Study of Inhibition Characteristics of Slurry Additives in Copper CMP using Force Spectroscopy

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Using a reference slurry, ammonium dodecyl sulfate (ADS), an anionic and environmentally friendly surfactant, was investigated as an alternative to BTA for its inhibition and lubrication characteristics. Results demonstrated that the inhibition efficiency of ADS was superior to that of BTA. Coefficient of friction (COF) was the lowest when the slurry contained ADS. This suggested that adsorbed ADS on the surface provided lubricating action thereby reducing the wear between the contacting surfaces. Temperature results were consistent with the COF and removal rate data. ADS showed the lowest temperature rise again confirming the softening effect of the adsorbed surfactant layer and less energy dissipation due to friction. Spectral analysis of shear force showed that increasing the pad-wafer sliding velocity at constant wafer pressure shifted the high frequency spectral peaks to lower frequencies while increasing the variance of the frictional force. Addition of ADS reduced the fluctuating component of the shear force and the extent of the pre-existing stick-slip phenomena caused by the kinematics of the process and collision event between pad asperities with the wafer. By contrast, in the case of BTA, there were no such observed benefits but instead undesirable effects were seen at some polishing conditions. This work underscored the importance of real-time force spectroscopy in elucidating the adsorption, lubrication and inhibition of additives in slurries in CMP.

Keywords : Chemical mechanical planarization(CMP), Inhibitors, Surfactants, Force spectroscopy

1. INTRODUCTION

Chemical Mechanical Planarization (CMP) of copper has emerged as a critical component for the fabrication of integrated circuits.[1] Several studies have been carried out to study the effect of inhibitors on copper CMP[1-5]. Deshpande *et al* examined the effect of benzotriazole (BTA) as inhibiting agent in the presence of hydrogen peroxide and glycine at low pH[1]. Attempts have been made to elucidate the mechanism of copper removal in the presence of oxidizer, complexing agent and Inhibitor[4]. Recent work[2] has shown that the inhibition characteristic of copper dissolution by sodium dodecyl sulfate (SDS) was better than that of BTA. It has been demonstrated that ammonium dodecyl sulfate, an environmentally friendly surfactant, can be used as an efficient corrosion inhibitor for Electrochemical Mechanical Planarization of copper in solutions containing hydrogen peroxide and glycine solutions[3]. Surfactants have also been investigated for their effect on dishing and polishing speed[5].

In this study, using a reference slurry, ammonium dodecyl sulfate (ADS), an anionic and environmentally friendly surfactant, was investigated as an alternative to BTA for its inhibition and lubrication characteristics. Measured parameters included real-time mean and fluctuating component of frictional force (both in terms of average shear force and variance) at the pad wafer interface, pad surface temperature and average copper removal rate. Spectral analysis (in frequency domain) of the shear force data was employed to determine the inhibition and lubrication of the additives in the slurry.

2. EXPERIMENTAL PROCEDURE

Three different types of slurries were tested, which were based on a reference slurry to which 3.0 mM concentration of ADS or BTA was added. The reference slurry was comprised of 1 percent by weight glycine, 5 percent by weight H_2O_2 and 3 percent by weight fumed silica at a solution pH of 4.0. The pH of the slurry was adjusted by the addition of dilute perchloric acid ($HClO_4$). Slurries, prepared with UPW and reagent grade chemicals, were tested for copper removal rate, thermal and frictional characteristics. In all cases, Rohm and Haas IC1000 K-groove pad was used to polish 200 mm electroplated blanket copper wafers. Copper removal rate was calculated by measuring wafer weight before and after polishing using a microbalance. Pad surface temperature was recorded by an infrared camera (Agema 550 infrared thermal imaging camera) which took three thermal images every second. Pad temperatures at five locations outside the leading edge of the wafer carrier were averaged throughout the polishing process to report the mean pad leading temperatures. The polisher and associated accessories are described elsewhere[6]. Shear force was measured with a precision of ± 10 percent using load cells which were attached to strain gauge amplifiers that would send voltage to a data acquisition board. Experimental procedure consisted of 30-minute initial diamond conditioning (100-grit TBW diamond disc) with UPW at a pressure of 0.4 PSI, rotational velocity of 30 RPM and oscillation frequency of 20 per minute. Conditioning was followed by a 5-min pad break-in with the reference slurry. The same rotational velocity and oscillation frequency were used for in-situ pad conditioning. Two sliding velocities, 0.31 and 0.94 m/s, were used in the study. Both wafer and pad rotated in the counter-clockwise direction during polishing. Polishing pressure was kept constant at 2 PSI. Slurry was injected at the center of the pad and the flow rate was maintained constant at 200 cc/min. Two wafers were polished at each polishing condition and average values are presented everywhere.

