Particle Adhesion and Removal in Semiconductor Processing

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Chemical Mechanical Polishing (CMP)

- Removes a thin surface layer to obtain planarity of wafers
  - Uses abrasive particles in aqueous solution in conjunction with relative motion between polishing pad and wafer
  - Surface removed mechanically and chemically

- Introduces contaminants onto wafer surfaces
  - Pieces of polished surface and polishing pad
  - Slurry particles
  - Contamination from the handler or handling device
  - Must be removed before further processing
Post-CMP Cleaning

» Must remove particles less than 1 micron in diameter
» Must not roughen wafer surface excessively
» Brush scrubbing and megasonic cleaning have potential for removing small particles
» Problems with
  • Resource consumption
  • Lack of understanding of cleaning mechanism
  • Inefficient and unreliable processes

Brush Scrubber

\[ r = \text{radius} \]
\[ \omega = \text{angular speed} \]
Brush Scrubbing Results†

Before Cleaning

After Cleaning

Post-CMP Cleaning Model Objective

Develop and validate scientifically-based cleaning models to optimize wafer cleaning processes and minimize water and chemistry use

Adhesion Model

1st Generation
Rough deformable spherical particles interacting with a rough flat surface

2nd Generation
Asymmetrical rough particles interacting with any surface

Use critical particle Reynolds approach to determine flow conditions needed to initiate particle removal

Removal Model
### Adhesion Mechanisms

<table>
<thead>
<tr>
<th>Bond Type</th>
<th>Interatomic Distance (Angstroms)</th>
<th>Dissociation Energy (Kcal/mole)</th>
<th>Effect of Temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td>Primary Covalent</td>
<td>1 to 2</td>
<td>50 to 200</td>
<td>None</td>
</tr>
<tr>
<td>H-H</td>
<td>0.8</td>
<td>104</td>
<td>None</td>
</tr>
<tr>
<td>C-H</td>
<td>1.1</td>
<td>99</td>
<td>None</td>
</tr>
<tr>
<td>C-C</td>
<td>1.5</td>
<td>83</td>
<td>None</td>
</tr>
<tr>
<td>Ionic</td>
<td>2 to 3</td>
<td>10 to 20</td>
<td>High</td>
</tr>
<tr>
<td>Hydrogen Bond</td>
<td>2 to 3</td>
<td>3 to 7</td>
<td>High</td>
</tr>
<tr>
<td>van der Waals Forces</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Dipole Interactions</td>
<td>2 to 3</td>
<td>1.5 to 3</td>
<td>High</td>
</tr>
<tr>
<td>London Forces</td>
<td>3 to 5</td>
<td>0.5 to 2</td>
<td>Low</td>
</tr>
</tbody>
</table>

*Always present*
AFM Force Measurement

- Laser
- Mounted cantilever
- Liquid cell
- Substrate
- Temperature plate

SEM of a R = 3 µm PSL Sphere

6.67 µm
AFM Force Curve

A = Approaching Curve
B = Removal Curve

Removal Force (nN)

Separation Distance (nm)

Applied Load
Particle – Surface Contact Radius

Elastic-plastic deformation

\[ a = 0.43 \cdot R^{0.53} \]

Adhesion-induced contact radius (\(\mu m\))
Particle radius (\(\mu m\))

PSL spheres on Silicon
Surface Mechanical Properties

Force / Depth profile from a Hystem Nanoindentor

30 nm Cu film on Ti/SiO₂/Si Structure

E = slope = 78 GPa
4 Parameters Determined

- Average asperity size ($\varepsilon_s$)
- Standard deviation in asperity size (std)
- Fractional coverage of the surface by asperities ($f$)
- Common shape, if any, among asperities

Asperities assumed to be hemispherical in this work
2\textsuperscript{nd} Generation Model (Gen 2)

