Colloidal Aspects of Chemical Mechanical Polishing

SFR Workshop & Review
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2002 GOAL: To integrate initial chemical models into basic CMP model. Validate predicted pattern development. (Dornfeld, Talbot)
Motivation

- Optimize slurries for high removal rates with adequate planarity
  - Current roles of slurry chemistry (additives, ionic strength, pH) not understood

- Reduce consumables
  - Slurries are expensive and mostly not recycled

- Environmental concerns
  - CMP and post CMP cleaning requires large water consumption
Role of Chemistry

• Chemical and electrochemical reactions between material (metal, glass) and constituents of the slurry (oxidizers, complexing agents, pH)
  – Dissolution and passivation

• Solubility

• Adsorption of dissolved species on the abrasive particles

• Colloidal effects

• Change of mechanical properties by diffusion & reaction of surface
Generic Chemical Reactions

• Dissolution: $M(s) + A \rightarrow M(aq) + B$
  $M(s) + A \rightarrow M^{n+} + ne^- + B$

• Oxidation: $M(s) + O \rightarrow M$-oxide$(s)$

• Oxide dissolution:
  $M$-oxide$(s) + A \rightarrow M(aq) + B$
  $M$-oxide$(s) + A \rightarrow M^{n+} + ne^- + B$

• Complexation (to enhance solubility)
  $M^{n+} + C \rightarrow MC^{n+}$
Colloidal Effects

- Surface charge (zeta potential or isoelectric point, IEP, the pH where the surface charge is neutral) of polished surface and abrasive particle is important

\[ \kappa = \left( \frac{2000F^2}{\varepsilon_0 \varepsilon_r RT} \right)^{1/2}, \quad I = \frac{1}{2} \sum q_i^2 \]

(Malik et al.)
Colloidal effects

- Maximum polishing rates for glass observed compound IEP ~ solution pH > surface IEP (Cook, 1990)

- Polishing rate dependent upon colloidal particle - W in KIO₃ slurries (Stein et al., J. Electrochem. Soc. 1999)
Synergistic Effects

- \[ \text{MRR} = k_{\text{chem}} (RR_{\text{mech}})_o + k_{\text{mech}} (RR_{\text{chem}})_o \]

- \((RR_{\text{mech}})_o = \text{mechanical wear} = K_e PV\)
- \((RR_{\text{chem}})_o = \text{chem. dissolution} = k_r \exp(-E/RT) \Pi C_i^n\)
- \(K_e\) affected by surface chemical modification
- \(C_i\) affected by mass transport (i.e., V)

Our Approach

A) Measurement of Zeta Potential
- Particles acquire charge when suspended in liquid
- Depends on various variables
  - pH of solution
  - Ionic strength
  - Temperature
- Stability of colloidal particles
  - coagulation
  - well dispersed

B) Measurement of particle size and distribution
Measurement of Zeta Potential

Particle Velocity measured through microscope using rotating prism technique

(Pen Kem Lazer Zee Meter)

Accuracy ± 5mV

Z.P. calculated using Smoluchowski eqn: (valid for kr>>1)

\[ \xi = \frac{v\eta\epsilon E}{\varepsilon} \]
Zeta Potential of Commercial Alumina Slurries (Met 202 & EKC Tech) and Alumina Particles vs. pH

*MET 202 Alumina Slurry from Solution Technology, 50 nm
**Pure Alumina from Ceralox, 300 nm
***EKC Tech Alumina Slurry, 120 nm
EKC Tech particles in DDI H$_2$O vs $10^{-2}$M Glycine

- Zeta Potential (mV)
- Ionic Strength (M)

ZP (H2O)
ZP (w/ Glycine)
2002 and 2003 Goals

- **Integrate initial chemical models into basic CMP model. Validate predicted pattern development by 9/30/2002.** (Dornfeld, Talbot)

- **Create comprehensive chemical and mechanical model. Experimental and metrological validation by 9/30/2003.** (Dornfeld, Talbot, Spanos)