3. RESULTS AND DISCUSSION

3.1 Removal rate analysis

The effectiveness of ADS in suppressing copper removal by mechanical polishing is compared with that of BTA as a function of polishing power. Figure 1(a) illustrates the mean removal rate of copper for reference slurry with and without BTA or ADS at additive concentration of 3.0 mM. This representation is followed in all the figures. The reference slurry exhibits the highest removal rate as expected. Addition of ADS or BTA reduces the removal rate thereby confirming the inhibition characteristics of the additives. The removal rate with ADS containing slurry is lower than that of BTA for both concentrations and polishing conditions establishing ADS to be a superior inhibitor than BTA. It has been reported that adsorption of ADS, which exhibits adsorption properties on metals very similar to those of SDS, is expected to follow the simple Langmuir or Frumkin type behavior on copper[7] and an electrostatic physisorption mechanism is likely to dominate over the chemisorption process[8]. The ionic head group of ADS ensures strong interaction with the copper and the hydrophobic tail acts as an effective barrier to diffusion of oxidants to the reacting surface. BTA, being a non-linear molecule may not form a complete closed packed adsorbed layer as ADS and hence provides deeper interaction zone. Based on removal rate results it appears that at 3.0 mM concentration of ADS the surface coverage is complete and there is sufficient availability of species for adsorption on the metal/metal oxide surface which results in significant suppression of removal of copper from the surface.

3.2 Frictional and thermal analysis

Figure 1(b) shows the mean coefficient of friction (COF) vs. V/p, a representative of the Sommerfeld number[9], where V is the sliding velocity and p is the polishing pressure. Results indicate that COF remains relatively constant for reference and ADS containing slurry, indicating boundary lubrication, and decreases for the slurry containing BTA where a transition from boundary lubrication to partial lubrication may be taking place[9]. It is possible that at lower velocity where boundary lubrication exists and pad-wafer interface is devoid of BTA containing liquid layer, the adsorbate films cannot equilibrate under sliding conditions. Therefore the COF determined is not the true COF of adsorbed BTA. At some higher transition velocity, the fluid film thickness increases which ensures the availability of BTA which replenishes a friction-damaged adsorbate film under the conditions of repetitive sliding contact, as observed at 3.0 mM BTA concentration, causing the COF

