Characterization of Thermoset and Thermoplastic Polyurethane Pads, and Molded and Non-Optimized Machined Grooving Methods for Oxide CMP Applications

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Objectives

• Investigate the effect of PU pad synthesis methods (i.e. thermoplastic and thermoset), grooving methods (i.e. molded and non-optimized machined grooving) and groove types (i.e. concentric and ‘logarithmic – positive – spiral – positive’) on:

  – Dynamic Mechanical Analyzer (DMA)
  – Coefficient of friction (COF)
  – Variance of shear force
  – Removal rate (RR)
  – Removal rate model

• Perform simulations using a two-step removal rate mechanism to estimate the chemical and mechanical rate constant
Polisher & Tribometer

\[ COF_{avg} = \frac{F_{Shear}}{F_{Normal}} \]
Experimental Conditions

- **Diamond disc conditioner**: TBW Industries 100 grit
- **Conditioning pressure**: 0.5 PSI
- **Conditioning**: *In-situ* at 30 RPM disc speed & 20 per minute sweep frequency
- **Break-in time**: 30 minutes
- **Wafers**: 100 mm blanket oxide
- **Wafer pressure**: 2, 3 and 4 PSI
- **Sliding velocity**: 0.32, 0.64, 0.96 and 1.24 m/s
- **Slurry**: Fujimi PL-4217
- **Slurry flow rate**: 80 cc/min
- **Pad**: - Thermoplastic non-optimized machined concentric groove
  - Thermoplastic molded concentric groove
  - Thermoset non-optimized machined concentric groove
  - Thermoset non-optimized machined logarithmic spiral positive groove
- **Polishing time**: 60 seconds
Thermoplastic and Thermoset Synthesis

**Single shot synthesis**

- Long chain diol/polyol + Diisocyanate + Chain Extender

**Prepolymer process (Two step synthesis)**

- Step 1: Long chain diol/polyol + Diisocyanate + Chain Extender
- Step 2: Low % NCO prepolymer

Domain 1: Hard segment
Domain 2: Soft segment

**Thermoplastic**

**Thermoset**
Pad Grooving Types

Logarithmic Positive Spiral Positive (LPSP)  Concentric
Lightly cross-linked polymers have a steeper modulus slope than more heavily cross-linked polymer. (Rodriguez, “Principles of Polymer Systems”, 1996)
The total energy loss during a stick-slip event is proportional to the damping factor (\( \tan \delta \)) of the material and that this energy must be equated to the external work of friction. (Moore, “Principles and Applications of Tribology”, 1975 and Bartenev & Lavrentev, “Friction and Wear of Polymers”, 1981)
Striebeck Curves

- Thermoplastic Non-Optimized Machined Concentric Groove
- Thermoplastic Molded Concentric Groove
- Thermoset Non-Optimized Machined Concentric Groove
- Thermoset Non-optimized Machined LPSP Groove

COF: 0.38
COF: 0.31
COF: 0.32
COF: 0.33

Pseudo-Sommerfeld Number
Removal Rate

Pressure x Velocity (Pa.m/s)

Thermoplastic Non-Optimized Machined Concentric Groove

Thermoplastic Molded Concentric Groove

Thermoset Non-Optimized Machined Concentric Groove

Thermoset Non-Optimized Machined LPSP Groove
Variance of Shear Force

- Thermoplastic Non-Optimized Machined Concentric Groove
- Thermoplastic Molded Concentric Groove
- Thermoset Non-Optimized Machined Concentric Groove
- Thermoset Non-Optimized Machined LPSP Groove
SEM Images and Conceptualization of Burrs

Molded Groove

Non-Optimized Machined Groove

Pad

Wafer

Pad
Removal Rate Model

• Oxide removal in the Langmuir-Hinshelwood model:

  – \( n \) moles of reactant \( R \) in the slurry react at rate \( k_1 \) with oxide film on the wafer to form a product layer \( L \) on the surface

  \[
  \text{SiO}_2 + nR \xrightarrow{k_1} L
  \]

  \( k_1 = A \cdot \exp\left(\frac{-E}{kT}\right) \)

  – Product layer \( L \) subsequently removed by mechanical abrasion with rate \( k_2 \)

  \[
  L \xrightarrow{k_2} \text{SiO}_2^* \quad k_2 = c_p \times p \times V
  \]

