High Performance, Ceria Post-CMP Cleaning Formulations for STI/ILD Dielectric Substrates

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OUTLINE

- Development of a low pH and high pH family of efficient ceria cleaners for STI and ILD dielectric surfaces (PETEOS, SiN, SiC, thermal oxide, etc.), PlanarClean® AG Ce-XXXX
- Mechanistic considerations specific to PlanarClean AG Ce-XXXX formulation design
  - Understanding CeO$_2$ surface chemistry and CeO$_2$-SiO$_2$ interactions: Raman, FTIR
  - Ce$^{4+}$/Ce$^{3+}$ oxidation state characterization: UV-VIS, Raman, potentiometric titrations
  - Ce$^{4+}$/Ce$^{3+}$ impact on the ceria cleaning mechanism
- Ceria particle defect count results by SEM, Dark field Microscopy (DFM) and ICP data on dielectric surfaces cleaned with PlanarClean AG Ce-XXXX formulation
- Conclusions and path forward
WHY FORMULATED CERIA CLEANERS VS. COMMODITY?

1. EHS/Safety concerns with traditional cleans (hot SPM, dHF, SC-1, TMAH + dHF)
2. One-step clean process requirement for throughput improvement
3. Need for improved particle removal
4. Need for improved metal removal
5. No damage to dielectric substrates
CERIA POST-CMP CLEANING FORMULATION – MECHANIC DESIGN CONCEPT

Formulation Design Options

1. High pH hydrolysis of -Ce-O-Si- bonds by HO⁻ nucleophilic attack to Ce⁴⁺ plus additives needed to stabilize –Ce-OH species and prevent re-deposition

2. High pH partial etch/dissolution of the surface –Si-O-Ce- groups plus re-deposition prevention

3. Bond-breaking additives, followed by CeO₂ complexation, particles stabilization and dispersion
INTERACTIONS OF ORGANIC MOLECULES WITH CERIA SURFACE AND SURFACE CHARGE VS. PH

- Surface modified CeO$_2$ particles in the CMP slurries: **positive or negative surface charge**
- Particle size: 15–200 nm
- Need to understand CeO$_2$ surface chemistry and types of interactions with the dielectric surfaces
- Six different types of CeO$_2$ particles tested – can we design a universal cleaner?

Surface-Modified Ceria in CMP Slurries

Various CeO$_2$ Particles (A-F) Tested

Different CeO$_2$ Particles Characteristics – $\zeta$ and PS

- Low pH $\zeta > 0$ mV
- High pH $\zeta < 0$ mV
TYPES OF CeO₂ SURFACE GROUPS

A. Hydroxyl groups by FTIR¹ and titration

CeO₂ - hydroxyls
CeO₂ - carbonates

B C D D

Particle B, pKₐ = 2.3
Particle C, pKₐ = 2.4
Particle D, pKₐ₁ = 2.2; pKₐ₂ = 8.4

PKₐ : 8–10 most basic
PKₐ₂ : 4–7
PKₐ₃ : <3- most acidic

Basic sites, pKₐ = 7–10
Acidic sites, pKₐ = 3–4

TYPES OF CeO$_2$ SURFACE GROUPS

B. Carbonates on reduced and stoichiometric ceria nanoparticles$^2$ (RAMAN)

Expect different CMP (RR) and post-CMP cleaning behavior!

DIFFERENT CLEANING FORMULATIONS FOR DIFFERENT CERIA SURFACE CHEMISTRIES?

- More acidic surface, partially hydroxylated
- Small amount of surface water H-bonded
- Surface exposed –OH for -Si-O- condensation
- Stronger Ce-O-Si bonds, difficult to break/clean

- More basic surface, more hydroxylated
- Outer-sphere shell of H-bonded water
- Reduced surface reactivity
- Weaker Ce-O-Si bonds, easier to break

Based on the FTIR-ATR UV-VIS and tritation experiments data
CERIA REACTS WITH $\text{H}_2\text{O}_2$ BY BOTH REDUCTION AND OXIDATION MECHANISMS

$\text{CeOH}^{3+} + \text{H}^+ + \text{e} \rightarrow \text{Ce}^{3+} + \text{H}_2\text{O} \ldots \text{E}_{\text{red}} = +1.715 \text{ V}$

$\text{H}_2\text{O}_2 \rightarrow 2 \text{H}^+ + \text{O}_2 + 2 \text{e} \ldots \text{E}_{\text{oxygen}} = -0.695 \text{ V}$

$\text{E}_{\text{red}} + \text{E}_{\text{oxygen}} > 0$, reaction can proceed

Reduction of Ce$^{4+}$ to Ce$^{3+}$
Oxidation of $\text{H}_2\text{O}_2$ to $\text{O}_2$

$\text{Ce}^{3+} + \text{H}_2\text{O} \rightarrow \text{CeOH}^{3+} + \text{H}^+ + \text{e} \ldots \text{E}_{\text{oxygen}} = -1.715 \text{ V}$

$\text{H}_2\text{O}_2 + 2 \text{H}^+ + 2 \text{e} \rightarrow 2 \text{H}_2\text{O} \ldots \text{E}_{\text{red}} = +1.776 \text{ V}$