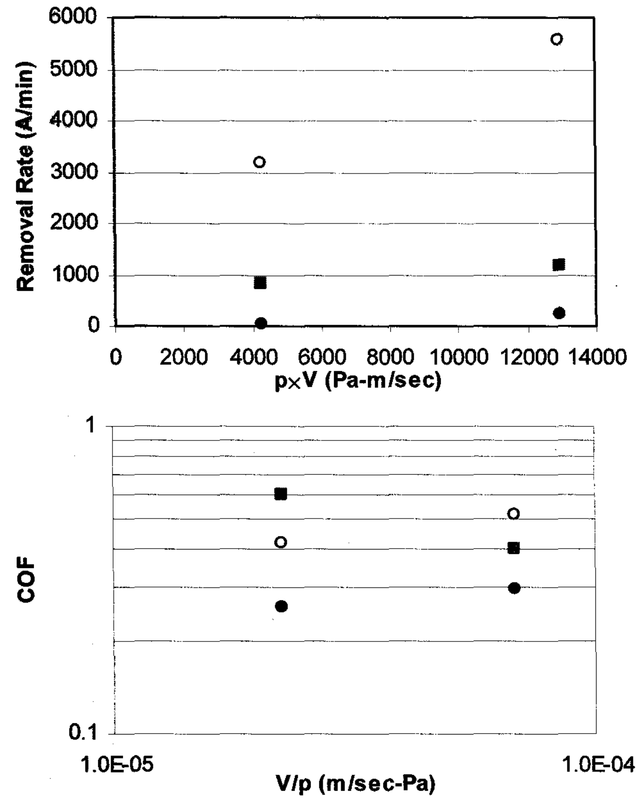

Fig. 1. Removal rate (top, a) and COF (bottom, b). Open circles represent reference slurry, filled circles represent reference slurry with 3.0 mM ADS concentration and squares denote reference slurry with 3.0 mM BTA.

to drop. The key point to note is the reduction in COF with the addition of 3.0 mM concentration of ADS. This suggests that adsorbed ADS provides lubricating action at the pad wafer interface by reducing the shear force and protecting the wafer and pad from chemical and mechanical wear. This lubricating effect is probably caused by the formation of low shear strength interface between the opposing surfaces[10]. On the other hand, at lower velocity addition of BTA to the reference slurry increases the shear force between the pad and the wafer surface and therefore results in higher energy dissipation due to friction. At higher velocity some benefits are observed with BTA but not as significant as with ADS. It is obvious that molecular structure or shape of the adsorbate has a strong influence on the effectiveness of lubrication. Presence of polar group, as in ADS, ensures strong adhesion to the metallic copper surface and long linear hydrophobic chain provides closed packed monolayers.

Figure 2(a) shows the measured mean pad leading temperature for slurries at different polishing conditions. As one can notice, the mean pad leading temperature increases with the polishing power as expected. It is interesting to note that ADS containing slurry shows the lowest mean pad leading temperature. Therefore addition of ADS lowers the friction force at the pad wafer surface due to its lubricating effect and consequently offers relatively lower temperature rise during polishing. This confirms the consistency in removal rate, COF and temperature results for ADS which exhibits its effect by formation of adsorbed barrier layer supplemented by reduction in both mechanical and chemical (by lowering the temperature) contributors to the removal rate of copper. In the case of BTA at lower velocity, it appears that the inhibition characteristics of BTA is predominantly by preventing the diffusion of the chemicals and oxidizers through formation of a barrier layer at the reacting surface and not by reduction in mechanical or thermal effects. Borucki et al have discussed the effect of viscous shear forces to the total shear force in the nanolubrication layer[11] which may exists for the ADS containing slurry. It was hypothesized that thermal softening of the asperity tip can increase the viscous element of the COF by decreasing pad modulus. The viscous contribution to the COF may therefore not only be partially contributory in creating a temperature increase but will also be affected by it. This effect may, to some extent, be observed in our

