Copper Surface Chemistry Relevant to Chemical Mechanical Planarization (CMP)

Karen L. Stewart Final Seminar August 13, 2008

Cu has replaced aluminum for interconnects in microelectronic devices because it possesses lower resistance, higher frequency capabilities, lower power requirements, and improved electromigration resistance.[1-3] Structures such as shallow trenches, plugs, vias, or interconnects are etched into a silicon wafer, and the structure is then filled with copper through an electroplating process.[4] Because there are many layers in microelectronic devices, each layer must be planar so that non-uniformities do not propagate throughout the layering process. This third processing step, termed chemical mechanical planarization or polishing (CMP), removes the Cu overburden produced by the electroplating process. The CMP slurry comprises a number of components, including chelating agents, oxidizers, corrosion inhibitors, buffers, surfactants, and abrasives.[4]

There are some models that attempt to describe the mechanisms involved in the polishing process. In the Preston model, removal rate is directly proportional to the velocity of the pad, the down pressure applied, and Preston's coefficient.[5, 6] This model, based on glass polishing, fails to explain metal polishing. Kaufman's model describes the CMP mechanism as three main steps: slurry components passivate the surface, abrasives and the polishing pad remove the passivated layer, and corrosion inhibitors protect recessed areas until the entire surface is planar.[7] However, recent and more demanding CMP implementations suggest that these models must be incomplete, since non-linear and non-zero origin pressure-velocity (PV) plots are now commonly observed.[8-10] A detailed understanding of the interplay between surface removal rates and slurry composition is desired both to control present-day formulations and to provide directions for future compositions necessary as circuit designs become more complex.

BTA is a well-known and commonly used Cu corrosion inhibitor. Numerous studies of the interaction of BTA with Cu reveal that the molecule forms a coordination polymer above the surface featuring a Cu(I) center bridging between two BTA molecules.[11-13] A detailed structure of the polymer is not yet known, however, anions are thought to coordinate to the Cu(I) center in some instances.

The effect of different anions in solutions containing benzotriazole (BTA) on copper removal rate was investigated. Corrosion inhibitor films thicknesses containing different anions were measured utilizing atomic force microscopy (AFM). Films grown from halide-containing solutions were found to be thicker than those grown from other anions. Ellipsometry was used as a secondary method of measuring film thicknesses and showed trends similar to AFM data. Films were also characterized with surface-enhanced Raman spectroscopy, which showed close association of BTA with the copper surface, and mass spectrometry showed halide inclusion in the Cu-BTA polymer. Open circuit potential measurements were also made to monitor copper oxide formation in halide and non-halide containing solutions. It was concluded that films grown in halide solutions have halide-inclusion and are thicker than those grown in other electrolytes. The thicker films correlated well with reduction in copper removal rates.[14]

In addition to being an oxidizing additive in Cu CMP slurries, hydrogen peroxide is an important intermediate in the oxygen reduction and corrosion processes.[15, 16] It is already known that Cu(I) formation would occur in basic conditions upon exposure to an oxidizer, but in acidic slurries where many Cu CMP slurries operate, little is known about the fate of the oxidizer. The electrochemical reduction of hydrogen peroxide on a copper surface in acidic sulfate solutions was investigated using cyclic voltammetry, rotating disk electrode experiments, surface-enhanced Raman spectroscopy, and density functional theory calculations.[17] The spectroscopy revealed that the hydrogen peroxide molecule was reduced at negative potentials to form a Cu-OH surface species in acidic solutions, a result consistent with the insight from Tafel slope measurements. Tafel slope plots were derived from data from the rotating disk electrode experiments and suggested that electron transfer is not the rate determining step for peroxide reduction. Density functional theory calculations support the instability of peroxide relative to the surface-coordinated hydroxide on both Cu(111) and Cu(100) surfaces. The proposed hydrogen peroxide reduction mechanism (Figure 1) involved H_2O_2 adsorption to the Cu surface. Then H_2O_2 is reduced, the Cu surface becomes partially oxidized, the O-O bond is cleaved, and two Cu-OH species form. The Cu-OH surface species are each reduced by one electron from the external circuit, leading to the cleavage of the Cu-O bond. The electron reduces the Cu center, and the resultant OH^- reacts with the H^+ in solution to yield H_2O.

