Mechanistic and Electrochemical Aspects of Copper Post CMP Cleaners for 5-7 nm Nodes

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WHAT IS CMP (CHEMICAL MECHANICAL PLANARIZATION)?

Challenges in Post CMP Cleaning

1. Variety of CMP slurry particle types
   - Silica (native, surface treated + or -)
   - $\text{Al}_2\text{O}_3$, $\text{CeO}_2$, $\text{TiO}_2$, $\text{ZrO}_2$, SiC, diamonds
2. Organic residue
   1. Corrosion inhibitors (BTA, ...)
   2. Dishing/erosion/selectivity additives (polymers, surfactants, small molecules)
3. Rate additives
4. Pad debris
5. Plating additives

Layers/Materials that need to be Cleaned

1. Copper/barrier
   - Ta, TaN, TiN, Co, Ru, Mn
2. Tungsten
3. Cobalt (bulk)
4. Aluminum
5. Dielectrics (including CeO$_2$ polishing)
   - TEOS, Si$_3$N$_4$, Low-k dielectric, SiC (SiOC, SiON, ...), Polysilicon, Single crystal silicon (wafer, various doping)

Source: International Roadmap for Semiconductors

PERFORMANCE GOALS FOR POST-CMP CLEANERS

1. Best in class defectivity
   1. Very low particle defects (silica, ceria, alumina, ...)
   2. Greater challenges arising as particle sizes decrease
   3. Low organic residue (Cu-BTA or other thick film formers, W or other metal inhibitors, pad debris, plating additives, ...)

2. Very low or no interfacial or surface metal/barrier corrosion or recess
   1. Advanced nodes <10 nm
   2. Low galvanic corrosion

3. Uniform, smooth etching with low roughness
   1. Affects thresholds for defectivity measurements
   2. No attack on low-k dielectric/dielectric loss

4. Low metallic impurities on wafer (<10^{10} atoms/cm^2) on dielectrics

5. Good buffering/no brush interactions to avoid ring scratches
THE RATIONAL DESIGN OF A POST CMP CLEANER PLANARCLEAN® AG COPPER CLEANING

PlanarClean® AG – Advanced Generation Copper Cleaning Mechanism

- **Cleaning additive** disperses silica and organic residue and prevents reprecipitation
- **Etchant** for controlled, uniform CuO_x dissolution to undercut particles
- **Organic additive** attacks and removes Cu-organic residue
- **Corrosion inhibitor package** controls galvanic corrosion
- **High pH** leads to charge repulsion between negatively charged silica and negative copper oxide surface

Cu(0)
PLANARCLEAN® AG PREVENTS SILICA AGGREGATION

- Particle adhesion mechanisms
  - **Physisorption** (van der Waals attraction – increases with PS)
  - **Electrostatic** attraction or repulsion (zeta potential)
  - **Chemisorption** (chemical reaction particle-surface)
  - **Capillary condensation**

\[
\zeta = 4\pi\gamma(\nu/E)/\varepsilon
\]

Silica Slurry Zeta Potential

IEP = 4

Zeta Potential

\[
\mathrm{SiOH} + \mathrm{HO}^- \rightarrow \mathrm{SiO}^- + \mathrm{H}_2\mathrm{O}
\]
DEFECTIVITY CORRELATED TO CHARGE REPULSION BETWEEN SILICA PARTICLES

Particle Size of 60 nm Silica CMP Slurry in Various Cleaners

Zeta Potential of 60 nm Silica CMP Slurry in Various Cleaners

The Effect of Coulombic Repulsion on Defectivity

Additive increases negative charge on silica surface

Zeta potential of all AG formulations is highly negative

BREAK-UP AND DISPERSION OF Cu(I)-BTA COMPLEXES

Cu(I)-BTA film

Additive tailored to attack Cu(I)BTA and similar films
- Fast kinetics
- Thermodynamically favored
- (Higher Cu binding constant than BTA)

Cu(I)-BTA can redeposit if Cu is not properly complexed or dispersed

Cu-BTA Film Removal for Various Cleaners

- Additive targeted to AG #1 and AG #2
- AG #1 has the highest % BTA removed

M(0)
Mox

Cu(I)

MOx

M (0)

H
N
N
BTAH

BTA

[Cu(I)-BTA]n
UV-Vis used to predict optimum complexant and ligand concentration.

