Self-Assemble Surfactant Structure Mediated Nanotribology for CMP Applications

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ABSTRACT

An atomic force microscope (AFM) was used to simulate the abrasive particles/surface interaction in the chemical mechanical polishing (CMP) process. Lateral forces measurements were performed between a silica particle and a silica wafer at the presence of surfactant dispersants and at pressures close to that exhibited in the CMP. In our previous study we have shown that the surfactant dispersants were effective at stabilizing the slurries but at the same time the material removal rate was negligible. The lateral force measurement reviled that the low removal rate is due to the boundary lubrication provided by the residing surfactant between the particles and the wafer. We showed that is possible to manipulate range in which the boundary lubrication is effective by simply changing the solution conditions as pH and electrolyte concentration. Base on that general founding we tried to push down the lubrication effectiveness limit by adding different type of counterions to the solution. A dramatic increase in the frictional force was found in the presence of multivalent counterions. Polishing test at that slurry conditions showed high material removal rate and at the same time the slurry were stable resulting at good surface finishing.

KEYWORDS
chemical mechanical polishing, lateral forces microscopy, surfactants

INTRODUCTION

The continuous developments in microelectronics device manufacturing necessitates the use of effective planarization techniques for successful deposition of metal and dielectric layers. Chemical mechanical polishing is preferred for planarization since it enables global planarity on the wafer surface, in spite of the fact that its fundamentals still need to be extensively studied. As the material removal and defect formation have to be controlled more precisely for the smaller device dimensions, it becomes important to create the knowledge base that will allow manipulation of the process for the requirements of the selected application.

CMP process has three primary components including the wafer surface (on which the microelectronic devices are built), the polymeric polishing pad and the
polishing slurry made of submicron size particles and chemicals. Polishing occurs as the slurry flows between the two rotating platens holding the wafer and the polishing pad. The ultimate goal of CMP is to achieve an optimal material removal rate while creating an atomically smooth surface finish with minimal number of defects. This can be accomplished by controlling the particle-substrate interactions leading to material removal as well as the particle-particle interactions controlling the slurry stability.

Self-assembled surfactant structures are dynamically formed at the solid-liquid interface from surfactant solutions at concentrations close or sometimes well below the critical micelle concentration (CMC). These structures allow surfactants to be effective dispersants under extreme conditions where traditional dispersion methods (i.e. electrostatic, polymeric, etc.) fail. Extremes in pH, electrolyte concentration and mechanical force are typically found in CMP processes. The physiochemical interactions of the dispersant molecules with the surface have a profound impact not only on the surface-finish quality but also on the material removal rates achievable in the process. The dispersant’s effectiveness for maintaining stability—and thereby surface quality—depends on the magnitude of the steric repulsive barrier manifested by the surfactant structures. In previous studies we have probed the solution conditions that regulate the magnitude of these barriers.\textsuperscript{1,2} In continuation of this work, the lateral interaction between a particle and a substrate under various solution conditions were probed using an atomic force microscope (AFM). This has allowed us to begin to understand the chemotribological synergism between dispersant chemistry and surface removal rate.

EXPERIMENTAL

Materials

Dodecyltrimethylammonium bromide and hexadecyltrimethylammonium (C\textsubscript{12}TAB and C\textsubscript{16}TAB) surfactants were obtained from Aldrich Chemical Co. and were at least 99% pure. NaCl, employed was of analytical grade and roasted for 4 hours at 400°C to remove organic contaminants. A silicon wafer with a 2 \textmu m thick coating of CVD silica was supplied by Silicon Quest International. The root mean square (RMS) roughness of the silica, as measured by AFM, was between 0.3-0.4 nm. 7.5 \textmu m monodispersed nonporous silica spheres were purchased from Bangs Laboratories Ltd. The water for all experiments was produced by a Nanopure filtration system and had an internal specific resistance less than 18.2 M\Omega.

Methods

All measurements were made using a Digital Instruments Nanoscope III multimode atomic force microscope equipped with a fused silica liquid cell. Rectangular tipless cantilevers (MikroMasch) with a normal spring constant in the range of $K_N = 2.8 \pm 0.3$ N/m were used for all experiments. The exact values of the normal spring constants were determined by the frequency method. Silica particles were attached to the cantilever end using a small amount of high temperature melting epoxy (Shell Epikote 1009).
Forces normal to the flat surface were measured according to the method introduced by Ducker et al.