- SEM
- SEM volume reconstruction
- 3-D Volume Reconstruction of Alumina/Silica Particles – Contact Area
- General Mathematical Description of Surface
  - Gen 2 \textit{van der Waals}
  - Removal Force Statistics
  - AFM-based force measurement
  - Compression/Deformation \textit{Surface asperities}
- Applied Load
- Settling of the Particle (tilting, shifting)
- Force Boundaries (Max, Min, Avg)
- AFM Topographic Data
- Nanoindentation Mechanical Data

\begin{itemize}
  \item 3-D Volume Reconstruction of Alumina/Silica Particles – Contact Area
  \item General Mathematical Description of Surface
  \item Gen 2 \textit{van der Waals}
  \item Removal Force Statistics
  \item AFM-based force measurement
  \item Compression/Deformation \textit{Surface asperities}
\end{itemize}
3-D Surface Reconstruction – Simulated Surface
Surface Interaction Force

Cylindrical Volume Elements

\[ F_A = - \frac{A \cdot (\text{Area cylinder})}{6 \cdot \pi \cdot D^3} \]
Roughness Effect – Monodisperse Particles

5 µm PSL in contact with a silicon substrate in DI water
Effect of Particle Diameter

PSL particles in contact with a silicon substrate in water

Removal Force (nN) vs. Particle Radius (µm)

- Experimental Data
- Model Predictions
Validation of Substrate Roughness

Average Measured Value 10 nN

Average Measured Value 127 nN

Range of Observed Values

Rough Silicon Surface

Smooth Silicon Surface

Removal Force (nN)

Frequency
Alumina/H_2O/Silicon Adhesion

3 µm alumina particle (contact radius = 350 nm) in contact with a silicon substrate in DI H_2O

Average Observed Force = 176 nN

Range of Observed Force = 139 - 201 nN

3 µm alumina particle (contact radius = 350 nm) in contact with a silicon substrate in DI H_2O
Alumina Adhesion – Effect of Substrate and Medium

- Experimental Data
- Ideal vdW Prediction

Average Simulation Prediction

Range of Simulation Prediction (+/- σ)

Removal Force (nN)

Al2O3/N2/SiO2 System
Al2O3/H2O/SiO2 System
Al2O3/N2/Cu System
Al2O3/H2O/Cu System
Geometry Effects

Current vDW models for a spherical 0.15 µm alumina particle (slurry particle) in contact with a silicon surface predict a removal force of 15 nN.

Our simulation accounting for the larger than expected contact area predicts a removal force of 108 nN.
Effect of Applied Load

Maximum contact area (0.15 μm alumina slurry = 282 nm)

<table>
<thead>
<tr>
<th>System</th>
<th>Force Prediction (nN)</th>
<th>Force Prediction (nN)</th>
<th>Force Prediction (nN)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Applied Load = 0 PSI</td>
<td>Applied Load = 0 PSI</td>
<td>Applied Load = 5 PSI</td>
</tr>
<tr>
<td></td>
<td>Smooth Films</td>
<td>Rough Films</td>
<td>Rough Films</td>
</tr>
<tr>
<td>Al₂O₃/Air/SiO₂</td>
<td>289</td>
<td>108</td>
<td>4058</td>
</tr>
<tr>
<td>Al₂O₃/Air/Cu</td>
<td>653</td>
<td>46.3</td>
<td>5876</td>
</tr>
<tr>
<td>Al₂O₃/Air/W</td>
<td>676</td>
<td>56.1</td>
<td>5335</td>
</tr>
<tr>
<td>Al₂O₃/H₂O/SiO₂</td>
<td>39.2</td>
<td>3.3</td>
<td>544</td>
</tr>
<tr>
<td>Al₂O₃/ H₂O/Cu</td>
<td>186</td>
<td>11.5</td>
<td>1674</td>
</tr>
<tr>
<td>Al₂O₃/ H₂O/W</td>
<td>200</td>
<td>16.6</td>
<td>1555</td>
</tr>
</tbody>
</table>
## Post-CMP Cleaning – Surface Characterization