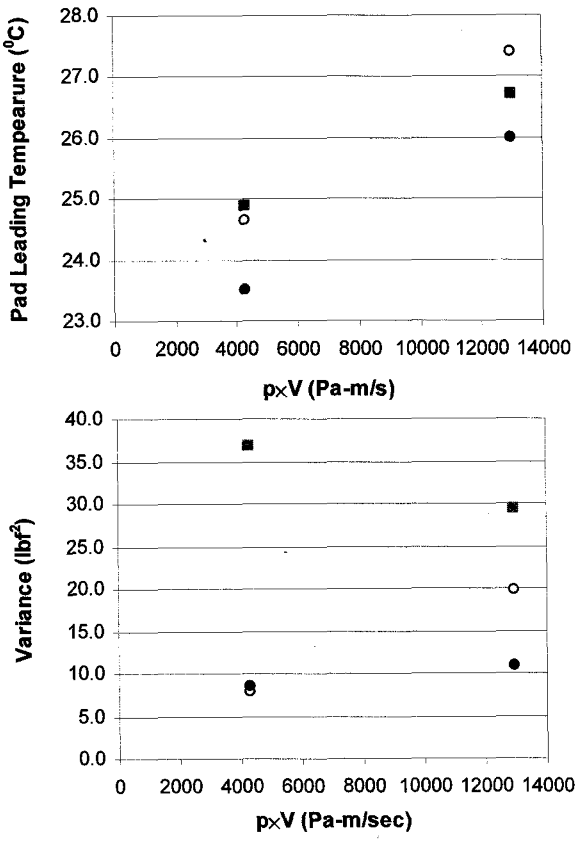

Fig. 2. Pad leading temperature (top, a) and Variance of shear force (bottom, b). Open circles represent reference slurry, filled circles represent reference slurry with 3.0 mM ADS concentration and squares denote reference slurry with 3.0 mM BTA

case of reference and ADS containing slurry where we observe a slight increase in COF with increasing velocity.

3.3 Shear force variance and spectra

In addition to removal rate, COF and temperature data, the variance of the shear force as well as its spectral characteristics may be used to further explore the adsorption, lubrication and inhibition of additives during CMP. The unidirectional shear force can be separated into two components, a mean component and a fluctuating component. Figure 2(b) summarizes the mean variance corresponding to all process conditions based on measured values of shear force (a total of 50,000 measured values per run). Results indicate that at higher sliding velocity, addition of BTA increases the variance of the shear force. On the other hand, addition of ADS reduces the extent of irregularity in the shear force. This signifies the dynamic nature of adsorption during the polishing process. The rate limiting step in the formation of an adsorbate film under sliding conditions is believed to be re-adsorption and typical uniqueness of the additive is required for this process to occur within the time available between successive sliding contacts[10]. ADS reduces this unsteady condition and hence lowers the variance of shear force in the polishing process. However, in the case of BTA it appears that it is the intrinsic characteristic of the molecule itself that creates the instability in the process. Hence BTA containing slurry exhibits large oscillations in the friction force demonstrating higher variability and unevenness of the system. Similar trends are noticed for BTA at lower polishing condition. At this condition, the variance of shear force for reference slurry is sufficiently low and therefore addition of ADS does not produce any further benefit. Variance has also been demonstrated to be a useful parameter in determining the lubrication regime as suggested from consistency in trends in COF and variance results[12].

The Fast Fourier Transform function is then utilized to convert measured shear force from time domain to frequency domain[13]. Normalized spectral amplitudes plots for different slurries at lower polishing power are shown in Fig. 3. The slurries at lower polishing power exhibit dominant peaks between 0-12 Hz and 40-60 Hz. Some of these peaks are assumed to be associated with stick-slip phenomena occurring due to fundamental processes at the microscopic (such as adsorption or desorption of surface active agents at an interface) and macroscopic (such as collision of wafer's advancing edge with neighboring grooves) level. Though these peaks normally signify elementary occurrences in the process, growth of these peaks can stipulate enhanced vibrations in the polishing process causing increased friction, wear and instability. On the other hand, suppression of these peaks suggests subdued vibrations thus resulting in smoother polishing. The emergence of peaks at lower frequencies (less than 12 Hz) is caused by the kinematics of the process including the rotational velocity of the platen, wafer and conditioner as well as by the collision event of groove and pad asperities with

