# Study on Interaction Single Particle-Substrate-Slurry with Help AFM in the CMP Process of the Surfaces with Selective Transfer

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*Abstract*—To understand the mechanism of Chemical Mechanical Planarization (CMP), an Atomic Force Microscope (AFM) was used to characterize polished layer surface formed by selective transfer (in which the copper (> 85%) is predominated) after a series of polishing experiments. In the presence of solutions with a known pH, the tribochemical friction and wear can be investigated. Simultaneous application of chemical agents and mechanical stress involving model single asperity and a solid surface. The experiments simulates several features of a single particle – substrate – slurry interaction in CMP. AFM tip was used to mimic a single abrasive silica particle, typical CMP slurry. Studying selective layer CMP we found that AFM scanning removes the surface oxide layer in different rates, depending on the removal depth and the solution pH. Friction forces acting between the AFM tip and surface during the polishing process were measured. Correlation between friction forces and removal rates is discussed.

Keywords—selective layer; AFM, CMP, model single asperity, particle – substrate - slurry interaction, pH

## I. INTRODUCTION

In spite of the fact that research in CMP has been conducted extensively, additional studies are still necessary for a better understanding of tribochemical and mechanical phenomena occurring at the interfaces between the pad and wafer, in the presence of the fluid slurry [1-5]. Studies have proved that the use of oxidizer helps the formation of an oxide film on the selective layer surface [4, 6, 7]. For a fundamental understanding of surface properties of the layers formed by selective transfer at nanoscale, it must be specified that there are materials which under optimal functioning conditions form a thin, superficial layer of copper (selective layer) in the contact areas, and therefore, can function in conditions of selective transfer.

These materials are used at various machine couples and have in common the fact that, in the friction areas special physic-chemical processes take place, which leads to the formation of a thin copper layer (selective layer), almost pure, with superior properties at minimal friction and wear[8-10]. This is a criterion for any friction couple of high efficiency and a normal process for the self-adjustment phenomena. In the process of friction of these materials and in the presence of own lubricants, the wear phenomenon itself manifests as a transfer of material from an element of a friction couple on the other (forming a selective layer), this phenomenon being contact areas, and therefore, can function in conditions of selective transfer.

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In many cases, our understanding of the mechanisms of material removal is largely empirical. Nevertheless, it is clear that the material removal often involves chemical as well as mechanical stimuli. Removal of a soft oxide film enables better planarization [11]. Oxide removal happens considerably faster than the copper CMP removal from selective layer. This is in correlation with the generally accepted model of copper CMP [10, 12, 13], by which surface of thin copper layer, formed by

selective transfer (selective layer) is oxidized while immersed in the slurry solution, forming the oxide layer.

Copper CMP studies in acidic and basic slurries were conducted and in the past. Current achievements in the study of copper CMP are reported in different papers [14-17]. Yet, the synergy of electrochemical, mechanical and tribochemical interactions is important to be understood. CMP is used to remove the excess of metal in the damascene processes for copper patterning from selective layer. Indeed, CMP seems to be the only effective technique to achieve both local and global planarization used in modern manufacturing.

To optimize the process of copper CMP from selective layer, various chemicals, abrasives, polishing pads etc. have been investigated. Due to the many parameters that can influence the CMP process, optimization of CMP by experimental means has been difficult. Modelling of the selective layer CMP can help to rationalize the CMP optimization. For this, we must know the behaviour of the pad and the wafer surfaces, and their interaction with the abrasive particles. The technique that is capable of measuring such information is AFM. We show here that the AFM technique can be used to study selective layer CMP under various conditions. Furthermore, to improve modelling, it is useful to study the mechanical/physical part of CMP separately from the chemical aspects.

By applying the slurry chemicals to the selective layer surface for some period of time and then removing the oxidizing agent from the slurry, we can study the mechanical action of the abrasives on the oxide layer separately from the chemical action. An AFM tip of radius of ~ 50 nm was used to mimic a single abrasive silica particle of the slurry stuck to the polishing pad [18].

During AFM scanning, the 'particle-like' tip moves over the surface being polished with a relatively high load force. This induces 'scratching' the surface akin to the CMP process. The AFM is used for both scratching while operating with a high load force and imagining while scanning with a small load force. At high contact forces, friction and wear can be induced by the tip of an AFM. Under these conditions, the AFM serves as an especially simple friction and wear system involving a single asperity translated across a well-characterized surface.