All axes are in nm

<table>
<thead>
<tr>
<th>Material</th>
<th>$\varepsilon_s$ (nm)</th>
<th>Std (nm)</th>
<th>Frac. Coverage</th>
<th>E (Gpa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO$_2$</td>
<td>1.7</td>
<td>0.7</td>
<td>56</td>
<td>55.8</td>
</tr>
<tr>
<td>Cu</td>
<td>0.8</td>
<td>0.5</td>
<td>45</td>
<td>78</td>
</tr>
<tr>
<td>W</td>
<td>1.1</td>
<td>.5</td>
<td>41</td>
<td>418</td>
</tr>
<tr>
<td>Al$_2$O$_3$ particle</td>
<td>1.6</td>
<td>0.7</td>
<td>33</td>
<td>500</td>
</tr>
</tbody>
</table>
CMP and Post-CMP Cleaning – Alumina Particles Interacting with Copper Films

Al₂O₃ particle may also dissolve in acidic solution
CMP and Post-CMP Cleaning – Alumina Particles Interacting with SiO₂ Films

**Chemistry Mean Std Dev Std Err Mean**

<table>
<thead>
<tr>
<th>Chemistry</th>
<th>Mean</th>
<th>Std Dev</th>
<th>Std Err</th>
<th>Mean</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂O</td>
<td>1.00</td>
<td>0.23</td>
<td>0.05</td>
<td></td>
</tr>
<tr>
<td>H₂O₂</td>
<td>2.72</td>
<td>0.68</td>
<td>0.13</td>
<td></td>
</tr>
<tr>
<td>NH₄OH</td>
<td>2.57</td>
<td>1.25</td>
<td>0.26</td>
<td></td>
</tr>
</tbody>
</table>

**Normalized Removal Force**

![Normalized Removal Force Chart](chart.png)

**SiO₂**

<table>
<thead>
<tr>
<th>Surface Species</th>
<th>Solubility</th>
<th>Al₂O₃</th>
<th>Solubility</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂O Si-O-Si, =Si(OH), Si(OH)x</td>
<td>Si(OH)₄ : 10 % dissociation</td>
<td>Al₂O₃</td>
<td>does not dissolve</td>
</tr>
<tr>
<td>H₂O₂ Si-O-Si, =Si(OH), Si(OH)x</td>
<td>Si(OH)₄ : 0 % dissociation</td>
<td>Al₂O₃, Al⁺³</td>
<td>dissolves</td>
</tr>
<tr>
<td>NH₄OH Si-O-Si, =Si(OH), Si(OH)x</td>
<td>Si(OH)₄ : 100 % dissociation</td>
<td>Al₂O₃, Al⁺³</td>
<td>dissolves</td>
</tr>
</tbody>
</table>
CMP and Post-CMP Cleaning – Alumina Particles Interacting with Tungsten Films

Chemistry Mean Std Dev Std Err Mean

<table>
<thead>
<tr>
<th>Chemistry</th>
<th>Mean</th>
<th>Std Dev</th>
<th>Std Err Mean</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂O</td>
<td>0.96</td>
<td>0.40</td>
<td>0.06</td>
</tr>
<tr>
<td>H₂O₂</td>
<td>1.87</td>
<td>1.97</td>
<td>0.29</td>
</tr>
<tr>
<td>NH₄OH</td>
<td>2.20</td>
<td>2.26</td>
<td>0.33</td>
</tr>
</tbody>
</table>
Adhesion Model Conclusions

» Expanded existing particle adhesion models to include
  • Chemical and morphological heterogeneities
  • Compression and deformation of surface asperities
  • Non-ideal geometries
» Obtained statistical information on particle adhesion
» Developed experimental procedure to measure particle adhesion for different particle/substrate systems as a function of
  • Aqueous environment
  • Contact time
  • Applied load
  • Solution temperature
Removal Model Objective

Assess mechanism(s) of micron-scale particle removal from semiconductor wafer surfaces using a critical particle Reynolds number approach