  – Abraded material \( L \) is carried away by the slurry

• The local removal rate in this mechanism therefore is a function of chemical and mechanical contributions

\[
RR = \frac{M_w}{\rho} \frac{k_2k_1}{k_2 + k_1}
\]
Pad Temperature

Pressure x Velocity (Pa.m/s)

Mean Pad Temperature (°C)

Thermoplastic Non-Optimized Machined Concentric Groove

Thermoplastic Molded Concentric Groove

Thermoset Non-Optimized Machined Concentric Groove

Thermoset Non-Optimized Machined LPSP Groove
Physical Temperature Model

\[ \bar{T} = T_p + \frac{2\zeta}{\sqrt{\pi\kappa\rho C_p}} \gamma_p \left( \frac{p_a}{p} \right) \frac{\mu_k p V}{V^{1/2}} \]

- Geometric factor
- Pad thermal properties
- Mean asperity tip contact pressure
- Fraction of heat conducted to pad
- Depends on contact area
- COF

Asperity removes layer at mechanical rate \( k_2 \)

Surface layer grows at chemical rate \( k_1 \).
Growth is fastest at the flash temperature

\( \text{(Borucki, CMPMIC 2005)} \)
Flash Heating Temperature

- $T \equiv$ hydrolyzed layer reaction temperature
- Reaction temperature is due to flash heating by passing slurry particle-laden asperity tips

\[
T = T_p + \zeta \frac{\gamma p \mu_k}{\sqrt{\kappa p C_p}} \left[ \frac{(p_a / p)}{V^{1/2}} \right] pV
\]

- The quantity in brackets depends on $V$ due to fluid dynamic effects. Assuming a power law dependence:

\[
T = T_p + \frac{\beta}{V^{1/2+e}} \mu_k pV
\]

- The model has five fitting parameters: $A$, $E$, $c_p$, $\beta$ & $e$:

\[
RR = \frac{M_w}{\rho} \left( c_p \cdot pV \right) \cdot Ae
\]

\[
\left( c_p \cdot pV \right) + Ae
\]
## Optimized Fitting Parameters

<table>
<thead>
<tr>
<th>Polishing pad</th>
<th>$c_p$ (moles/J)</th>
<th>$\beta$ (K/Pa-(m/s)$^{1-a}$)</th>
<th>RMS Error (Å/min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thermoplastic machined concentric groove</td>
<td>1.64E-8</td>
<td>2.15E-3</td>
<td>77</td>
</tr>
<tr>
<td>Thermoplastic molded concentric groove</td>
<td>1.74E-8</td>
<td>2.15E-3</td>
<td>78</td>
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<tr>
<td>Thermoset machined concentric groove</td>
<td>2.59E-8</td>
<td>1.45E-3</td>
<td>81</td>
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<tr>
<td>Thermoset machined LSP</td>
<td>2.52E-8</td>
<td>1.45E-3</td>
<td>65</td>
</tr>
</tbody>
</table>

$E = 0.53$ eV \textit{from Sorooshian et al., Journal of Tribology, 127, 639 (2005)}

$e = 0.66$

$A = 1.02 \times 10^5$ moles m$^{-2}$ s$^{-1}$
Sensitivity of ‘e’

Effect of varying e between 0 and 1

Removal Rate (A/min)

Pressure x Velocity (Pa.m/s)
Contribution of Flash Heating Temperature

Temperature Increment (°C)

Pressure x Velocity (Pa.m/s)

- $e = 1$
- $e = 0$

$T - T_a$

$T_p - T_a$
Thermoplastic pads exhibit higher chemical reaction rate constant than thermoset pads
Mechanical Abrasion Rate Constant, $k_2$

Thermoplastic pads exhibit lower mechanical abrasion rate constant than thermoset pads
Summary

• Thermoplastic pads induce higher COFs than the thermoset pads due to their inherently higher degree of energy loss.

• Since thermoplastic pads exhibit more reduction in storage modulus, the variance of shear force associated with thermoplastic pads is higher than thermoset pads.

• Un-optimized machined grooves produce rougher edges than molded grooves, thereby inducing a higher COF and a higher shear force variance.

• LPSP groove is designed to bring slurry towards the pad center, resulting in a higher mean pad temperature. In addition, the LPSP pad induces a higher shear force variance.

• Simulation results indicate that thermoplastic pads produce a more mechanically controlled removal than thermoset pads.