In a recent paper, we have characterized the friction and wear of silicon nitride tips on the selective layer surfaces in aqueous solution [10]. Similarly, references [15, 19] characterized the wear of silicon nitride tips on the copper surfaces [15] and on the glass surfaces [19] and it have been found that, no significant differences occur, with order to make a qualitative or quantitative comparison. Nevertheless, the friction and wear of silicon nitride AFM tips on selective layer surfaces in basic solution gradually slows, during prolonged linear scanning. Observations of tip and substrate wear suggest that the tip contact area and stress are mainly controlled by substrate wear during linear scanning. In this paper, we monitor

the friction and wear of the selective layer substrate in basic solution. As one might expect, the friction and wear of the AFM tip affects the friction and wear of the underlying substrate. An understanding of nanometer friction and wear must incorporate the mutual removal of material from asperity and substrate.

## II. MATERIALS AND METHODS

One big advantage of using the AFM tip as an abrasive silica particle is that we can measure forces acting between the particle-tip and the surface being polished. Here we report measurement of the friction force while scratching and polishing. A Dimension 3100 Nanoscope IIIa AFM by Digital Instruments was used in this paper. Standard integrated silicon nitride NP-S V shaped AFM tips by Digital Instruments were utilized for the AFM 'scratching and polishing'. The AFM allows examining the effects of applying highly localized stress to a surface. Nanoprobe RTESP7 silicon rectangular cantilever tips were used for measurement of friction forces. Spring constants of both types of cantilevers were measured [20-23], and they have $k$ of $\sim 0{\cdot}15$ N m$^{-1}$ (it was determined by resonance method using built-in option in the AFM software).

Slurry solution used for selective layer oxidation was prepared as aqueous solutions 5 wt% of peroxide and 1 wt% of glycine with different pH values of 3, 4, 5, 8, and 8.5. The pH of the slurry solution was adjusted with either HCl or KOH with 10 mM ionic strength. Oxidation of the selective layer wafer was done by placing a droplet of about 2–3 cm diameter of the slurry solution on the selective layer surface for 10 or 15 min. The AFM scanning/scratching was done with no oxidizing agents, and took place in aqueous solutions of HCl and KOH of 0.01mol/L mixed to maintain the same pH as in the slurry solution.

Fundamental studies on the simultaneous application of chemical agents and mechanical stress involving model single asperity and a solid surface. At the same time, we show the consequences of combining highly localized mechanical stress (due to contact with the AFM tip) and exposure to aqueous solutions of a known pH. The method simulates several features of a single particle – substrate – slurry interaction in CMP. Friction coefficients were measured as described, *e.g.*, in Meyer et al. [24]. Specifically, friction force was measured against 5 to 8 different load forces. The friction coefficient was calculated as the averaged ratio of the friction force to the total vertical force, which include the load force and the force adhesion.

To optimize the CMP process, we need to obtain information on the interaction between the abrasive slurry particles and the polished surface. To study such interactions, we used all AFM. An AFM tip of radius of ~ 50 nm was used to mimic a single abrasive silica particle, typical of those used in CMP slurry. Surface analysis of selective layer using the AFM revealed detailed surface characteristics obtained by CMP. Quantitative models explain the modifications observed to the surface at manometer-scale. At the

same time, it complements observations of tip – induced friction and wear and growth in a number of inorganic surfaces in aqueous solutions.

## III. EXPERIMENTAL RESULTS AND DISCUSSIONS

The surface morphology and friction response to AFM probes were studied to reveal the tribochemical mechanisms. Surface characterized using AFM was conducted after CMP. AFM topography scans were used to find the surface roughness ($S_a$) values for the scanned areas. The observed $S_a$ values were considered as an index for planarization quality after CMP. Figure 1 shows the AFM topography scan for a pit on the surface.
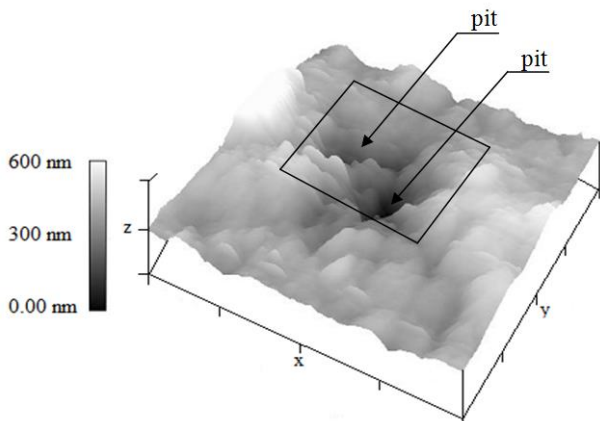