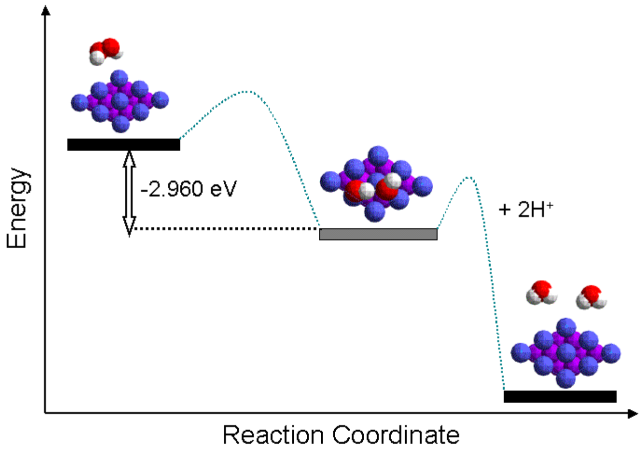

Figure 1. Proposed hydrogen peroxide reduction mechanism on a Cu(111) surface. The blue, purple, red, and white spheres represent Cu surface atoms, bulk Cu atoms, O atoms, and H atoms, respectively.

References

1. Andricacos, P. C., Uzoh, C., Dukovic, J.O., Horkans, J., Deligianni, H. Damascene Copper Electroplating for Chip Interconnections. *IBM J. Res. Develop.* **1998**, *42*, 567.

2. Carpio, R., Farkas, J., Jairath, R. Initial Study on Copper CMP Slurry Chemistries. *Thin Solid Films* **1995**, *266*, 238.

3. Edelstein, D. C., Sai-Halasz, G. A., Mii, Y.-J. VLSI On-Chip Interconnection Performance Simulations and Measurements. *IBM J. Res. Develop.* **1995**, *39*, 383.

4. Oliver, M. R. *Chemical-Mechanical Planarization of Semiconductor Materials*; Springer: Berlin, 2004; pp 7-131.

5. Li, Z., Ina, K., Lefevre, P., Koshiyama, I., Philipossian, A. Determining the Effects of Slurry Surfactant, Abrasive Size, and Abrasive Content on the Tribology and Kinetics of Copper CMP. *J. Electrochem. Soc.* **2005**, *152*, G299.

6. Preston, F. W. The Theory and Design of Plate-Glass Polishing Machines. *J. Soc. Glass Technol.* **1927**, *11*, 214.

7. Kaufman, F. B., Thompson, D. B., Broadie, R. E., Jaso, M. A., Guthrie, W. L., Pearson, D. J., Small, M. B. Chemical-Mechanical Polishing for Fabricating Patterned Tungsten Metal Features as Chip Interconnects. *J. Electrochem. Soc.* **1991**, *138*, 3460.

8. Chen, K.-W., Wang, Y. L. Study of Non-Preston Phenomena Induced from the Passivated Additives in Copper CMP. *J. Electrochem. Soc.* **2007**, *154*, H41.

9. Paul, E., Kaufman, F., Brusic, V., Zhang, J., Sun, F., Vacassy, R. A Model of Copper CMP. *J. Electrochem. Soc.* **2005**, *152*, G322.

10. Zhao, B., Shi, F. G. Chemical Mechanical Polishing: Threshold Pressure and Mechanism. *Electrochem. Solid-State Lett.* **1999**, *2*, 145.

11. Cotton, J. B., Scholes, I.R. Benzotriazole and Related Compounds as Corrosion Inhibitors for Cu. *Brit. Corros. J.* **1967**, *2*, 1.

12. Rubim, J., Gutz, I.G.R., Sala, O., Orville-Thomas, W.J. Surface Enhanced Raman Spectra of Benzotriazole Adsorbed on a Copper Electrode. *J. Mol. Struct.* **1983**, *100*, 571.

13. Vogt, M. R., Nichols, R. J., Magnussen, O. M., Behm, R. J. Benzotriazole Adsorption and Inhibition of Cu(100) Corrosion in HCl: A Combined in-situ STM and in-situ FTIR Spectroscopy Study. *J. Phys. Chem. B* **1998**, *102*, 5859.

14. Stewart, K. L., Zhang, J., Li, S., Carter, P. W., Gewirth, A. A. Anion Effects on Cu-benzotriazole Film Formation. *J. Electrochem. Soc.* **2007**, *154,* D57.

15. Adzic, R. R. In *Electrocatalysis*; Lipkowski, J., Ross, P. N., Eds., Wiley-VCH, Inc.: New York, 1998; p. 197-242.

16. Hariharaputhiran, M., Zhang, J., Ramarajan, S., Keleher, J. J., Li, Y., Babu, S. V. Hydroxyl Radical Formation in H_2O_2-Amino Acid Mixtures and Chemical Mechanical Polishing of Copper. *J. Electrochem. Soc.* **2000**, *147*, 3820.

17. Stewart, K. L., Gewirth, A. A. Mechanism of Electrochemical Reduction of Hydrogen Peroxide on Copper in Acidic Sulfate Solutions. *Langmuir* **2007**, *23,* 9911.