The frictional force measurements were performed using the “friction force” mode of the AFM. In this mode the colloidal probe is pressed against the substrate at a constant applied load while the substrate slides horizontally underneath the cantilever. Further details of the measurement procedure are given elsewhere. The magnitude of the lateral frictional force, $F_L$, was determined from half of the difference in the lateral force detector signal in one complete scan (cycle). The lateral sensitivity of the detector $S_L = 3.1 \times 10^{-4}$ rad/V was determined using the method of Meurk et al. $K_L = 11.0 \pm 1.3$ nNm/rad was calculated from the experimental value of the normal spring and the cantilever dimensions.

Before each experiment the silica wafer samples were rigorously washed with acetone, ethanol and boiled for four hours in Nanopure DI water. Colloidal probes were washed in ethanol and exposed for one hour to a short wave UV source. All experiments were done at a room temperature of approximately 23°C.

Each experimental series is taken at a fixed position on the sample. After each increase in the normal force, ten friction force cycles were allowed to transpire in order to allow the lateral force magnitude to stabilize prior to taking a reading. Consecutive runs taken over different areas show good reproducibility with a maximum deviation of about ±5%. It should be noted that the experimental results from different probes have similar features with regards to lateral and adhesive force interactions under the given solution conditions, although some difference in the magnitude might appear.

RESULTS AND DISCUSSIONS

Polishing performance and lubrication effect

In previous studies, self-assembled surfactant structures have been shown to impart stability in colloidal systems in extreme chemical environments where the more traditional electrostatic stabilization and polymeric dispersion techniques may not perform adequately (Adler, et al, 2000). Self-assembled structures of C$_{12}$TAB a cationic surfactant, have been demonstrated to prevent agglomeration in silica suspensions at extremes in ionic strength and pH. The efficacy of C$_{12}$TAB surfactant as a dispersant under CMP conditions, as well as its impact on CMP performance was subsequently investigated (Basim, et al., 2003). The surface quality response of wafers polished with C$_{12}$TAB mediated slurries was observed to be optimal with minimal surface roughness and deformation. However, material removal rate was determined to be only 70 Å/min—an unacceptable value. This observation made it clear that there was more to slurry performance than its stability alone. Initially it was suspected that the micellar aggregates that promote stability were strong enough to inhibit surface engagement; however, it was later found that the force per particle experienced during polishing (~750±150 nN) was two orders in magnitude greater than the force required to destroy these adsorbed micellar structures. Therefore, the reduction in material removal rate has been attributed to a boundary layer lubrication effect imparted by the individual dispersant molecules. Figure 1 shows the lateral versus normal force response of the baseline (pH=10.5) and
surfactant mediated solutions without added salt (140, 68 and 32 mM, C₈TAB, C₁₀TAB and C₁₂TAB). It can be seen that for the baseline solution, the friction force increases with the increasing normal loads. On the other hand, the extent of friction in the surfactant mediated slurries in the absence of salt remained nearly constant. Polishing experiments conducted at the given concentrations of these surfactants in the absence of NaCl have confirmed these results. Negligible material removal rates were found in all cases (61, 53 and 56 Å/min for C₈TAB, C₁₀TAB and C₁₂TAB, respectively).

Figure 1. Frictional force in surfactant solutions without salt. Reproduced with permeation from (Basim, et al., 2003a)