Fig. 1 AFM topography showing pit

The image of Fig. 1 is a 6 x 6 µm$^2$ AFM topography scan area. One can see a pit formed in the same area, after *ca.* 70 s of scanning/scratching over a 3 x 3 µm$^2$ area in the middle of 6 x 6 µm$^2$ area, with a load force *ca.* 30 nN at pH 6. Depth of the pit depends on scanning/scratching time and the pH of the slurry solution. The removal mechanism in selective layer CMP can be understood by studying the AFM topography and by controlling the synergy between mechanical wear and electrochemical interaction on the surface, good planarization can be achieved.

The reasoning for better planarization can be seen as the synergy of the controlled oxidation and subsequent removal process of the oxide at the selective layer surface. In case of excessive mechanical wear or excessive corrosion action, surface planarization is poor.

The copper from selective layer potential was varied from anodic side to cathodic side. Surface characterization using an AFM was conducted after CMP under the same conditions of potential. We found that the AFM scanning removes the surface oxide layer in different rates depending on the depth of removal and the pH of the solution. The depth of removal is one parameter uncontrolled and depends on scratching time and pH solution.

In accordance with Steigerwald et al. [1], it is well known that removal rate is proportional to the speed of polishing. So, to obtain the value of mechanical removal of the oxide layer in the real CMP process, the AFM removal rate can be changed proportionally to the increase in the polishing speed.

To compare with the AFM removal rate, one must evaluate the measured CMP removal rate per single abrasive particle. Because the concentration of the abrasives particles is of the order of a few per cent, one can estimate the removal rate per particle to be about two orders of magnitude larger than the observed CMP rate [10]. Here, we do not take into account pure chemical dissolution, which can only decrease the part removed by the abrasives.

Therefore, this estimation of the removal rate per abrasive particle gives somewhat higher values than can be in reality, if we consider the chemical dissolution. Even this high estimation is still much smaller than the scaled AFM removal rate. In the CMP process, the abrasive particles can roll over the surface, not necessarily stick to the pad, and scratch the surface. This depends on the interaction between the particle pads. This effect can bring some effective increase to the CMP removal rate per particle (no rolling). However, it is unlikely that such an increase can result in the high removal rates of the oxide layer as estimated by AFM.

Comparing the qualitative behaviour obtained of the removal rates as a function of pH with CMP data reported [10, 12], one can see definite correlation, as shown in Fig. 2.
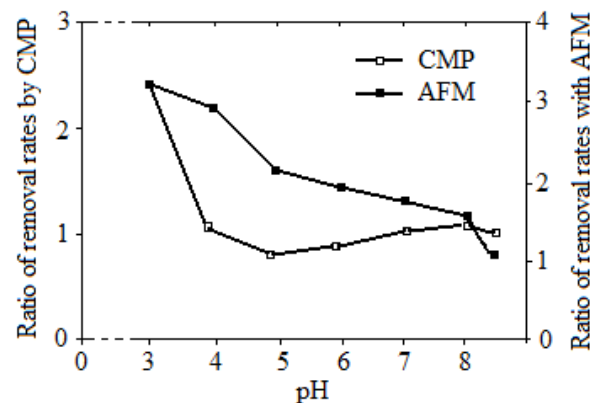


Fig. 2 Comparision of CMP removal rates and the AFM mimicked (rates for pH3 taken to be the same)

It is interesting to compare these data with the observed removal rates in the actual selective layer CMP process. One can noticed that for all the pH values studied, the scaled AFM removal rates are much higher than the estimations per single abrasive particle in the selective layer CMP. A large difference in the removal rates leads to a conclusion that the abrasive particle can remove the oxide layer at a much higher rate than actual CMP rate. So, we can conclude that the abrasives serve mainly to expose the selective layer surface to the slurry chemicals by removing the oxide layer rapidly, and the limiting factor is likely the chemical oxidation of the selective layer surface.

For the qualitative comparison, we put the same rates for the pH level of 3. Quantities comparison

reveals the following: oxide removal with the AFM happens considerably faster than the CMP selective layer removal. This confirms, essentially, a generally accepted model of copper CMP [10, 12, 13, and 25], and defines the following model for the selective layer CMP: the originally corrugated/patterned selective layer surface is oxidized while immersed in the slurry solution.

A fast rotating pad and the abrasive particles touch and remove of oxide layer from the top areas of the corrugated/patterned copper surface, because the pad touches these areas first. Because the rate of removal of the oxide layer is much higher than the actual CMP removal rate, the rate of oxidation must be much slower that the rate of oxide layer removal.

