

## Controlled Stabilization of Nanoparticulate Suspensions

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**ABSTRACT:** Stabilization of nanoparticulate systems in extreme processing environments requires new approaches. The increase in the total surface area of the nanoparticulate systems with the decrease in the particle size results in ineffective application of the conventional stabilization techniques, such as electrostatic stabilization and polymeric dispersion. In this investigation, self-assembled surfactant structures were utilized to stabilize nanosize silica suspensions at extreme environments of pH, ionic strength and reactive additives of the chemical mechanical polishing (CMP) process. The strong repulsive force barriers provided by the cationic surfactant stabilized the silica CMP slurries under high pH and ionic strength conditions. In addition, it was observed that stabilization must be achieved by controlling not only the particle-particle interactions but also the particle-substrate interactions, to meet CMP performance criteria. The knowledge base created in this investigation can be extended to the future stabilization requirements of the paint and paper production and mineral processing applications.

### 1 INTRODUCTION

Several emerging technologies such as chemical mechanical polishing (CMP), high speed coatings, inks, nanocomposites, and biomedical applications are increasingly relying on nanoparticulate dispersions to achieve optimum performance. Many of these technologies operate under extreme conditions such as high salt (CMP, biofluids in medical applications), high pressure (CMP, high speed coatings), and in the presence of complex additives (CMP, nanocomposites, bio applications).

Traditionally used dispersing methods such as electrostatic repulsion and steric stabilization using polymers may not perform adequately under severe processing conditions. Electrostatic repulsion is effective in stabilizing homogeneous, low ionic strength suspensions, where pH can be controlled in order to provide sufficient surface charge. The repulsive energy due to electrostatics decreases proportionally with particle size, and hence a greater surface potential is needed to disperse nanoparticles than relatively larger particles. This effect, coupled with the severe environment may be great enough that pH adjustment, or addition of inorganic dispersant such as sodium silicate, may not lead to suspension stability. In case of polymeric dispersants, polymer layers increase the effective volume fraction, and hence prevent the use of

nanoparticles in concentrated suspensions. Additionally, many polymeric dispersants are polyacrylate based and may perform poorly under extremes of pH and ionic strength. These limitations have motivated the search for alternative dispersants to stabilize suspensions in extreme environments and maintain fluidity in concentrated suspensions. Surfactants can provide a feasible alternative for stabilization of ultrafine particles under extreme conditions. The barrier to aggregation in presence of surfactant aggregates, measured using atomic force microscopy (AFM) was found to be several orders of magnitude higher as compared to barrier expected from electrostatic interactions alone. The onset of this barrier was correlated to dispersion of nanoparticles under extreme conditions. The results indicated that the strength of the barrier increased with increasing compactness of the adsorbed self-assembled surfactant structure at the solid-liquid interface (Adler et al., 2000).

' CMP process is a specific example in which stabilization has to be achieved under extreme chemical and dynamic environments. This process is widely used to achieve multi level metallization in microelectronic device manufacturing. Figure 1 schematically represents the CMP process. In CMP, the main objective is to planarize the metal or dielectric layers

deposited on the wafer surfaces by using slurries containing submicrometer size particles and chemicals. An effective polishing requires an optimal material removal rate with minimal surface deformation. Therefore, it is important to control the particle-substrate interactions that are responsible for the material removal and the particle-particle interactions, which control the slurry stability and consequently the defect density.

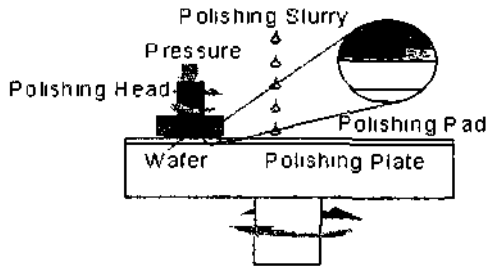


Figure 1. Schematic representation of CMP process.

