<table>
<thead>
<tr>
<th>Agenda</th>
</tr>
</thead>
<tbody>
<tr>
<td>Market trends in PCMP</td>
</tr>
<tr>
<td>Copper PCMP</td>
</tr>
<tr>
<td>W PCMP</td>
</tr>
<tr>
<td>CeO$_2$ PCMP</td>
</tr>
<tr>
<td>Trends in brush technology</td>
</tr>
<tr>
<td>The future of PCMP cleaning</td>
</tr>
</tbody>
</table>
Post-CMP Cleaning Challenges

- New materials/film types
  - Diversification of dielectric materials
  - New barrier materials

- Feature size decreasing
  - 10 nm ubiquitous
  - Working on 3-5 nm for most customers

- Increasingly complex CMP slurries
  - New particle types
  - Small particles
  - Advanced organic additives

- Defect detection thresholds decreasing
  - Current state of the art → 18 nm

- Environmental laws/customer EHS more stringent
  - Country to country variations
  - Customer EHS requirements vary
  - Tetramethylammonium hydroxide increasingly forbidden

New Materials Lead to Cleaning Complexity

**Conductors**
- Copper
- Barrier/liners (Ta, TaN, TiN, Co, Ru, Mn)
- Tungsten
- Cobalt
- Ruthenium
- Aluminum
- Molybdenum, Chromium
- Pt Group (Rh, Ir, Ru, Os, Pt, Pd)
- Binary compounds (MoN, Re2C, ...)

**Dielectrics**
- TEOS
- Thermal oxide
- Si3N4
- Low-k dielectric, SiC (SiOC, SiON, etc.)
- Polysilicon, single crystal silicon (wafer, various doping)
- Doped glass (BPSG, PSG, etc.)

*Samsung N14 Technology*
Fumed silica (older ILD, W slurries)

Colloidal silica
- Controlled growth from “silicic acid”
- High purity particles via Stober process – controlled hydrolysis of Tetraalkyloxysilicate

Surface functionalized silica
- Anionic functionality (carboxyl or sulfonic acid)
- Cationic (amines, quaternary ammonium)

Ceria
- Cationic surface
- Adsorbed additives for selectivity can modify surface properties

Alumina

Titania, zirconia

Nanodiamonds

SiC

Challenges/Diversity in Particle Cleaning

\[ \text{SiOH} + \text{HO}^- \rightarrow \text{SiO}^- + \text{H}_2\text{O} \]

\[ \text{IEP} = 4 \]

Zeta potential \( \zeta = 4\pi\gamma(\nu/E)/\varepsilon \)
Formulation Characteristics for Proper Cleaning

- Controlled undercut of particles/dissolution of substrate
  - Break Lewis-acid-base and H-bonding interactions
  - Typically want 1-2 atomic layers
  - No change in low k film dielectric constant
- Dissolution or dispersion of the particles
- Dissolution or dispersion of the organic residue
- Chemical attack on organic residue
- Mechanical action by brushes
- Surface wetting
- Charge repulsion between particles and surface

Complicated 4-way interactions present challenges for Post-CMP cleaning.

More predictive simulation/models needed
Challenges in Cu PCMP

- Advanced generations requiring very low or no defects
  - Organic residue
  - Silica particles
  - Metal particles
- Minimal/zero corrosion to exposed metals (Cu, TaN, Co, Ru)
  - No galvanic corrosion or barrier attack
  - Low Cu recess/etch rates → 3–10 nm technology
- Minimal Cu surface roughness
- Extended queue time
- EHS friendly/green chemistry
  - No TMAH
- Low COO
  - Higher POU dilution
  - Low chemical consumption
Types of organic Residue Encountered in Post-CMP Cleaning

- Corrosion-inhibitor – metal complexes (i.e., Cu-BTA)
- Surfactant residues
- Interactions between slurry additives and cleaning additives
- Pad debris (polyurethane – hydrophobic or hydrophilic)
- Brush debris (crosslinked PVA – hydrophilic)
- Plating additives
- Filter or tubing shedding/residues
- Biological debris (bacterial, skin cells, etc.)

Advanced defect metrology has enabled detection of smaller defect sizes

- Soluble organic or surfactant residue

Pad or brush debris
EDX = C, N, O → polyurethane pad
EDX C, O only → brush

Precipitated organic such as from the interaction of cleaner with slurry components
PlanarClean® AG - Advanced Generation Copper Cleaning Mechanism

Cleaning additive disperses silica and organic residue and prevents re-precipitation

**Etchant** for controlled, uniform CuO_x dissolution to undercut particles

**Organic additive** attacks and removes Cu-organic residue

**Corrosion inhibitor package** controls Cu galvanic corrosion

**High pH** leads to charge repulsion between negatively charged silica and negative copper oxide surface

**Etchant** for controlled, uniform CuO_x dissolution to undercut particles

**Organic additive** attacks and removes Cu-organic residue

**Corrosion inhibitor package** controls Cu galvanic corrosion

**High pH** leads to charge repulsion between negatively charged silica and negative copper oxide surface

Etchant for controlled, uniform CuO_x dissolution to undercut particles

Organic additive attacks and removes Cu-organic residue

Corrosion inhibitor package controls Cu galvanic corrosion

High pH leads to charge repulsion between negatively charged silica and negative copper oxide surface