If we are dealing with polishing rather than etching, the exposed selective layer is oxidized faster that the areas passivity by the oxide layer. If the area is still high, the oxide layer is removed again, and the process repeats until the high area disappears, i.e., is polishing away. These results lead to a faster dissolution of higher areas than the lower ones, i.e., in the planarization. So, one result of this study is the first direct quantitative confirmation of this idea.

The advantage of the AFM technique is in its ability to measure forces in situ [26], acting between the slurry particles and the polishing surfaces while scratching/polishing [27]. Because it is plausible to know the direct correlation between the removal rate and the force of friction, between the AFM tip and surface, we measure the friction force. Such measurements were done on the selective layer surface treated as before, immersed in the aqueous solution of the corresponding pH. Friction loops [24, 26] were captured in 10-20 different points on the surface. At each point the loops were measured for a range of load forces.

To exclude a possible contribution of topology into the measuring lateral force [28], each point was chosen as a relatively flat area of at least 250×250 nm. The calculated friction coefficient was averaged over those measurements and is presented in Fig. 3.
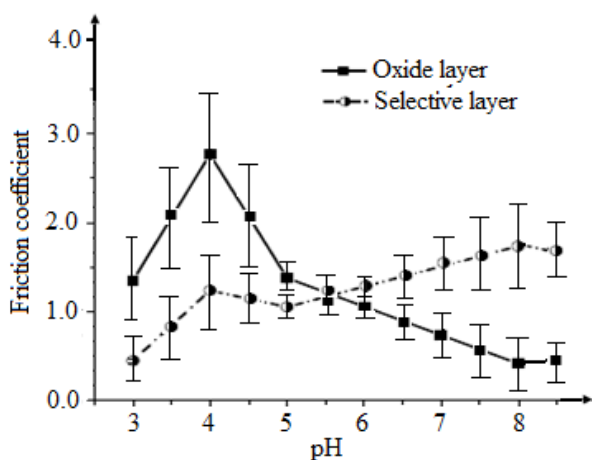


Fig. 3 Dependence of the friction coefficient on the slurry pH for selective layer and oxide layer

Figure 3 shows the variation of friction coefficient (normalized by the lateral spring constant of the cantilever [18], between the AFM tip and selective layer surface, with the slurry pH. The error bars represent the root-mean-square (RMS) of the calculated friction coefficients.

The values of the friction coefficient are somewhat higher than for a typical material. This may be explained by the measurements being done with the vertical forces typical for the scratching, i.e., wearing. Wearing usually leads to increase of friction [24].

As one can see from Fig. 3, the friction coefficient decreases as pH grows from 4 to 8, for oxide layer, which confirms the hypothesis that the removal rate directly correlates with the friction. However, the friction coefficient increases while the pH changes from 3 to 4. This happens even though the removal rate seems to be higher for pH3, as seen in Figs. 3 and 4.
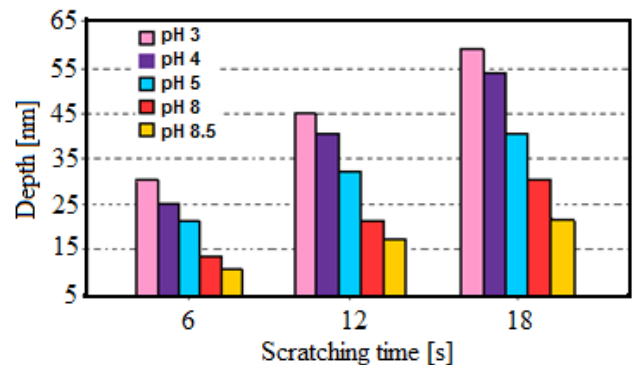


Fig. 4 Depth of the pit for different pH values as a function of time of the AFM scratching

The average depth was calculated using roughness analysis provided by Nanoscope software. The error bars presented in the graphics are the RMS values of the height variations inside the pit. It can be seen that the depth decreases monotonically with the increase of pH. The pit depth for pH3 was measured unambiguously only after 18 s of scratching because of the high surface roughness. The reason was that the oxidized surface was much more corrugated for pH3 than for other pH s values, where the depth of the pit was ca. 56 nm after 18 s. It is interesting to note that pH3 is a special case. Nevertheless, the friction coefficient - removal rate dependence is highly nonlinear.

