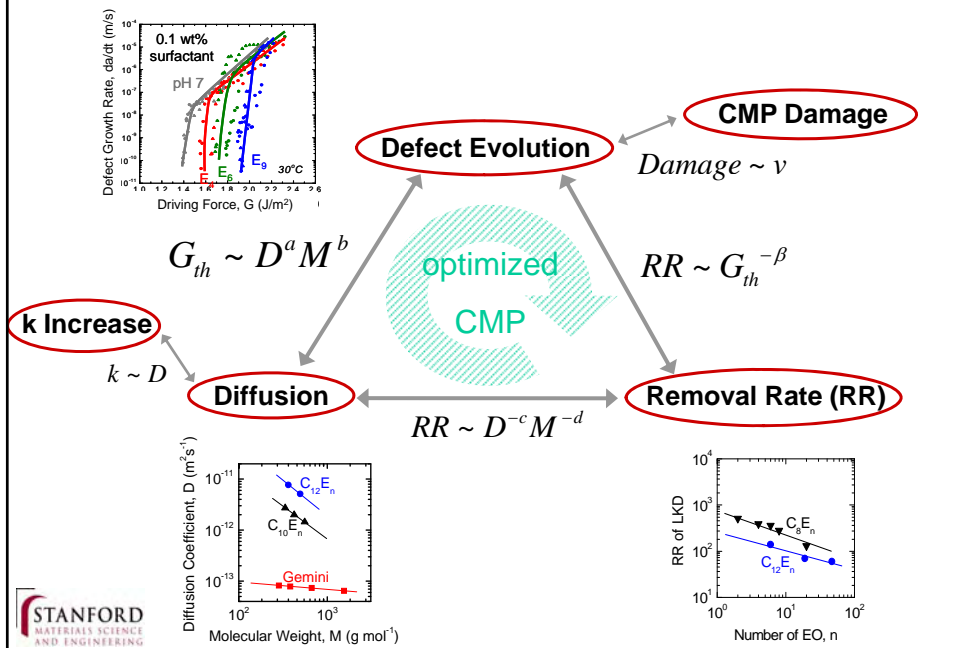
*RR is inversely proportional to D. RR is inversely proportional to  $G_{th}$ .*



$$RR \sim D^{-c} M^{-d}$$

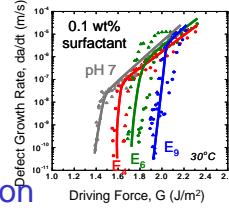
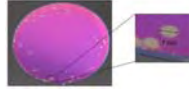
$$RR \sim G_{th}^{-\beta}$$

# Road Map for Optimized CMP of Nanomaterials

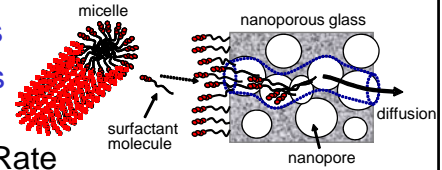


# Summary

- Defect Evolution and Damage
  - fracture of ULK materials
  - slurry chemistry effects on damage evolution



- Diffusion of Chemically Active Solutions
  - diffusion of aqueous solutions
  - effects of nonionic surfactants



- Correlations with CMP Removal Rate
  - role of slurry chemistry and surfactants
  - removal, diffusion and defect evolution rates