It is suggested that a perfectly planarized surface with minimal deformation can be achieved by using monosized particulates (Cook, 1990). In practical applications, however, there may be oversized particles in the slurries in the form of larger size particles (hard agglomerates), or the agglomerates of the primary slurry particles (soft agglomerates). The polishing tests conducted in the presence of hard agglomerates (at parts per million concentration) verified a significant degradation in the polishing performance (Basim et al., 2000). The Atomic Force Microscopy (AFM) analysis showed increasing surface roughness and deformation (scratches and pit formations) on the wafer surfaces with significant variation in the material removal rate response. CMP slurries are filtered before polishing to remove hard agglomerates. Nevertheless, even after filtration significant defect counts have been observed on the polished surfaces (Ewasiuk et al., 1999). These are attributed to the possibility of particulate agglomeration during the polishing operations due to the local variations in the particle concentration, ionic strength or pH. Systematic analysis conducted in the presence of soft agglomerates showed significant surface deformations and variation in the material removal rates leading to the conclusion that the CMP slurries must remain stable to obtain optimal polishing performance (Basim & Moudgil, 2002).

The self-assembled structures of  $C_{12}$ TAB (cetyl trimethyl ammonium bromide), a cationic

surfactant, have been shown to provide stability to silica suspensions at high ionic strengths and extreme pH by introducing a strong repulsive force barrier (Singh et al., 2000). In the present study, this concept was utilized to stabilize the CMP slurry at high pH and salt concentration and under the applied pressure. It was observed that not only the particle-particle interactions but also the particle-substrate interactions must be taken into consideration in stabilizing the CMP slurries.

## 2 MATERIALS & METHODS

The baseline polishing slurries were prepared from 0.2Dm monosize sol-gel silica powder obtained from Geltech Corporation. Slurry pH was adjusted to 10.5 and the solids concentration was kept at 12wt.%. To stabilize the baseline slurry, dry silica powder was ultrasonicated in deionized water while maintaining the pH at 10.5 with NaOH addition. Preparation of the slurries from a dry powder was necessary to enable the control of system chemistry. To simulate the extreme CMP slurry environment, 0.6 M NaCl salt was added into the baseline slurry, which resulted in coagulation of the abrasive particles. Under these conditions,  $C_{12}$ TAB ( $n=8, 10, 12$ ) surfactants were added into the suspension. Particle size analyses of the slurries were conducted using Coulter LS 230 instrument utilizing light scattering technique with small volume module. The background water used to run the size analysis was prepared to have the same chemical composition as the modified slurries.

Polishing tests were performed on p-type silicon wafers on which a 2.0Dm thick  $SiO_2$  layer had been deposited by PECVD (supplied by Silicon Quest International). The 8-inch wafers were cut to square samples of 1.0 in. x 1.0 in. and Struers Rotopol 31 tabletop polisher was used for polishing with IC 1000/Suba IV stacked pads supplied by Rodel Inc. A grid-abrade diamond pad conditioner was utilized to abrade the pad before conducting each polishing test. The downforce was set to 7.0 psi ( $492 \text{ gr/cm}^2$ ) and the rotation speed was kept at 150 rpm both for the pad and the wafer. Slurry flow rate was 100 ml/min and polishing tests were conducted with 50ml slurries for 30 seconds. The thickness of the oxide film on the wafers was measured via spectroscopic ellipsometry method before and after polishing to calculate the material removal rate. Atomic Force Microscopy (AFM) technique was selected for the surface characterization of the polished wafers. For all the selected conditions, a minimum of four polishing tests were conducted and five 100m x10Dm size images were taken on each polished wafer to

evaluate the surface roughness and maximum surface deformation responses.

To measure the interparticle forces and the particle-substrate friction in the presence of surfactants, a silica particle was attached to the AFM tip. The details of the force and friction measurements with the AFM technique were discussed elsewhere in detail (Basim et al., 2003).

