

**PARTICLE-SURFACE INTERACTIONS IN CHEMICAL
MECHANICAL POLISHING*****RECEIVED****SEP 26 1996****OSTI**M.T. Dugger⁺, J.S. Jeon⁺⁺, S. Raghavan⁺⁺, C.L.J. Adkins⁺, P.J. Resnick⁺⁺Sandia National Laboratories, Albuquerque NM USA 87185⁺⁺Dept. of Materials Science and Engr., Univ. of Arizona, Tucson AZ USA 85721**1.0 INTRODUCTION**

Material removal in chemical mechanical polishing (CMP) occurs by a pressure accentuated chemical attack of the surface. The polishing slurry typically consists of abrasive particles and reactive chemicals that may or may not include an oxidant. Post-CMP cleaning processes must remove both the ionic contaminants and any remaining polishing slurry particles. Central to the effectiveness of a clean is the use of conditions that will minimize the binding force between the residual particles and the wafer surface. The morphology and composition of the particle, the surface from which it must be removed, and the environment surrounding the wafer will determine the magnitude of forces that hold a particle to the wafer surface. At the Sandia/SEMATECH Center for Contamination Free Manufacturing, two techniques -- atomic force microscopy (AFM) and electrokinetic deposition -- are being used to explore these interactions for CMP of both oxide and tungsten surfaces. A basic understanding of particle-surface interaction forces and how they are affected by the chemical/physical environment of the particle and surface is the objective of this task. Modification of the binding forces between particles and wafer surfaces may be used to maximize post-CMP cleaning effectiveness.

2.0 APPROACH

The focus of the AFM work to date has been investigation of conditions relevant to oxide polishing and post-CMP cleaning. The probe tip is used to simulate a slurry particle because its shape, radius of curvature (on the order of 10 nm) and composition approaches that of slurry particles. Using an atomic force microscope in the force versus distance mode, data can be collected that show the attractive or repulsive nature of the wafer/tip interaction in various liquid chemistries. In lateral force mode, information can be obtained about the friction coefficient between the wafer and tip under various contact pressures. In both of these modes, the effect of addition of a nonionic surfactant was investigated and a series of experiments was performed to determine the effects of pH and ionic strength on particle binding forces.

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The electrokinetic deposition studies were performed using LPCVD tungsten films. Two kinds of alumina particle dispersions were used in this study: (1) a dispersion made from high purity alumina particles; and (2) a commercially available alumina slurry used in tungsten CMP. The effects of a nonionic surfactant and the addition of hydrogen peroxide on alumina deposition on the tungsten have also been investigated.

3.0 RESULTS AND DISCUSSION

The role of adsorbed surfactants on particle binding forces was explored with Triton X-100. The binding force between an oxide probe and a thermal oxide film, polished and etched in dilute HF to remove organic contamination, was measured in deionized water (DIW) and DIW with 1000 ppm of Triton. The results are shown in Figure 1. The attractive force observed on approach in DIW is suppressed in the presence of the surfactant. However, once contact is made, the surfactant does not significantly alter the adhesive force of the probe. Suppression of the attractive force on approach is attributable to steric hindrance. The probe is apparently able to displace the surfactant under sufficient pressure, so that van der Waals attraction dominates. Nanoscale friction measurements using lateral force microscopy, as well as bulk friction and wear measurements, indicate no effect of the addition of Triton to surface sliding forces or material removal rates.

Measurements under a variety of pH and ionic strength conditions show that repulsive forces are generated between oxide probes and oxide surfaces in high pH polishing and cleaning environments, consistent with the zeta potential of surfaces under these conditions. These results indicate that reduced particle levels may be realized by maintaining a pH such that electrostatic repulsion prevails throughout the polishing and cleaning steps. Control of the ionic strength appears to be a secondary effect modulating the attractive/repulsive forces. The extent of the electrostatic double layer is inversely proportional to the ionic strength. The ionic strength must therefore be large enough to provide charge carriers, but not so large that the electrostatic double layer becomes small enough to permit van der Waals forces to bind particles to the wafer surface.

Measurements of probe forces in DIW containing 200 ppm of Triton indicate attractive force between the probe and wafer of approximately 1 nN magnitude, which is similar to that observed with DIW alone. High concentrations of surfactant are apparently required to provide steric repulsion in neutral water. In KOH solutions of pH 10, repulsive force between the probe and wafer was observed. This observation is consistent with the presence of large electrostatic double-layers, which provide repulsion of similarly-charged surfaces beyond the extent of any adsorbed surfactant.

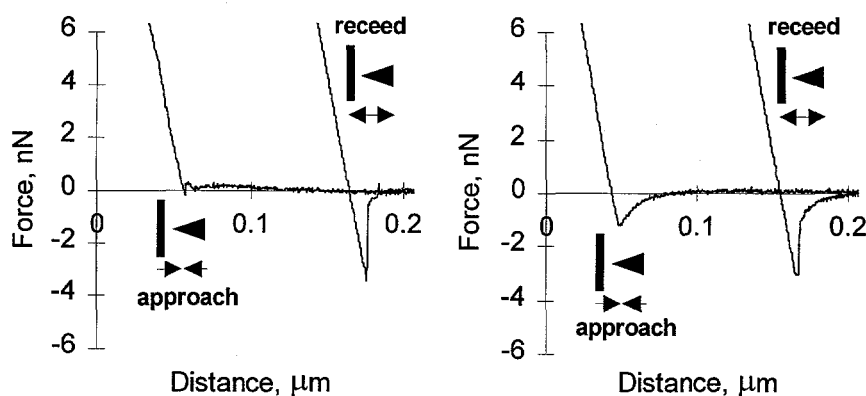


Figure 1. Force versus distance in DIW (left) and in DIW + 1000 ppm of Triton X-100 (right).