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 5167 Å/min for C₁₂TAB, C₁₀TAB and C₈TAB, respectively). When AFM friction force measurements were conducted in the presence of salt, an interesting behavior was observed. It can be seen in Figure 2 that, C₈TAB and C₁₀TAB mediated solutions started to exhibit higher friction values above 750 nN. 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, form a compact adhesion layer due to the electrostatic interaction between the negatively charged silica surface and positively charged surfactant head group. However, addition of salt resulted in competitive adsorption of the salt molecules, weakening the adsorbed surfactant and hence possibly desorbing the surfactant lubrication layers above a certain applied load. The impact of competitive adsorption of the salt molecules was less effective on the longer chain length surfactants, perhaps due to their ability to form more densely packed and well-ordered
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 strength of adsorption of the surfactant at the interface also increases with the increased chain length, resulting in denser adsorption of the surfactant. Thus, it is possible that NaCl addition does not affect the lubrication layers created by C_{12}TAB mediated slurries to the same extent as surfactants with shorter chain lengths as seen in Figure 2. Accordingly, C_{12}TAB yielded negligible material removal of 66 Å/min, whereas the shorter chain length C_{10}TAB surfactant, resulted in material removal of 650 Å/min indicating that the slurry silica particles were able to engage with the silica wafer surface up to some extent due to the removal of the surfactant. C_{8}TAB 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_{8}TAB mediated slurries (5167 Å/min) should be attributed not only to easier removal of the loosely packed 8-carbon chain surfactant layer but also to the increase in abrasive particle size due to the absence of a repulsive force barrier for C_{8}TAB at 0.6 M salt concentration.

Figure 2. Frictional force in surfactant solutions with added salt. Reproduced with permeation from (Basim, et al., 2003)
Manipulation of the surfactant mediated friction

It has become evident that an appreciable frictional interaction between slurry particles and the wafer surface is a fundamental requirement for material removal. In that section we tailor the lubrication effects in conditions different from the conditions of the CMP slurries (high pH and electrolyte concentration). The results shown in Figures 3 and 4 respectively indicate that by manipulating the amount of salt or the pH of the solution phase the friction between silica surfaces in the presence of surfactant can be altered (Vakarelski, et al., 2004).

![Figure 3. Effect of the added electrolyte. Reproduced with permeation from (Vakarelski, et al., 2004)](image)

As in the previous polishing experiments, 32mM of C_{12}TAB was used as the dispersing surfactant. The friction force versus loading force for deionized water at a pH of 5.6 is given to represent the engagement of silica surfaces under natural condition in the absence of surfactant. The results illustrate that in the presence of surfactant there exists a critical loading force at which the friction coefficient changes from essentially zero to some finite value, indicative of a change in the state of surface engagement. Additionally, the loading force at which this occurs is shown to decrease with an increase in the amount of monovalent electrolyte or a decrease in pH. It is known that the number of negatively-charged, electrostatic adsorption sites on silica decreases with pH and that the number of ions competing for these sites increases with electrolyte concentration. Therefore, it was speculated that residual surfactant monomer were more easily desorbed
from the surface at lower pH values and under higher salt concentration—possibly resulting in the higher frictional forces experienced under these solution conditions.

Figure 4. Effect of the solution pH. Reproduced with permeation from (Vakarelski, et al., 2004)

To enhance the frictional engagement between the silica surfaces in the presence of surfactant, several ions of different states of hydration and valences were screened. As indicated by results in the previous sections, it was imperative that these ions did not cause coagulation in the slurry. Secondly, the ions should allow for significant material removal at the same ionic strength (0.6M) of the salt in the negligible-polishing slurries—as an indicator of performance. From these initial investigations, it was found that multivalent ions could significantly enhance the polishing performance of silica.

The surfactant-stabilized slurries with added multivalent ions shown to have higher removal rates and improved surface finish in comparison to baseline slurry and the surfactant-mediated slurries containing NaCl. This is preposed to be due to a bridging mechanism (enhance adhesion) between the silica surfaces mediated by the multivalent ion in the absence of surfactant causing additional wear. Furthermore, by changing the multivalent ions content in the formulation both the material removal rate and the onset of increased friction can be changed as indicated in Figure 5. This illustrates that by altering the concentration of competitive ions in the slurry solution, the material removal rates and possibly the planarity of these systems can be manipulated. Further details on the multivalent ions effect will be published elsewhere.
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 maybe in other applications. To enable an optimal material removal rate, it is also necessary to have the abrasive particles engage with the substrate. It has been shown that the particle-substrate interaction forces could be modified by addition of surfactants to the slurries, which tend to form a lubrication layer on the wafer surface and vary the material removal response. The adsorption/desorption of the surfactant molecules were observed to be a function of the slurry ionic strength and the applied normal forces. In summary, it was observed that the stability of the CMP slurries must be tailored by controlling both the lateral (particle-
particle) and normal (particle-wafer surface) interactions, which can be manipulated by varying the surfactant chain length, slurry ionic strength and the valence of the added salt.

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REFERENCES