- Relate adhesion models to particle removal
- Relate flow characteristics to particle removal
- Develop model for removal processes by combining adhesion and flow models
  - Determine effect of Hamaker constant (A) on model
  - Determine effect of particle size distribution on model
  - Determine effect of roughness on model
Preliminary Work


- Studied detachment of spherical glass particles from a flat glass surface
- Used laminar channel flow over a range of flow rates to remove adhering particles
- Percentage adhering as a function of wall shear stress ($\tau_w$) presented graphically

- System Properties
  - Fluid: solution of distilled water, HNO$_3$, and NaNO$_3$
    - Ionic strength: $1 \times 10^{-3}$ mol/L
    - pH: 3
  - Particle (mean) diameters: 2, 5, 10, 15 µm ($\sigma \sim 12\%$)
  - Estimated maximum roughness of surface: 0.8 nm
  - Hamaker constant (A): $1.14 \times 10^{-20}$ J
Flow System

Channel Dimensions
- Width (2A): 1 cm
- Height (2B): 0.5 mm
- Hydraulic Diameter (d_H): 0.952 mm

Flow Properties
- Flow Rates: 0.02 – 25 cm³/s
- Re: 4 – ~5000
- Type of Flow: laminar
- Velocity in x-direction only: u = u(y,z)
- Boundary Conditions:
  u(B,-A) = u(B,A) = 0
  u(-B,-A) = u(-B,A) = 0

† J. Colloid Interface Sci. 176, 74-85 (1995)
Velocity Profile, $Q = 0.02 \text{ cm}^3/\text{s}$

$$\text{Re} = \frac{d_H \rho \langle u \rangle}{\mu} = 4$$
Particle Adhesion/Removal Model

\[ \mu = \frac{2 \rho u d}{Re} \]

\[ F_A = \text{Gen 2 adhesion force} \]
\[ F_L = \text{Lift force} \]
\[ M_D = \text{External moment} \]
\[ F_D = \text{Drag force} \]

Point around which rolling occurs for a rough surface

Point around which rolling occurs for a smooth surface

\[ \text{Re}_p = \frac{d \rho u}{\mu} \]
Rolling Particle Removal Criteria

\[ \bar{M}_D + \bar{F}_D \cdot l_1 + \bar{F}_L \cdot l_2 \geq \bar{F}_A \cdot l_2 \]

- **External moment of surface stresses about center of particle**
  \[ M_D \propto d \text{Re}_p \]

- **Drag force**
  \[ F_D(\text{Re}_p < 1) \propto \text{Re}_p \]

- **Lift force**
  \[ F_L \propto d \frac{du}{dz} \left| \frac{d}{2} \text{Re}_p \right. \]

- **Adhesion force**
  \[ F_A \propto \text{Ad} \]

- **Horizontal lever arm**

- **Vertical lever arm**
Assessing Particle Removal

- Removal occurs when $Re_p(\text{Flow}) \geq Re_{pc}(\text{Rolling})$
  - $Re_p(\text{Flow})$ constant at constant flow rate (for this system)
- **Ideal system** of smooth, deformable spherical particles of identical radius adhering to a smooth, flat, deformable surface
  - → Single adhesion force
    - ⇒ Single value of $Re_{pc}$
    - ⇒ All or none of the adhering particles should be removed
- **Real system** of deformable particles with non-uniformly distributed roughness and a finite size distribution adhering to a deformable surface with a non-uniform roughness distribution
  - → Multiple adhesion forces and multiple points around which rolling can occur
    - ⇒ Multiple values of $Re_{pc}$
    - ⇒ All, some, or none of the adhering particles can be removed
Illustration: Critical Particle Reynolds Number Approach

Ideal System

$Q = \text{High } [\text{cm}^3/\text{s}]$

All particles are removed

$Re_{pc} (\text{Rolling})$

$Q = \text{Low } [\text{cm}^3/\text{s}]$

No particles are removed

horizontal position, $y (\text{m})$
Adhesion Profile, $d = 2$ and $15 \, \mu m$

- Yiantsiros and Karabelas
- Prediction (Ideal System)
Effect of Hamaker Constant on $\text{Re}_{pc}$, $d = 2 \, \mu\text{m}$