Etchant for controlled, uniform CuO_x dissolution to undercut particles

Organic additive attacks and removes Cu-organic residue

Corrosion inhibitor package controls Cu galvanic corrosion

High pH leads to charge repulsion between negatively charged silica and negative copper oxide surface
IMEC Reflexion Data
Shows lower organic and silica defects compared to the competitor

300 mm Reflexion at IMEC w/ SP3 at 80 nm Threshold, SEM Review

Copper Wafers
PlanarClean® AG Formulations show improved galvanic corrosion

Controlled Electrochemical Properties
- Ligands to control OCP gap
- Passivation to modify resistivity

\[ \text{Co} \rightarrow \text{Co}^{2+} + 2e^- \]
\[ 0.5O_2 + H_2O + 2e^- \rightarrow 2OH^- \]

Anodic Co corrosion
\[ \Delta V = 0.32 \text{ V} \]

Nearly zero galvanic corrosion
\[ \Delta V = -0.001 \text{ V} \]
PlanarClean® AG Formulations maintain higher film integrity on both Cu and Co

Additional novel Cu inhibitor in AG Formulations improves Cu passivation

Evolution of AG surface passivation

Calculated Cu Film Resistance for Various PCMP Formulations

Higher impedance storage and loss components → higher film integrity

When \( w \to 0 \)

\[
Z' = R_n + \frac{R_{ct} + \sigma \omega^{-1/2}}{(\sigma \omega^{1/2} C_{dl} + 1)^2 + \omega^2 C_{dl}^2 (R_{ct} + \sigma \omega^{-1/2})^2}
\]

\[
Z'' = -\frac{\omega C_{dl} (R_{ct} + \sigma \omega^{-1/2})^2 + \sigma^2 C_{dl} + \sigma \omega^{-1/2}}{(\sigma \omega^{1/2} C_{dl} + 1)^2 + \omega^2 C_{dl}^2 (R_{ct} + \sigma \omega^{-1/2})^2}
\]
SEM Cross-Section Analysis
IMEC 45nm Cu/Co patterned wafers show no evidence for corrosion
In-Situ Electrochemistry shows OCP shift under brushing conditions

Old formulation - no brush

Old formulation dynamic with 60 RPM brush

Good formulation with 60 RPM brush

Developed in conjunction with Prof. D. Roy and C. Johnson at Clarkson University
Challenges for Ceria
Post-CMP Cleaning Formulations

- Many different ceria types
  - Calcined
  - Precipitated/colloidal
- Organic additives vary depending on goals
  - Rate additives (ILD)
  - Polymeric or small molecule selectivity additives
    - Stop on nitride or poly
    - Reduce feature size dependence

Current industrial POR (commodity clean): inefficient and environmentally unfriendly
- DHF
- SC-1
- SC-1 + DHF
- SPM (H₂O₂ + H₂SO₄)
- TMAH + SC-1
  - Highly toxic
  - Unformulated
  - Environmentally unfriendly
  - Damage to dielectric

Entegris AG Ce-XXXX formulations
- Improved particle and metal removal
- Replace toxic commodity cleaners
- Environmentally friendly
- No damage to dielectric surfaces
- Ce residue post-CMP cleaning < 10¹⁰ atoms/cm²
Higher pH vs. low pH Cleaning Mechanism for Negative Ceria

**Acidic Approach**
- pH = 1 - 4
- Strong electrostatic attraction

**Neutral/Basic Approach**
- pH = 5 - 13
- Strong electrostatic repulsion

**Steps**
1. Bond breaking
2A & 2B: Modification of surface charge
3A & 3B: Complexation
4: Removal of soluble ceria

**Chemical Structures**
- $\text{CeO}_2$
- $\text{Si}$
- $\text{OH}$
- $\text{CeO}_2\text{Si}_2$

**Notes**
- Higher pH vs. low pH Cleaning Mechanism for Negative Ceria
- Strong electrostatic attraction
- Small molecule charge modifier
Ceria Particle Surface Chemistry Enables the Design of Efficient Ceria Cleaners

Ce$_3^{3+}$O$_3$
Few carbonates physisorbed
FTIR IR Spectra of Cerium Silicate Shows the Effectiveness Bond Breaking Agent

Si – O – Ce solid sample + CeXXXX sample  →  Solid material isolated + filtrate isolated

IR of sample before and after treatment

Relative Ce – O – Si intensity is greatly reduced with CeXXXX
Full Wafer Cleaning Data shows significant cleaning improvements.
Advanced Products Have Higher CeO$_2$ Dissolution Efficiency

Why is increased ceria dissolution desirable?

