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

Reinhold H. Dauskardt (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

ULK damage → Defect Evolution → CMP Damage

k Increase → Diffusion → Removal Rate (RR)

ULK damage
Defect Evolution
CMP Damage
Diffusion
Removal Rate (RR)
Optimized CMP

Micelle
Surfactant molecule
Nanoporous glass
Nanopore
Diffusion
**Crack Driving Force and Subcritical Cracking**

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

\[ G_{\text{total}} \geq G_c \quad (J/m^2) \]

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

\[ G_{\text{total}} < G_c \quad (J/m^2) \]

**Reliability and Implications for Processing Yield**

- Depends on defect size and fracture energy, \( G_c \)
- CMP slurry accelerates defect evolution
- Frequency of Occurrence, \( g(S) \)
- Strength Level, \( S \)
- Surface or interfacial defects
- Device or process stress
- Cracking probability
Automated Crack Velocity Testing

Load Relaxation Crack Growth Technique

Aquous solution container
Thermocouple
DTS Delaminator System

Accelerated Cracking

Relevance to CMP Damage

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!
Surfactant Effects on Defect Growth and Diffusion

Dimeric surfactant accelerates crack growth
\( C_m E_n \) surfactants suppressed crack growth!

Dimeric surfactant decreases diffusion
\( C_m E_n \) 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

**AFM tip removal**

- DI water pH10 (NH₄OH)
- pH10 (NH₄OH) + 0.1wt% C₁₈E₂₀

**Long range surfactant bridging**

- Si₃N₄ tips
- Spring constant ~ 0.22N/m
- Images taken in soft contact mode

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**Molecular Bridging Contribution**

\[ G_{\text{tip}} = G_{\text{applied}} - G_{\text{bridging}} \]

**From AFM measurements:**

\[ \Delta G_{\text{th}} \sim 0.75 \text{ J/m}^2 \]

\[ F_{\text{max}} \sim 13.3 \text{ pN} \]

Bridging stress:

\[ \sigma_{\text{b}} = F_{\text{max}} \cdot A = 2.6 \text{ pN/nm}^2 \]

Bond Areal density:

\[ A \sim \frac{1}{\pi (C \cdot r)^2} \sim 2 \cdot 10^{-4} \text{ nm}^{-2} \]

\[ G_{\text{bridging}} = \sigma_{\text{b}} \delta \int_0^1 \chi(\varepsilon) d\varepsilon = 0.93 \text{ J/m}^2 \]
Concentration Effects on Crack Growth

Phase diagram of water-C12E6 binary mixture

Crack Growth in Commercial Slurries

<table>
<thead>
<tr>
<th>pH</th>
<th>BMS-B1</th>
<th>BMS-B3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oxidizing agent</td>
<td>0.4 wt% H₂O₂</td>
<td>1.0 wt% H₂O₂</td>
</tr>
<tr>
<td>Inhibitor</td>
<td>BTA</td>
<td>BTA</td>
</tr>
<tr>
<td>Surfactant</td>
<td>O</td>
<td>O</td>
</tr>
<tr>
<td>Chelate</td>
<td>O</td>
<td>O</td>
</tr>
<tr>
<td>Abrasive (silica)</td>
<td>12.5 – 15 wt%</td>
<td>1 - 30 wt%</td>
</tr>
</tbody>
</table>
Effect of Low-k Film Density/Dielectric Constant

- **Crack Growth Rate, \( \frac{da}{dt} \) (m/s)**
- **Crack Propagation Rate, \( \frac{da}{dt} \) (m/s)**

**Materials**:
- MSSQ/SiC
- CDO/TaN
- Bulk SiO₂
- CrN (200 nm)
- Epoxy

**Applied Strain Energy Release Rate, \( G \) (J/m²)**

- Guyer, Patz and Dauskardt, JMR 2006

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

**Failure near the bottom interface**

- \( G_c = 3.1 \text{ J/m}^2 \) (FPB)
- \( G_c = 1.6 \text{ J/m}^2 \) (FPB and DCB)

**Notes**:
- Delaminated at the bottom
- DI Water 23°C
Road Map for Optimized CMP of Nanomaterials

- ULK damage
- Defect Evolution
- CMP Damage
- k Increase
- Diffusion
- Removal Rate (RR)
- Optimization of CMP

Diffusion of Solutions into ULK Films

- Cleaved edge
- Diffusion front
- Solutions diffuse into porous films → change RI

- \( D = 4.88 \times 10^{-8} \) for \( k = 2.5 \)
- No diffusion for \( k = 2.6 \) and \( 3.0 \)

Fick’s law: \( x = \sqrt{Dt} \)
Diffusion of CMP Slurry: Effect of H$_2$O$_2$ Addition

**With H$_2$O$_2$ (1 wt.%)**
- Uniform Fickian diffusion
- No buckling

**Without H$_2$O$_2$**
- Severe buckling

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

Watch solutions diffuse, change in RI

SiNₓ
Porous MSSQ
Silicon

Diffusion front

diffusion distance, x

pore dia ~ 2.1 nm

Surfactant Solution Diffusion

0.1 wt% solution

100 wt% surfactant

Ar ion etching
(2 mm x 2 mm)

SiNₓ
Nanoporous thin film
Silicon

XPS scan
(0.1 mm x 0.1 mm)

Increase in k-value after direct CMP

(Kondo et. al., IITC, 2007)
Mechanism Likely Related to Polymer Reptation

\[ D \sim M^{-\alpha} \]

\( \alpha = 2 \)  

polymer reptation theory

\( D \sim M^{-2.3} \)

Data for poly(butadiene)

\[ n_t, D (m^2 s^{-1}) \]

CmEn

polymer melt


surfacetant in nanopores


deck.png

Dynamic tube  
(polymer entanglement)

Road Map for Optimized CMP of Nanomaterials

ULK damage

Diffusion

Removal Rate (RR)

k Increase

Defect Evolution

CMP Damage

optimized CMP

si.png

ULK shear load

CMP Slurry

PAD
Correlations with CMP Removal

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

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

Diffusion Coefficient, $D$ ($m^2 s^{-1}$)

Molecular Weight, $M$ (g mol$^{-1}$)

Removal Rates, RR

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

Threshold of $G$, $G_{th}$ (J/m$^2$)

Number of EO, $n$

Road Map for Optimized CMP of Nanomaterials

Growth Rate, $da/dt$ (m/s)

Defect Evolution

 CMP Damage

Damage $\sim v$

$G_{th} \sim D^a M^b$

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

Removal Rate (RR)

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

$k$ Increase

$k \sim D$

$0.1$ wt% surfactant

pH 7

$E_9$

$E_4$

$E_6$

$E_9$

$E_4$

$E_6$

$E_9$
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