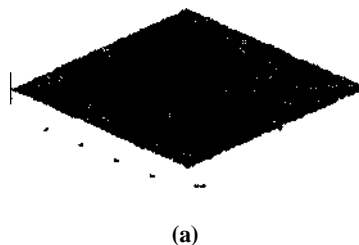
### 3 RESULTS & DISCUSSION

To stabilize the silica slurry in the presence of 0.6M NaCl at pH 10.5, C<sub>12</sub>TAB surfactant was used at 1, 8 and 32 mM concentrations according to the previous findings reported (Adler et al., Singh et al., 2000). The baseline polishing slurry contained 12wt%, 0.20μm monosize silica particles at pH 10.5. Addition of 0.6 M NaCl destabilized the particles by screening the surface charge. As a result, the mean particle size of the slurry increased to 4.30μm. When 1mM C<sub>12</sub>TAB was added into the coagulated slurry, the mean particle size was measured to be 4.8Dm. At 8mM C<sub>12</sub>TAB concentration, a jump was observed in the repulsive force barrier due to the formation of the self-assembled surfactant aggregates. The increase in the repulsive force barrier initiated the stabilization of the particles and the mean size of the slurry began to decrease (1.6Dm) with the addition of 8mM C<sub>12</sub>TAB. Finally, at 32mM C<sub>12</sub>TAB concentration, the high ionic strength polishing slurry was completely stable (mean particle size- 0.2 Dm) since a strong enough repulsive force barrier was reached for the particle-particle interactions.

Polishing experiments were conducted with the stable slurry to evaluate the CMP performance. Initially, surface quality response was analyzed in terms of surface roughness and maximum surface deformation by imaging the polished wafer surfaces using AFM technique. Slurries containing 0.6M NaCl resulted in 4.8nm surface roughness and 70nm deep pitting (maximum surface deformation) as compared to 0.85nm and 35nm obtained with the baseline slurry. The poor surface quality in the presence of salt was due to the coagulation of the slurry (Basim & Moudgil, 2002). Since the 1mM and 8mM C<sub>12</sub>TAB concentrations were not able to stabilize the slurries completely, surface qualities were also observed to be poor at these concentrations. However, when complete stabilization was reached with the addition of 32mM C<sub>12</sub>TAB at high ionic strength, surface roughness reduced to 1.5nm and the maximum surface deformation was recorded to be only 20nm. Figures 2-a and b illustrate the surface images of the wafers polished with the 0.6M NaCl containing unstable slurry and slurry stabilized by addition of 32mM

C<sub>12</sub>TAB in the presence of 0.6M NaCl.

To evaluate the overall polishing performance, material removal rate responses of the slurries were also measured simultaneously. Addition of 0.6M NaCl resulted in 7600 Å/min material removal rate as compared to the 4300 Å/min with the baseline pH 10.5 slurry. The increase in the material removal rate in the presence of salt is suggested to be due to the increased pad-particle-substrate interactions as a result of the screening of negative charges in the system. This phenomenon was reported to enhance the frictional forces by conducting in-situ friction force measurements (Mahajan et al., 1999). The increase in the friction forces is believed to result in enhanced material removal. When 1mM C<sub>12</sub>TAB was added to the high ionic strength slurry, the material removal rate decreased to 5500Å/min but still remained higher than the baseline result of 4300 Å/min. On the other hand, at 8mM and 32mM C<sub>12</sub>TAB concentrations a removal rate of only 70 Å/min was obtained. Two reasons can be suggested for the negligible material removal in the presence of 8 and 32mM C<sub>12</sub>TAB. First, it is known that the presence of surfactants in the system results in lubrication between the abrasive and the surface to be polished and therefore decreases the frictional force (Klein et al., 1994). Therefore, the addition of C<sub>12</sub>TAB in the polishing slurries at relatively high concentrations may be resulting in negligible material removal by reducing the frictional forces required for polishing. Second alternative is that, the high repulsive force barrier induced by the C<sub>12</sub>TAB self-aggregated structures may be preventing the particle-surface interaction and therefore resulting in a very low material removal rate. The concentration of C<sub>12</sub>TAB, where negligible material removal rate response was obtained coincides with the observation of the jump in the maximum repulsive force barrier as described previously (Adler et al., Singh et al., 2000).



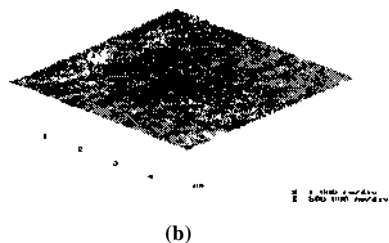


Figure 2. Atomic Force Microscopy images of the wafers polished with (a) 0.6M NaCl containing unstable slurry and (b) 0.6M NaCl + 32mM C<sub>12</sub>TAB containing stable slurry.