**Ideal System**

- **Lower limit of literature values**
- **Upper limit of literature values**

Graph showing the relationship between $A \times 10^{20}$ (J) and $\text{Re}_{pc} \times 10^6$.
Effect of Particle Size Distribution on $Re_{pc}$

Ideal System

![Graph showing the relationship between particle diameter and $Re_{pc}$ with mean and $\pm 3\sigma$.]
### Effect of Roughness on Adhesion Force

<table>
<thead>
<tr>
<th>System</th>
<th>Mean $F_A$ (N)</th>
<th>Standard Deviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ideal</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Smooth particle/Smooth surface</td>
<td>$1.3 \times 10^{-8}$</td>
<td>-</td>
</tr>
<tr>
<td>Real</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Rough particle/Rough surface</td>
<td>$2.2 \times 10^{-9}$</td>
<td>$3.1 \times 10^{-11}$</td>
</tr>
</tbody>
</table>

### Assumptions for Roughness

<table>
<thead>
<tr>
<th></th>
<th>Average Height (nm)</th>
<th>Standard Deviation (nm)</th>
<th>Fractional Coverage</th>
</tr>
</thead>
<tbody>
<tr>
<td>Particle</td>
<td>0.4</td>
<td>0.4</td>
<td>0.25</td>
</tr>
<tr>
<td>Surface</td>
<td>0.4</td>
<td>0.4</td>
<td>0.25</td>
</tr>
</tbody>
</table>
Roughness affects $Re_{pc}$ by affecting
- Adhesion force
- Point around which rolling can occur

Length of horizontal and vertical lever arms ($l_1$ and $l_2$) depend on $\varepsilon_1$
Effect of Roughness on $Re_{pc}$, $d = 2 \, \mu m$

Contact area controls the point around which rolling occurs.

Surface roughness controls the point around which rolling occurs.

Real System

$Re_{pc}$ vs. roughness height, $\varepsilon$ (nm)
Removal Analysis Procedure

Roughness Characteristics
\[ f_s, \varepsilon_s, \sigma_s, f_p, \varepsilon_p, \sigma_p \]

Use Gen 2 to predict adhesion force for each particle size

Calculate \( \text{Re}_{pc} \) (Rolling) Distribution

Particle Size Variation

Roughness Effects

Velocity Profile
\[ V_p, \frac{du}{dz} \]

Calculate \( \text{Re}_p \) (Flow)

Calculate percentage adhering

Compare with data from Yiantsios and Karabelas
Calculating the Adhesion Force using Gen 2, d = 2 µm

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hamaker constant (A)(^1)</td>
<td>1.14 x 10(^{-20}) J</td>
</tr>
<tr>
<td>Lennard-Jones separation distance ((D_{LJ}))(^2)</td>
<td>0.4 nm</td>
</tr>
<tr>
<td>Bulk modulus (E)(^1)</td>
<td>4.86 x 10(^{10}) N/m(^2)</td>
</tr>
<tr>
<td>Applied load (P) = weight of particle(^2)</td>
<td>1.03 x 10(^{-13}) N</td>
</tr>
<tr>
<td>Fraction of surface covered with asperities (f_s)(^3)</td>
<td>0.25</td>
</tr>
<tr>
<td>Average roughness height on surface ((\varepsilon_s))(^3)</td>
<td>0.4 nm</td>
</tr>
<tr>
<td>Standard deviation in surface roughness height ((\sigma_s))(^3)</td>
<td>0.4 nm</td>
</tr>
<tr>
<td>Fraction of particle covered with asperities (f_p)(^3)</td>
<td>0.25</td>
</tr>
<tr>
<td>Average roughness height on surface ((\varepsilon_p))(^3)</td>
<td>0.4 nm</td>
</tr>
<tr>
<td>Standard deviation in surface roughness height ((\sigma_p))(^3)</td>
<td>0.4 nm</td>
</tr>
<tr>
<td>Contact radius (a), calculated using the DMT theory</td>
<td>6.46 nm</td>
</tr>
</tbody>
</table>

