Motivation

- An understanding of copper removal mechanism’s is important for developing CMP models and for optimizing CMP process parameters and slurry compositions
- Steigerwald’s removal mechanism is applicable to copper CMP: there must be a balance between passivation of recessed regions of the copper surface, mechanical removal of protruding surface layers and the chemical dissolution of surface layers and debris

2003-04 Main Objectives

- Preparation of idealized two phase surfaces, characterization of differential etching behaviors (Milestone 6)
- Develop a basic understanding of the effects of H$_2$O$_2$ concentration and glycine on passivation
- Propose a mechanism for the passivation of copper in glycine-containing solutions with H$_2$O$_2$
- Model the contribution of chemical action in overall CMP performance

The Problem

- Currently can’t quantitatively explain why H$_2$O$_2$ induces passivation under conditions that give active dissolution in the absence of H$_2$O$_2$
- Cannot satisfactorily model a process that we don’t understand
- Future understanding and modeling of the removal and passivation mechanism needs dynamic kinetic information which we are now gathering for the copper-glycine-water-H$_2$O$_2$ system

Approach

- The electrochemical quartz crystal microbalance utilizes frequency changes to track extremely small weight changes
- This can provide dynamic information on both the thickness of adsorbed/dissolved layers. Electrochemical information can be acquired simultaneously
- Quartz Crystal Microbalance (QCM) measurements were made in solutions containing a chemical oxidant (H$_2$O$_2$)
- Electrochemical QCM measurements were made in electrochemical/chemical systems

Experimental Apparatus

- EQCM measurement
- QCM measurement

Experimental Study

- Solution system
- pH 9 carbonate/bicarbonate buffer solution
- 0.01M glycine (added after stabilization of EQCM)
- Oxidation using either H$_2$O$_2$ or externally applied potential (added after stabilization, to observe transient effects)
- Sample
- AT-cut 5MHz Cu crystal (MaxTek, Inc.)
- Rinsed with acetone and Millipore water, then dried with compressed air

In-situ Corrosion Potential Measurement

- Addition of glycine: to capture and compare the effect of glycine on etching/passivation of copper
- Varying H$_2$O$_2$ concentration: 2.09 wt% and 0.3 wt%, to explore the effect of H$_2$O$_2$ concentration on passivation
- EQCM measurement
- In-situ corrosion potential measurement
- QCM measurement at $E_{corrosion}$ without H$_2$O$_2$ in solution

EQCM measurement at corrosion potential $E = 185$ mV vs. SCE

- Accurate reproducible EQCM results (develop procedure to attain prompt mixing of reagent additions without affecting crystal frequency)
- AFM/STM measurement of dynamic structural evolution, combining simultaneously the electrochemical measurements
- Characterization of the phases on the surface by XPS, XRD, SEM, etc.