In order to distinguish the effect of lubrication and the repulsive force barrier on material removal response, it was planned to alter the magnitude of the repulsive force barrier. Accordingly, the force barriers of different chain lengths of the CTAB surfactant were measured by AFM above the critical micelle concentration (CMC), where they form the self-assembled structures. The repulsive force barriers created on a 0.2Dm particle by C<sub>12</sub>TAB, C<sub>10</sub>TAB and C<sub>8</sub>TAB surfactants at 32, 68 and 140mM concentrations in the presence of 0.6M NaCl at pH 9 were 0, 2.2 and 6 nN respectively (Basim et al., 2003). This finding indicates that decreasing the chain length of the surfactant leads to a smaller repulsive barrier. In agreement with the measured force barrier values, none of the slurries prepared by the C<sub>8</sub>TAB surfactant, which gave the minimum repulsive barrier, (at 1mM, 35mM and 140mM concentrations) were stable. Therefore, the maximum surface deformation values were higher than desired (50-60nm). On the other hand, the surface roughness values were reasonable (-0.9 nm), which may be attributed to the decreased frictional forces due to the lubrication introduced by the surfactant molecules (Xiao et al., 1996). Most importantly, all the C<sub>8</sub>TAB containing slurries yielded high material removal rates (6000-7000 Å/min). Finally, when C<sub>10</sub>TAB surfactant was added into the unstable slurry, stability was reached at 68mM concentration but the material removal rate was only 500 Å/min. It was observed that the stability responses obtained as a function of surfactant chain length strongly correlated with the measured force barrier values. However, to evaluate the impact of the repulsive force barrier on particle-substrate interactions, or in other words the material removal response, it was necessary to know the force applied on a single abrasive particle during polishing. This value was calculated to be 750+150 nN for a 0.2Dm size

particle by determining the pad-substrate contact area at the applied head pressure and the particle concentration at the area of contact of the pad (Basim et al., 2003). Since the measured force barriers for all the CTAB surfactants were much less than this value, the pressure applied per particle is expected to easily overcome the repulsion introduced by the self-assembled CTAB aggregates. Hence, it was more likely that the lubrication effects introduced by the surfactants controlled the material removal by varying the frictional forces between the abrasive particles and the substrate.

In order to understand the surfactant lubrication effect on material removal rate at particle-wafer interaction level, AFM friction force measurements were conducted. A silica particle attached to the cantilever tip was made to raster on the silica wafer surface in the presence of surfactants to simulate the single particle-wafer interaction. The preliminary analysis showed a significant decrease in the friction coefficient of the particle-substrate interaction in the presence of the C<sub>12</sub>TAB surfactant. Figure 3 illustrates the AFM friction force measurements in the absence and presence of C<sub>12</sub>TAB and 0.6 M NaCl. The measurement of the lateral friction force as a function of the normal load was conducted from which friction coefficient was calculated based on the Amonton's law. It can be seen that for baseline solution, frictional forces increased with an increase in normal forces. On the other hand, with the C<sub>12</sub>TAB addition, the frictional interactions were minimal.

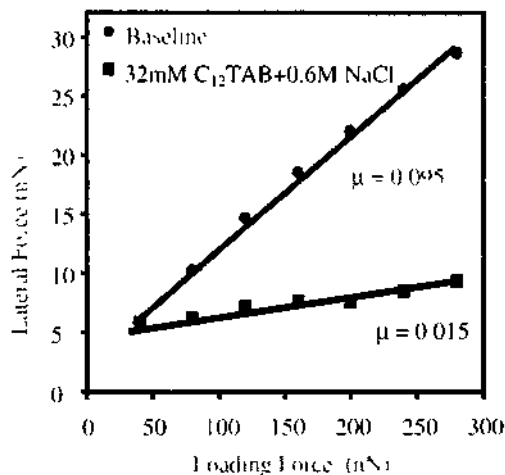


Figure 3. Atomic Force Microscopy friction coefficient measurements with baseline pH 9 solution and 0.6M NaCl + 32mM C<sub>12</sub>TAB solution.