Figure 2 shows the results of zeta potential measurements carried out on high purity alumina powder, alumina particles in a commercial CMP slurry, and a CVD tungsten wafer. Differences in composition as well as shape may contribute to the differences in zeta potential for high purity alumina and slurry particles. Interestingly, the profile of zeta potential vs. pH for alumina particles in the diluted slurry shows a flat region of small negative zeta potential in the pH range of 4 to 6. The tungsten wafer zeta potential was negative at pH 4. It may be concluded from this figure that the high purity alumina particles will adhere to tungsten at pH values less than 8 and the alumina in the commercial slurry would exhibit a weak tendency to adhere to a tungsten surface below a pH value of 4.

The importance of electrostatic interactions between alumina particles and tungsten surfaces in particulate contamination during CMP was investigated by carrying out controlled deposition experiments in the absence or presence of an applied potential. Experiments under an applied potential were carried out to create a "worst-case scenario" for particle deposition/adhesion. Additionally, application of an anodic bias during deposition allowed the simulation of contamination on WO_x , which is known to form on tungsten in the presence of an oxidant. Under a cathodic bias, the surface of W was covered with positively charged alumina particles in a dispersion maintained at a pH of 4 and these particles were difficult to remove by a DI rinse. Under anodic bias significantly less contamination was observed indicating a lack of attraction between positively charged alumina particles and a positively charged surface. Thus, one strategy to reduce alumina contamination on W would be to add an additive to the slurry that would provide a zeta potential of the same sign to both the surface and the particles.

The feasibility of controlling particle adhesion by steric repulsion of adsorbed layers on the particles and the W surface was investigated using nonionic surfactants. Of the surfactants investigated, octylphenol polyethylene oxide (OPEO) with a ethylene oxide chain length of 9 to 10 was found to be effective in controlling particle deposition. As shown in Figure 3, the surfactant did not

reverse the zeta potential of alumina from positive to negative; the beneficial effect was mainly due to steric repulsion.

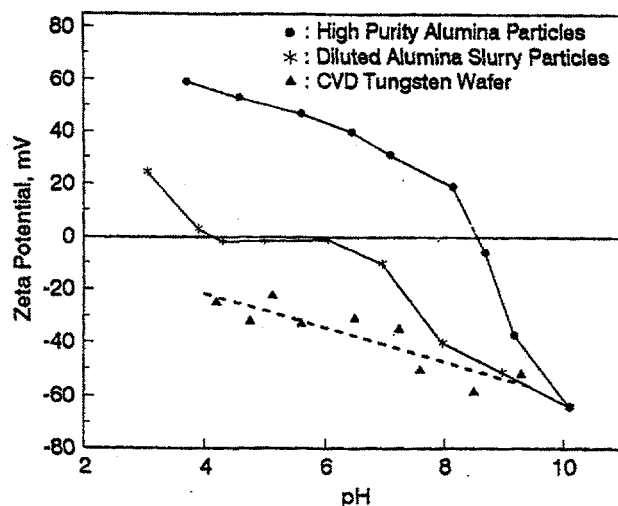


Figure 2. Zeta potential of LPCVD tungsten wafer and alumina particles in 0.001 M KCl solution as a function of pH.

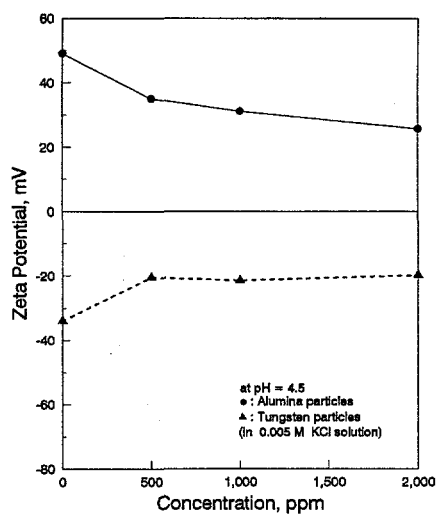


Figure 3. Zeta potential of tungsten and alumina particles as a function of OPEO ($n = 9.5$) concentration at a solution pH of 4.5.

4.0 CONCLUSIONS

Particle/wafer attraction and particle deposition were found to be consistent with electrostatic attraction forces for both oxide and tungsten wafers. Both AFM and electrokinetic techniques can be used to study the origins and magnitudes of particle/wafer interactions relevant, at the laboratory scale, to CMP processing. Electrostatic interactions are important in the adhesion of particles during CMP operations. It is possible to influence particle deposition by modifying the electrostatic charge characteristics of wafer or particle surfaces, or by introduction of a non-ionic surfactant. The processing implications of this work are: (1) the oxide polish/rinse/clean process should be maintained at high pH in order to minimize particle deposition (this has been observed experimentally [3]); (2) the effectiveness of nonionic surfactant additions to prevent particle deposition in polishing/cleaning solutions is dependent on the zeta potential of surfaces in the system at the working pH, and may require concentrations greater than 1000 ppm. These laboratory findings are being tested on full-scale polishing equipment.

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