Ligands complex copper as soluble Cu(II) and prevent redeposition as CuOx defects or reprecipitating BTA.
PLANARCLEAN AG: LOWER DEFECTS THAN COMPETITORS

Cu Blanket Defects [SP2]

Additive forms weakly interacting film that prevents silica (re)attachment

SiO$_2$

CuO$	ext{x}$

Cu(O)

AG #3
8× lower defectivity

Competitor
AG #1
AG #2
AG #3

50% lower

Competitor
AG #1
AG #2
AG #3

SEMI Defect Review
# defects pareto (≥100 nm defects)

- Pit
- 2D Al
- 2D Si
- 2D organic
**ELECTROCHEMISTRY REVEALS PLANARCLEAN® AG EXHIBITS IMPROVED CORROSION PERFORMANCE**

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

Co OCP < Cu OCP:
Co not protected

AG #1
\[ \Delta V = 0.079 \]
(Cu 1.210 Å/min)

AG #2
\[ \Delta V = 0.005 \]
Nearly zero galvanic corrosion
(Cu 0.078 Å/min)

AG #3
\[ \Delta V = 0.022 \]
Very low galvanic corrosion
(Co 0.270 Å/min)

**Controlled Electrochemical properties**

- Ligands to control potential gap
- Passivation to modify resistivity
IMPEDEANCE SPECTROSCOPY SHOWS THAT AG COPPER INHIBITOR IMPROVES Cu PASSIVATION

Higher impedance storage and loss components → higher film integrity

With Cu inhibitor

Without Cu inhibitor

With Cu inhibitor

Without Cu inhibitor
PLANARCLEAN® AG FORMULATIONS PROVIDE BETTER PASSIVATION ON BOTH Cu AND Co

**Impedance Spectroscopy**

**Cobalt**

**AG #1**

**Older formulation**

**Copper**

**AG #1**

**Older formulation**

**Additional Novel Cu Inhibitor Improves Cu Passivation**

**Calculated Cu Film Resistance for Various PCMP Formulation**

- Evolution of AG surface passivation

When $\omega \to 0$

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

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

Ref:
ELECTRON MICROSCOPY SHOWS SIGNIFICANTLY IMPROVED Cu/Co CORROSION PERFORMANCE FOR PLANARCLEAN® AG

SEM on Sematech® 754 Wafers

Older technology

PlanarClean AG #1

PlanarClean AG #2

PlanarClean AG #3

TEM on 45 nm Cu/Co Wafers

Corrosion near Cu-Co interface

Older Technology

PlanarClean AG #1

PlanarClean AG #2

PlanarClean AG #3

Minimal corrosion near Cu-Co interface

Controlled, smooth etching with minimal galvanic/edge corrosion
IMPROVED CORROSION ADDITIVES REDUCE SURFACE ROUGHNESS BY 2-4×

AFM Roughness of Cu Etched with Various Cleaners

- Older tech
- AG #1
- AG #2
- AG #3
- AG #4

$R_a$ (nm)

$4\times$
CONCLUSIONS

- Charge repulsion shown to be a key driver towards cleaning performance

- Rate of attack on Cu(I)-BTA polymer, dispersion and complexation important for removal and preventing re-deposition of organic residues and particles

- OCP gap must be minimized by optimal ligand selection to minimize galvanic corrosion

- Impedance spectroscopy and Tafel plots have been used to Optimize corrosion inhibiting package

- Very low Cu roughnesses can be obtained with the correct inhibitor (4 Å)