When the friction measurements were conducted on the baseline (pH=10.5) and surfactant mediated solutions in the absence of NaCl (140, 68 and 32 mM, C<sub>8</sub>TAB, C<sub>12</sub>TAB and C<sub>18</sub>TAB), it was observed that all the surfactant mediated slurries resulted in minimal friction. Indeed, when polishing experiments were conducted at the corresponding surfactant concentrations in the absence of NaCl, the material removal rate values were observed to be negligible for all the chain lengths (61, 53 and 56 Å/min for C<sub>8</sub>TAB, C<sub>12</sub>TAB and C<sub>18</sub>TAB, respectively). This result indicated that at any chain length, CTAB surfactant was able to form a lubrication layer in the absence of salt. Consequently, minimal particle-surface interactions occurred in these systems resulting in negligible material removal. It is also important to note that all the slurries were stable without salt addition.

The polishing results in the presence of 0.6 M NaCl, however, showed an increase in the material removal with decreasing chain length of the surfactant (66, 650 and 6167 Å/min for C<sub>12</sub>TAB, C<sub>18</sub>TAB and C<sub>8</sub>TAB, respectively). When AFM friction force measurements were conducted in the presence of salt, an interesting behavior was observed. It was observed that C<sub>8</sub>TAB and C<sub>18</sub>TAB mediated solutions started to exhibit higher friction values above 750 nN. This type of a behavior was also observed on the mica surfaces modified with 2, 5, 7 and 17 chain lengths alkylsilanes (Xiao et al., 1996). It appears that the lubricating surfactant layer is desorbed/destroyed beyond a certain loading force. In the absence of salt, all the surfactants, regardless of the chain length, seems to form a compact adhesion layer due to the electrostatic interaction between the negatively charged silica surface and positively charged surfactant head group. However, the addition of salt appears to screen the electrostatic interactions thereby resulting in weaker adhesion of the adsorbed surfactant layer and possibly desorption of this layer above a certain applied load (Chen et al., 1992). The impact of salt molecules was less effective on the longer chain length surfactants, perhaps due to their ability to form more densely packed and well-ordered layers (Xiao et al., 1996). As the length of the hydrocarbon chain increases, the lateral interactions between the hydrocarbon chains become more pronounced resulting in formation of more compact layers. In addition, the driving force for the surfactant adsorption on the substrate surface also increases with the increased chain length, resulting in denser surfactant layer (Clear & Nealey, 1999).

Thus, it is possible that NaCl addition does not affect the lubrication layers created by C<sub>12</sub>TAB mediated slurries to the same extent as surfactants with shorter chain lengths. Accordingly, C<sub>8</sub>TAB yielded negligible material removal of 66 Å/min, whereas the shorter chain length C<sub>18</sub>TAB surfactant, resulted in material removal of 650 Å/min indicating that the silica particles were able to engage with the silica wafer surface up to some extent due to the removal of the surfactant. Finally, QTAB mediated slurries also showed an increase in the frictional forces at single particle-surface interaction level, suggesting that they as well should polish the silica surface. However, the significantly high removal rate for the C<sub>18</sub>TAB mediated slurries (5167 Å/min) should be attributed not only to the easier removal of the loosely packed 8-carbon chain surfactant layer from the wafer surface under applied load, but also to the coagulation of the particulates in the absence of a repulsive force barrier for QTAB at 0.6 M salt concentration resulting in more mechanical interactions.

#### 4 CONCLUSIONS

Robust dispersion of the CMP slurries in extreme ionic strength and high pH environments is a must for optimal polishing performance, which requires the introduction of high enough repulsive forces between the slurry particulates. However, in this study, it was observed that to design optimally performing CMP slurries, the control of particle-particle interactions is not sufficient as it has been in other applications. To enable an optimal material removal rate, it is also necessary to achieve sufficient particle-substrate interactions. In summary, the stability of the CMP slurries must be tailored by controlling both the lateral (particle-particle) and normal (particle-wafer surface) interactions and this can be achieved by utilizing self-assembled surfactant structures and manipulating the frictional interactions by changing the surfactant chain length and slurry ionic strength.

#### ACKNOWLEDGMENTS

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