Analysing the data with reference to the variation of process parameters, interesting results were depicted. At both low and high pH of slurry and in anodic potential conditions, planarization achieved was of high quality, whereas with remaining combinations of parameters under study, insufficient surface planarization was observed. An example of selective layer CMP produced by AFM scanning/scratching is show in Fig. 1.

The removal mechanism in the selective layer CMP can be understood by studying the AFM topography, and by controlling the synergy between

the mechanical wear and electrochemical interaction on the surface, good planarization can be achieved. Therefore, the reasoning for better polishing can be seen as the synergy of the controlled oxidation and subsequent removal process of the oxide at the selective layer surface. In case of excessive mechanical wear or excessive corrosion action, surface polishing is poor.

For the qualitative comparison, we put the same rates for the pH of 3 (see Fig. 3). Quantative comparison reveals the following: oxide removal with the AFM happens considerably faster than the CMP selective layer removal. This confirms, essentially, a generally accepted model of copper CMP [10, 12, 13] and brings the following model for the selective layer CMP: the originally corrugated/patterned selective layer surface is oxidized while immersed in the slurry solution.

As one can see from regular AFM topology images (see Fig. 3), the oxide is much rougher for the case of pH3 vs. the other considered pH values, because removal rates have higher values, respectively of the high surface roughness. Analyzing the removal noise by the AFM, we can speculate that the oxide is being removed through grinding into nanosize particles of the oxide, which are noticeably smaller than in the case of the other pHs. These particles, sliding between the AFM tips and polishing surface, effectively lubricate the tip-surface contact, and consequently, decrease the friction coefficient. The surface morphology and friction-wear response to AFM probes were studied to reveal and intuition of tribochemical mechanisms.

The AFM scratching was done over a 1.5 x 1.5 $\mu m^2$ area has been smoothed by 10 square scans with 256 lines/scan with a load force of *ca.* 20-30 $\mu N$. This is about the estimate a force for a single abrasive particle during CMP (this force can also be estimated as a result of pressure of the order of 10 psi was spread over particles of slurry that contain 5% abrasives) [26, 29].

Figure 5 shows a 9 x 9 $\mu m^2$ deflection image of a polished, selective layer surface in slurry solution, where the inner 3 x 3 $\mu m^2$ square was smoothed by 10 raster scans at a nominal contact force of 200 nN. Deflection images often reveal small surface structures that are obscured in topographic images.
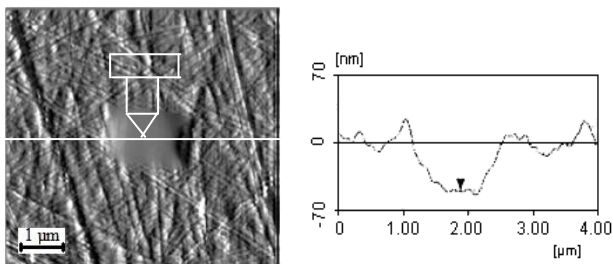


Fig. 5 Vertical deflection image of a polished, selective layer surface (left) and its cross section (right)

The root-mean-square (RMS) roughness of the diamond polished selective layer (outside the central smooth area) was typically 1.8 ± 0.7 nm. Small area AFM scanning typically reduces the RMS roughness of the surface to 0.25 ± 0.1 nm, about twice the minimum surface roughness of this material due to its atomic structure [19]. In the middle of image of Figure 5 are a 3 x 3 $\mu m^2$ AFM scan area and its cross section. One can see a pit formed in the scratched area. During the linear scanning, the shape of pit remains constant, while the shape of the AFM tip evolves constantly. After ref. Maw et al. [18], under these conditions the area of tip substrate contact is roughly proportional to time. As noted below, the friction and wear rate drops with time due to this increase in tip area.

Wear measurements during linear scanning are complicated by imagining issues. Since the width of the wear track is often comparable to the tip dimensions, wear track profiles can appear to be narrower than they really are. Figure 6 shows track and the tip profiles across the thin dimension of the wear track, perpendicular to the direction of linear scanning.
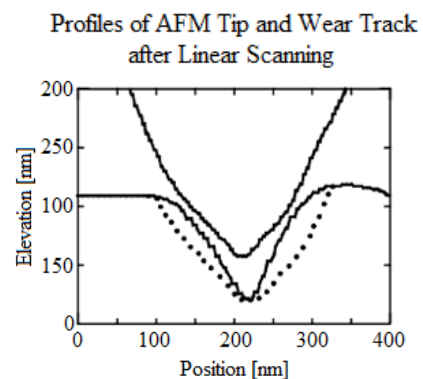