\(^1\)Taken from Yiantsios and Karabelas

\(^2\)Set by Gen 2

\(^3\)Estimated values based on information given by Yiantsios and Karabelas
Calculating the Adhesion Force using Gen 2

\[ F_{\text{real}} = 0.1563 F_{\text{ideal}} \]

\[ R^2 = 0.9984 \]

\[ \frac{F_{A_{\text{real}}}}{F_{A_{\text{ideal}}}} = K \]
Calculating the Adhesion Force using Gen 2

\[ \frac{F_{A_{\text{real}}}}{F_{A_{\text{ideal}}}} = K \]

\[ F_{A_{\text{real}}}(A, D, E, P, f_s, \varepsilon_s, \sigma_s, f_p, \varepsilon_p, \sigma_p, a) = K(\varepsilon_s, \varepsilon_p) \cdot F_{A_{\text{ideal}}}(A) \]

A, \varepsilon_s, \varepsilon_p have the most influence on the adhesion force for this system
Adhesion Profile, $d_{\text{mean}} = 2 \, \mu m$

- Yiantsios and Karabelas (t = 4 h)
- Yiantsios and Karabelas (t = 8 h)
- Prediction (Real System)

- $A = 1.14 \times 10^{-20} \, J$
- $A = 6.8 \times 10^{-20} \, J$
- $A = 8.2 \times 10^{-20} \, J$
Adhesion Profile, $d_{\text{mean}} = 5 \, \mu m$

- Yiantsios and Karabelas (t = 4 h)
  - $A = 1.14 \times 10^{-20} \, J$
- Yiantsios and Karabelas (t = 8 h)
  - $A = 6.8 \times 10^{-20} \, J$
- Prediction (Real System)
  - $A = 8.2 \times 10^{-20} \, J$
Adhesion Profile, $d_{\text{mean}} = 10 \, \mu m$

- $A = 1.14 \times 10^{-20} \, J$
- $A = 6.8 \times 10^{-20} \, J$
- $A = 8.2 \times 10^{-20} \, J$

Yiantsios and Karabelas

Prediction (Real System)
Adhesion Profile, $d_{\text{mean}} = 15 \, \mu m$

A = $6.8 \times 10^{-20} \, J$

A = $8.2 \times 10^{-20} \, J$

A = $1.14 \times 10^{-20} \, J$

- Yiantsios and Karabelas
- Prediction (Real System)
Removal Model Conclusions

» Accurate particle removal models require accurate particle adhesion models
  • Removal is highly dependent on adhesion model through
    › Particle size distribution
    › Roughness
    › Hamaker constant
» Rolling is the controlling removal mechanism
» Roughness and particle size distribution affect the point around which rolling can occur
» (Rolling) theoretical adhesion profiles for real adhesion system in agreement with those of Yiantsios and Karabelas
» Critical particle Reynolds number approach validated
» Predictive model for particle removal established
  Independent of particle size and cleaning (flow) system
Ongoing Work

Use channel flow system to experimentally validate removal model (critical Reynolds number approach)

- Vary particle diameter, particle composition, fluid flow rate, and fluid viscosity
- Experimentally measure adhesion force and Hamaker constant
- Experimentally determine particle and surface roughness
- Determine effect of roughness on particle adhesion (through validated models)
Future Work

» Use critical particle Reynolds number approach for
  • Asymmetrical particle analysis
  • Embedded particle analysis
  • Effect of particle agglomeration on removal
  • Tool based studies
    › Brush scrubbing
    › Megasonic cleaning

» Determine effect of turbulent flow on particle removal

» Use results in fab to optimize post-CMP cleaning
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