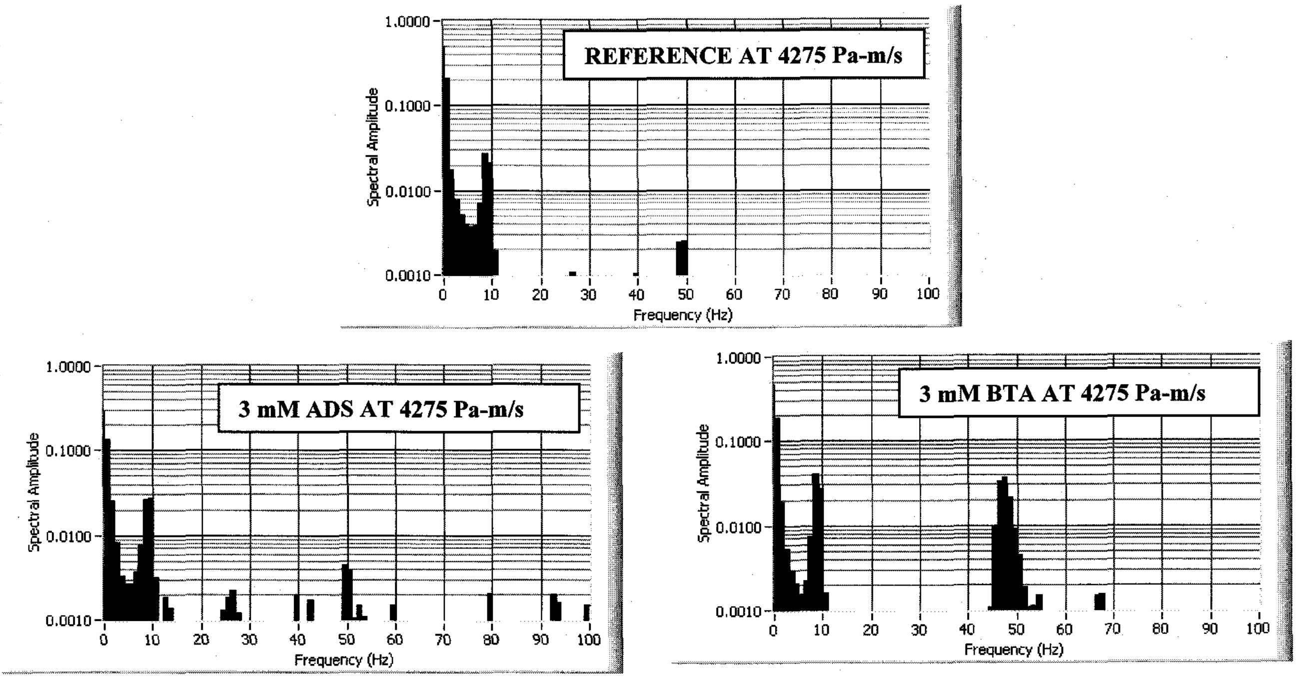

Fig. 3. Stick-Slip phenomena distribution in frequency domain for investigated slurries at relative pad wafer sliding velocity of 0.31 m/s.

polished wafer. The other frequencies with lower spectral amplitude may be considered as noise of the polish process that has no significant implication.

The high frictional characteristic of the BTA is evident from Fig. 3 where addition of BTA transforms high frequency spectral peaks. In the presence of BTA these spectral peaks (40-60 Hz) grow and become outsized indicating high variance, shear force and unsteadiness in the process. Conversely, addition of ADS does not significantly alter the spectra. However, one can notice development of low amplitude peaks at different frequencies which may be reflective of different mechanistic microscopic behavior exhibited by ADS, due to its inherent surface active attributes. Currently there is not enough information to predict these phenomena and further investigation will be required to explore the details. Normalized spectral amplitudes plots at higher polishing power are shown in Fig. 4. Increasing polishing power shifts the spectral peaks from higher frequency to lower frequency regime. Therefore, on comparing spectral peaks at the two different polishing powers, one can observe an increase in population of peaks at frequency lesser than 12 Hz at higher polishing power. As mentioned earlier, these peaks below 12 Hz, are caused by the kinematics of the process and therefore it is typical to detect an increase in peak masses with an increase in the polishing power or relative pad wafer sliding velocity. However, unfortunately these lower frequency high amplitude peaks restrain the appearance of other peaks at higher frequency. Therefore the spectral peaks which were present at higher frequency in lower velocity spectra disappeared in higher velocity spectra.