$\text{E}_{\text{oxygen}} + \text{E}_{\text{red}} > 0$, reaction can proceed

Oxidation of Ce$^{3+}$ to Ce$^{4+}$
Reduction of $\text{H}_2\text{O}_2$ to $\text{H}_2\text{O}$

Commodity cleaners as controls

- SC-1: $\text{H}_2\text{O}:\text{H}_2\text{O}_2:\text{NH}_3$ (1:1:5)
- SPM: $\text{H}_2\text{SO}_4:\text{H}_2\text{O}_2$ (1:4), $T > 100^\circ\text{C}$

Why $\text{H}_2\text{O}_2$?
RAMAN SPECTRA FOR BIG CERIA PARTICLES C (>100 nm) IN REACTION WITH H$_2$O$_2$/SC-1

No changes on the surface ratio Ce$^{4+}$/Ce$^{3+}$ upon addition of SC-1/H$_2$O$_2$
RAMAN SPECTRA FOR SMALL CERIA PARTICLES A (15 nm) IN REACTION WITH H₂O₂/SC-1

- Reduced fluorite Ce⁴⁺O₂ surface species
- Vo.. Vacancies
- Peroxo/reduced Ce³⁺ species

Ce³⁺ + H₂O₂ → Ce⁴⁺

- Fully oxidized Ce³⁺ to Ce⁴⁺ (only peroxo-Ce⁴⁺ species)
- No Vo.. vacancies
- No remaining Ce⁴⁺-O₂--Ce⁴⁺ fluorite structure
- No remaining reduced peroxo-Ce³⁺ species
THE NEGATIVE EFFECT OF H₂O₂ IN COMMODITY CLEANERS ON DIELECTRIC SUBSTRATES

- Spherical deposits from peroxymonosulfuric acid
- PETEOS surface damaged after H₂O hot rinse
- PlanarClean AG Ce-XXXX-1 and -3 leave very clean, undamaged PETEOS surfaces
Commodity cleaners such as hot SPM and SC-1 potentially damage and leave agglomerated ceria particles and residue on dielectric surfaces.
# PlanarClean AG CE-XXXX Formulation Additives List – Function and Mechanism

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<tr>
<th>Component</th>
<th>Function</th>
<th>Mechanism</th>
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| A         | Non-TMAH pH adjustor     | ◦ Provides the hydroxyl anions and adjust pH needed for surpassing CeO$_2$ pH$_{\text{IEP}}$
                | ◦ Ensures negative surface charge on both dielectric surface and ceria & organic contamination, by being adsorbed on inorganic and organic residues. |
| B         | Complexing reagents       | ◦ Adsorption at the ceria surface
                | ◦ Stabilization of ceria particles via electrosteric repulsion, preventing agglomeration and re-precipitation |
| C         | Bond-breaking reagent     | \[- \text{Ce} - \text{O} - \text{Si} - C - \text{Ce} - \text{OH} + \text{HO} - \text{Si} -\]
| D         | Cleaning Additives Package | ◦ Interacts with particles and dielectrics surfaces to prevent particles aggregation and organics re-deposition |
EXPERIMENTAL PROCEDURE

Beaker-dip experiment

PETEOS → CeO₂ particles A-E → Beaker dip → Ceria contaminated substrate → AG Ce-XXXX cleaner → Beaker dip → Cleaned substrate

Polishing experiment

Wafer carrier → Pressure → Slurry → Pad → Beaker dip → Cleaner → Round table → Rotation

Metrology for Characterization
- Dark Field Microscopy (DFM)
- ICP-MS
- SEM
- AFM
- TOF-SIMS
- XPS
- FTIR-ATR (Mechanism)
- Raman
- UV-VIS (Mechanism)
- NMR (Mechanism)
## FORMULATION DEVELOPMENT (PERFORMANCE = CERIA CONTAMINATION AFTER CLEANING)

### Dark Field Microscopy Data

2nd generation cleaner: 3.5× more efficient than SC-1 and 2× than the 1st generation
Developed cleaner showed extremely good performance – 150× better than SC-1
SEM AND ICP-MS CHARACTERIZATION

Process: Beaker dip/PETEOS/Particle C

- ICP-MS supports the dark field microscopy data and it shows >150× improvement over SC-1
- SEM data strongly supports DFM and ICP data
CONCLUSIONS

Several low-pH and high-pH high-performance ceria cleaning formulation PlanarClean AG Ce-XXXX were developed at Entegris based on in-depth mechanistic understanding on silica-ceria surface interactions.

All ceria cleaning formulations contain complexing reagents, silica-ceria bond breaking reagents and dispersing reagents for particles agglomeration and re-deposition prevention.

Low-pH PlanarClean AG Ce-XXXX-2 and PlanarClean AG Ce-XXXX-3 formulations perform well on dielectric surfaces polished with both low- and high-pH ceria dispersions.

High-pH PlanarClean AG Ce-XXXX-1 ceria cleaning formulations perform best on dielectric surfaces polished with high-pH ceria dispersions.

We demonstrated that commodity cleaners such as hot SPM and SC-1 are the root cause for defective and damaged dielectrics surfaces, also highly contaminated with ceria aggregated particles.

PlanarClean AG Ce-XXXX formulations show improved ceria particles removal vs. commodities by as much as 150× (ICP-MS).
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