Ceria-Slurry (CeO$_2$) Dissolution
Challenges for W Post-CMP Cleaners

Slurry particles and organic residue removal from W and dielectric surfaces (PETEOS, Silicon Nitride, Polysilicon);
Metal residue in any form (Ions, Salts, Metal Oxide)

Cleaning Requirements:
- W ER < 1 Å/min
- TiN ER < 1 Å/min
- Dielectrics ER < 1 Å/min
- Dielectrics: Si$_3$N$_4$, TEOS, SiC, etc.
- Defect counts DDC ≥ 0.065 mm lower than commodities: dAmmonia, SC-1
- Low W/TiN galvanic corrosion
- Mt atoms < 10$^{10}$ Mt/cm$^2$

- No increased roughness
- Market increasingly challenged by W recess
  - High pH commodities (SC1, dIl NH$_3$)
  - Traditional low pH cleaners
- Low W etch rates (<2 Å/min) cannot be achieved with commodity cleaners
- No organic Residue
- Nitride cleaning is particularly problematic
- No silica particles or clusters
- Green chemistry (TMAH free)
Post-CMP W Cleaning Mechanisms vs. pH

Low pH
- Silica brush imprints
- Good Mt removal
  \( \sim 10^{10} \text{ atoms/cm}^2 \)

High pH
- No Silica brush imprints
- Poor Mt removal
  \( 4-6 \times 10^{10} \text{ atoms/cm}^2 \)

CA = Mt complexing agent
D1 = SiO\(_2\) dispersant
D2 = organic residue dispersant

STERIC repulsion
ELECTROSTATIC repulsion

Removed by DIW Rinse
Higher Tungsten Etch Rates Observed

Increasing pH due to dissolution as Polyoxotungstate Keggin ions

The Effect of pH on W Etch Rate with No W Inhibitor

\[ y = 0.9708 \ln(x) - 0.6731 \]
\[ R^2 = 0.9951 \]

WO\(_3\) negative at all pHs of interest

Improving Organic Residue Removal from Si₃N₄ Contact Angle and FTIR

**Electrostatic Repulsion during CMP**

Si₃N₄ surface typically highly contaminated by cationic dishing and erosion control agents.

Cleaning additive removes cationic contamination from dielectric surface and disperses.

**Contact Angle**

- **pH < pH_{IEP}, \zeta = +30 mV**
- **pH > pH_{IEP}, \zeta = -15 mV**

For example, the following graph shows the contact angles for clean, hydrophilic and dirty Si₃N₄:

**FTIR**

- Organic residue
- Silica NP
Defectivity Correlated to Charge Repulsion between silica particles and various surfaces (W, SiO$_2$, Si$_3$N$_4$)

Additive increases negative charge on silica surface

Zeta Potential

\[ \zeta \approx 4 \pi \eta \left( \frac{v}{E} \right) / \varepsilon \]


Acknowledgements:
Thomas Parson, Daniela White, Michael Owens
PlanarClean AG-W formulations exhibit lower defects and organic residues over traditional cleans.

Si$_3$N$_4$ – EDR Review – Defect Pareto
# defects pareto (≥ 65 nm defects)

PC AG-W Series show improved performance over SC-1 on all substrates.

SiO$_2$ – EDR Review – Defect Pareto
# defects pareto (≥ 65 nm defects)

W – EDR Review – Defect Pareto
# defects pareto (≥ 100 nm defects)
SEM Images of PETEOS Coupons

Polished with W CMP slurry and cleaned with Formulations A and B

- Tabletop polishing
- Colloidal silica Ludox, PS = 20-30 nm
- pH = 2.3
Correlation SEM vs. Calculated Adhesion

Based on contact angle measurements
Planarcore® Improved Manufacturing for Reduced Particles

LPC 2.8 Micron

>70% Particle Count reduction

LPC 0.2 Micron

>40% Particle Count reduction

Total IC

>65% Ion content reduction
Process Can Often Play a Large Role
Impact of the Brush Gap

**Brush cleaning:**
physical + chemical cleaning

**Brush Pressure:**
- Too low: insufficient physical cleaning
- Too high: particles stick to PVA brushes and lead to brush marks

# defects pareto (>= 100 nm defects)
Conclusions

Entegris believes that advanced metrology and better simulations of customer processes are the key to designing more effective PCMP cleaners

- In situ electrochemistry (Tafel, impedance) under brushing conditions
- Model reactions such as cerium silicate bond-breaking studies
- Synthesis of Cu-BTA residues
- Measurement of particle-wafer interaction energies
- Spectroscopic analysis of surfaces, particles and side reactions
  (UV-Vis, FTIR, TOF-SIMS, XPS, Raman, 1H/13C/multinuclear NMR)

Proper mechanistic studies have led to superior defectivity and advanced node patterned wafer corrosion performance
Thank you!

Q&A
Appendix