Fig. 6 Profiles of tip and track after linear scanning in basic solution

During the linear scanning, the area of tip-substrate contact depends critically on substrate wear, in addition to tip wear. To compensate for tip size effects, the wear track profiles were manually deconvoluted (a mathematical deconvolution carried with a computer) using the tip profile shown. The wear rate can be strongly affected, when there is a difference between the stresses applied. The dots indicate the shape of the wear track profile given by deconvolution. Each track was formed by 15 linear scans with 1024 lines/scan at a nominal contact force of 200 nN. A sequence of wear depth measurements as a function of number of 500 nm linear scans appears in Fig. 7.

Each individual depth measurement was made with a new tip; the points with error bars indicate averages of two or more measurements. It was observed that the profiles of AFM tip and wear track after linear scanning showing conformal wear of tip and track, while what wear depth is function of force applied to the tip. Both wear rates vary approximately

with the square root of the number of scans. Significantly, wear of linear scans is a linear function of force applied to the tip. Models accounting for these results suggest that the local stress is controlled by substrate wear during linear scanning. However, as the track gets wider and wear deeper, the volumetric wear could still be constant over time.
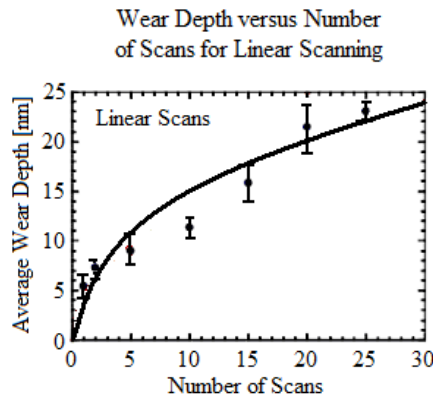


Fig. 7 Wear depth depending number of scans for 500 nm linear scans with 1024 lines/scan with nominal contact force of 150 nN

## IV. CONCLUSIONS

* Removal mechanisms in copper CMP in generally and selective layer CMP in particularly can be understood by studying the AFM topography. Good planarization can be achieved by controlling the synergy between mechanical wear and electrochemical interaction on the surface.

* AFM technique is able to measure all forces (including the force of friction) acting between the slurry and the polishing surfaces while polishing/scratching. Measurements based on friction in CMP can help to identify the interactions between the pad and different materials (with different friction coefficients) and surface topography as these are exposed and evolve during planarization.

* AFM technique was used to study fundamentals of CMP of selective layer. Oxidation of the selective layer surface was done in aqueous solutions of 5% wt of glycine at different pH of 3, 4, 5, 8 and 8.5. An AFM tip of radius of ~ 50 nm was used to mimic a single abrasive silica particle of slurry.

* During the AFM scanning/scratching, such a silica particle moves over the surface being polished with a load force of 20...30 nN, which is about the estimated force for a single abrasive particle during CMP. Such scanning/scratching removes the surface layer at different rates. This rate is lower for higher pH, and for longer polishing times. The pH dependence of the observed removal rates is consistent with CMP results reported previously.

* Comparing the obtained AFM removal rates of the oxide layer with the CMP experimental rates, we conclude that the oxide removal happens considerably faster than the actual CMP selective layer removal.

* This suggests a model for copper CMP, in which an originally corrugated selective layer surface is planarized by fast oxide removal from the tops of the oxidized selective layer surface by the abrasive particles stuck to the polishing pad. The exposed top selective layer areas oxidized further and scratched away by the abrasive again. This process repeats itself until no tops on the selective layer surface remain, i.e., planarization is complete.

* AFM allows examining the effects of applying highly localized stress to a surface, and in the presence of slurry solutions, wear can be investigated. This wear appears during linear scans and depends on number of scans.

* The friction and wear of silicon nitride AFM tips on selective layer surfaces in basic solution gradually slows during prolonged linear scanning. Observations of tip and substrate wear suggest that the tip contact area and the stress are mainly controlled by substrate wear during linear scanning.

* Characterizing the AFM tip before and after wear allows as incorporating the evolution of the asperity shape into microscopic modelling of single asperity wear and improving our understanding of polishing and micromachining process.

* AFM technique was also used to monitor forces acting between the slurry particle and surface while being polished. The friction forces acting between the AFM tip and surface being polished were measured. With the exception of pH 3, the smaller friction coefficient corresponds to a slower removal rate. However, quantitatively the friction removal rate dependence is highly nonlinear.

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