Post Tungsten CMP Cleaner Development with Improved Organic and Particle Residue Removal on Silicon Nitride and Excellent Tungsten Compatibility

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Summary
**Problem statement**

- There are four types of defectivity after post tungsten cleaning.
- Improve tungsten compatibility and cleaning efficiency to improve defectivity.
Zeta Potential Measurements on Wafer Substrates and Defect Sources

Zeta Potential vs. pH

- Adjust formulation pH to measure zeta potential
- High pH value provides higher electronic repulsive force between contaminant particles and SiNx and tungsten wafers
Method to Estimate Cleaning Efficiency

- W & SiN wafer pre-treatment method:
  - Cut 3 cm square cubic area wafer coupons
  - Apply the slurry (with or without centrifuge) on the W & SiN wafer coupon surface and allow it to dry it overnight.
  - Put the wafer coupon in 100 mL of post-CMP formulation for 1, 5 or 10 minutes. (500 RPM @ 50°C). Dry the coupon and analyze by SEM
A technique using AFM (atomic force microscopy) was developed to measure the adhesion forces between colloidal silica particles (50 – 80 nm) and wafer surfaces in the cleaning solution. Additionally, by attaching a polystyrene bead (~5μm) to the AFM cantilever and measuring the force-distance curve to Si$_3$N$_4$, Cu and W wafers the adhesion force between polystyrene and the wafer substrate was obtained.
**Tungsten compatibility analysis**

- Pretreatment tungsten wafers
  - Cut 3 cm square cubic area tungsten wafer coupons
  - Immerse the coupon in 100 mL formulation for 10 minutes.
  - Measure the amount of tungsten dissolved in the formulation with ICP-MS

Immerse the tungsten coupon for 10 minutes in the cleaning solution

Remove the coupon and analyze the tungsten ion concentration by ICP-MS
Chemical A and Chemical C shifted the zeta potential of Si$_3$N$_4$. Increased levels of Chemical A raised the pH of the formulation and the zeta potential of Si$_3$N$_4$ became more negative. Chemical C decreased the pH of the formulation as its concentration was increased and the zeta potential of Si$_3$N$_4$ was increased.
Chemical A and Chemical C concentrations affected the zeta potential of SiO₂. Higher concentrations of Chemical A raised the pH and the zeta potential of SiO₂ became more negative. Chemical C had the reverse behavior and decreased the pH and increased the zeta potential of SiO₂.
The best cleaning efficiency was observed at high pH where the adhesion force between polystyrene and Si₃N₄ was reduced. Slurry residues would be more dissolved in an alkaline environment and the lower adhesion force will facilitate particle and organic residue removal.
From main effects plot, we found that increased amount of **Chemical A** would enhance clean efficiency but increased amount of **Chemical C** would decreased clean efficiency. The clean efficiency improvement came from pH effect or zeta potential effect because when we increased the amount of **Chemical A** the pH would increase at the same time.
**Tungsten compatibility improvement by added chemical A**

- Added chemical **A** could improve tungsten compatibility and reduce tungsten loss in the formulation. It is well known tungsten is easy to corrode in high pH region. However, chemical **A** showed good tungsten compatibility in the high pH region. When we added chemical **C** amount higher than middle level, it will increase tungsten loss.
We could find lower W-loss and better clean efficiency on pH 8 to 9. If zeta potential of SiN is less than -40 mV, it will showed better clean efficiency in the formulations. We also observe same trend on SiO\(_2\) when zeta potential is less than -38 mV. Zeta potential effect maybe come from pH effect.
Summary

- In the high pH region, lower adhesion force between polystyrene and Si$_3$N$_4$ will result in better clean efficiency.

- Chemical A could show good tungsten compatibility in the high pH region.

- If the zeta potential of Si$_3$N$_4$ & SiO$_2$ is less than -40 mV, the formulations yielded better cleaning efficiency.