4. CONCLUSION

Results demonstrate that the inhibition efficiency of ADS is superior to that of BTA. COF obtained from frictional force measurement is the lowest when the slurry contains ADS. This suggests that adsorbed ADS on the surface provides lubricating action thereby reducing the wear between the contacting surfaces. ADS containing slurry shows the lowest temperature rise again confirming the softening effect of the adsorbed surfactant layer, thereby resulting in less energy dissipation due to friction. Spectral analysis (in frequency domain) of the shear force data is employed to determine the inhibition of the additives in the slurry. It is noticed that increasing the pad-wafer sliding velocity at constant wafer pressure shifts the high frequency spectral peaks to lower frequencies and also increases the variance of the frictional force at the pad-wafer interface. Addition of ADS reduces the fluctuating component of the shear force and the extent of the pre-existing stick-slip phenomena caused by the kinematics of the process and collision event between pad asperities with the wafer. By contrast, in the case of BTA, there are no such observed benefits but instead undesirable effects are seen in some polishing conditions. This work underscores the importance of real-time force spectroscopy in elucidating the adsorption, lubrication and inhibition of additives in slurries in CMP.

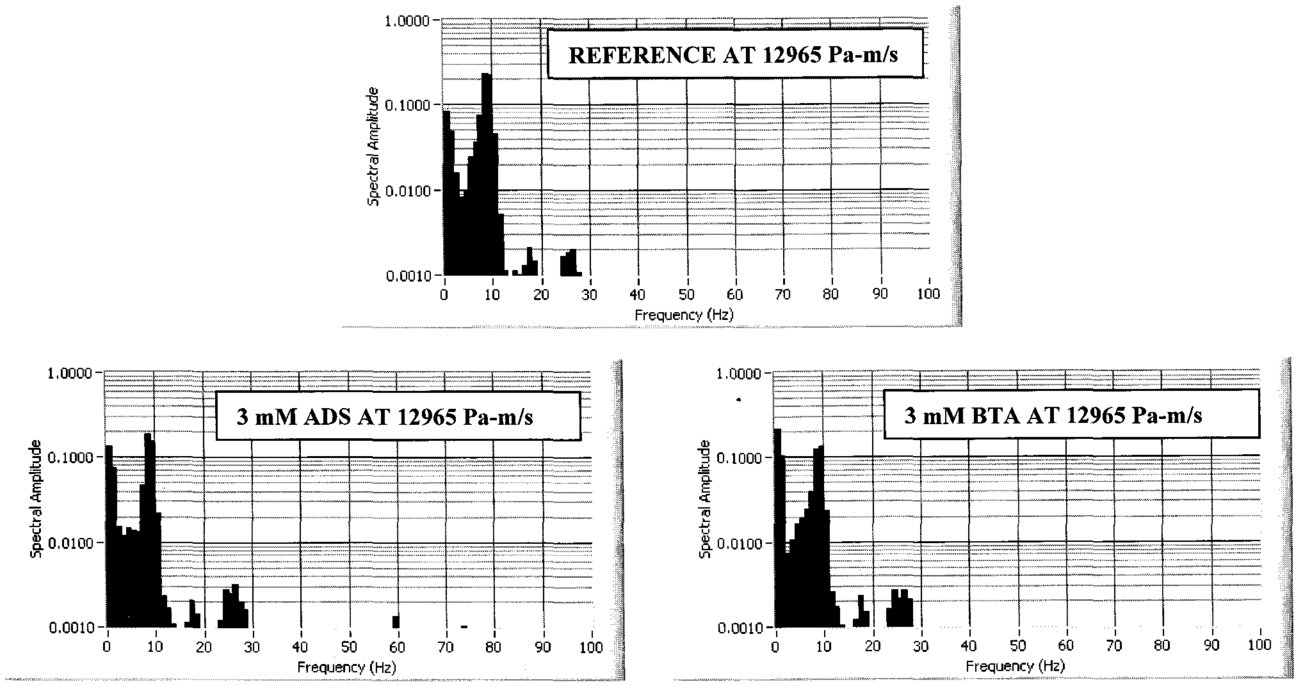

Fig. 4. Stick-Slip phenomena distribution in frequency domain for investigated slurries at relative pad wafer sliding velocity of 0.94 m/s.

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