Effects of CMP Slurry Chemistry on Agglomeration of Alumina and Copper Surface Hardness

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Workshop
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Motivation
Prediction of material removal rates (MRR)
• Predictive CMP models - optimize use of process consumables
• Improve understanding of effects of CMP variables

Reduce cost of CMP
Better process control
• Understand role of slurry chemistry (additives, pH, etc.)
• Develop slurries that provide adequate removal rates and global planarity

Reduce defects
• Control of abrasive particle size
• Control of interactions between wafer surface and slurry

2007 Main Objectives
Understand effects of agglomeration/dispersion of slurry on Cu CMP
• Colloidal behavior measured by zeta potential and agglomeration size distribution
• Effects of chemical additives and presence of copper
• Copper surface hardness as function of chemistry
• State of the Cu (Cu, CuO, Cu2O, etc.) in slurry and on surface
• Use colloidal behavior in model of CMP

Experimental Procedure

Zeta Potential
Copper aluminia in 10⁻⁴M KNO₃ solution with and without 0.12M copper
• IEP ~6.5 with and without Cu
• IEP ~9.2 for alumina from literature

Material Removal Rate (MRR) is affected by:
• Abrasive size and size distribution
• Wafer surface hardness
Cu is the interconnect of choice - our research focus

Copper Water System
Potential-pH for Copper-Water System
• IEP ~9.5°

Agglomeration behavior is consistent with the Pourbaix diagram

Average (nm) of Agglomerate size of bimodal distributions in a 1 mM KNO₃ solution

Copper Glycine-Water System
Potential-pH for Copper-Glycine-Water System
[Cu⁺]=10⁻⁴M, (Glycine)=10⁻¹M at 25°C and 1atm
• Agglomeration behavior is consistent with Pourbaix diagram

Average (nm) of Agglomerate size of bimodal distributions in a 1 mM KNO₃ solution with various additives

Future Goals
Continue to investigate effect of copper on zeta potential and particle size
• Determine state of Cu in solution
• Study agglomeration as a function of time

Initial hardness measurements show large differences in copper surface with pH and chemical addition

Modeling - Luo and Dornfeld Model*
• Incorporate experimental measurements (hardness and agglomerate size distribution) into model and compare with experimental CMP data

Conclusions
Colloidal Behavior
• pH has greatest effect on colloidal behavior
• Glycine acts as a stabilizing agent for alumina
• Presence of Cu nanoparticles can increase or decrease agglomeration depending on the state of copper in solution

Agglomeration behavior with copper is consistent with potential-pH diagrams

Nanohardness of Copper Surface
• pH of the slurry affects copper surface hardness
• Addition of chemical additives has large effect on the surface hardness
• State of copper on surface is consistent with potential-pH diagrams

Under certain conditions glycine may cause decrease in copper surface hardness