

A New Approach for the Study of Chemical Mechanical Polishing

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The process of chemical mechanical polishing (CMP) can be studied using *in situ* atomic force microscopy (AFM) by intentionally using a high tip/sample interaction force. The nominal removal rate of Al during AFM scratching is studied under a range of conditions including varying tip/sample force, solution pH, and electrode potential. This approach should be useful for CMP process development and furthering the fundamental understanding of CMP mechanisms.
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The process of chemical mechanical polishing (CMP) of metal involves hard particles suspended in an aqueous slurry that interact with a metal surface because of mechanical force applied between the particles and surface by the polishing pad.^{1,2} The interaction may result in physical removal of metal or just breaking of a surface film, followed by electrochemical dissolution and reformation of a protective film. In order to understand better the mechanism of CMP, it is instructive to consider the process at its most basic level, *i.e.*, a single abrasive particle being forced against the metal surface in the presence of an electrolyte. The premise of this paper is that this particle/metal interaction can be simulated by the interaction of an atomic force microscope (AFM) tip with a sample surface, thereby allowing a new approach to the study of the fundamental mechanisms of CMP.

Characterization of surface topography by AFM is typically performed under conditions that minimize the tip/sample interaction. However, in order to simulate CMP with the AFM, the opposite approach is followed. Instead of minimizing the tip/sample interaction, the tip is intentionally pushed against the sample surface with a higher tip force than usual. Guay *et al.* showed that the dissolution rate of pure aluminum thin films was locally enhanced during controlled AFM rastering in dilute chloride solutions.^{3,4} The loss of material was followed by determining the average roughness as a function of time. A relation between the applied force and the decrease of roughness was observed.⁴ Schmutz and Frankel used *in situ* AFM scratching of pure Al and an Al alloy in chloride solutions to study localized corrosion and repassivation processes.⁵ Under certain conditions, even in 0.5 M NaCl, contact mode rastering of the AFM tip at a high force resulted in the formation of a deep, smooth-bottomed trench in the pure Al surface. Clearly, the interactions between an AFM tip and the sample surface in an electrolyte can result in accelerated material removal.

The analogy of AFM scratching with metal CMP is as follows. An AFM cantilever, made of any of a number of materials (Si and Si₃N₄ cantilevers are readily available), is rastered across a metal sample *in situ* in contact mode using a high applied force. The metal sample is analogous to the metallized wafer in CMP, and metals such as Al, W, or Cu could be studied. The AFM tip with a contact diameter of about 50 nm pressing against the sample is analogous to the action of a single abrasive particle. The exact CMP slurry, but without particles, can be used in the AFM cell to simulate the environment. It is also possible to remove the oxidizing agent from the CMP slurry and use a potentiostat to control the sample potential, which provides an extra degree of freedom in designing a process. The force applied at the tip by the spring constant of the cantilever is analogous to the action of a polishing pad pushing an abrasive particle against the surface. The AFM allows much better control of the force than that achievable in a real CMP process. However, by accu-

rately controlling the force, potential, and solution chemistry it is possible to use *in situ* contact mode AFM rastering to simulate and study CMP at its most basic level.

Experimental

A Digital Instruments Nanoscope IIIa AFM was used in these experiments. Bulk pure Al (99.99%) samples were polished to 6 μm with diamond paste and then finished with colloidal silica to a final roughness of 2 nm. They were studied in different environments, including sulfate and borate solutions with a range of pH levels. The solutions were pumped continuously at a rate of about 10 mL/h through the electrochemical cell, which had a volume of about 0.1 mL. The potential was either left at open circuit or controlled using a saturated mercurous sulfate electrode (MSE) and a Pt counter electrode located downstream of the cell. A square region of a given size, *e.g.*, 5 × 5 μm, was rastered with a Si tip for 1 h in contact mode at a specific applied force, as monitored by the setpoint voltage on the AFM photodiode. The scan region was then opened up, *e.g.*, to 15 × 15 μm, and the result of the high force scratching was imaged at low force. The nominal removal rate was determined as a function of setpoint voltage by measuring the depth of the trench created by the rastering and dividing by the raster time. This process was repeated sequentially with increasing setpoint voltage at nearby areas. The nominal removal rate of the scratched area determined in this fashion was referenced to the unscratched surface. It should be noted that under certain conditions the dissolution rate of the unscratched surface was relatively high.

Results and Discussion

An example of Al CMP produced by *in situ* AFM scratching is shown in Fig. 1. The central square region was rastered for 1 h in 0.5 M Na₂SO₄ + 0.01 M Na₂B₄O₇ (pH 9.2) at open circuit (-1.7 to -1.9 V MSE) at a setpoint force of 3 V. This resulted in the formation of a trench approximately 50 nm deep. The image shown in Fig. 1 was made *in situ* at a low setpoint force that itself did not result in any change in the surface as determined by AFM. A cross section of the smooth-bottomed trench formed by the rastering is shown in Fig. 1b. The trench is localized to the area that was rastered at the high setpoint and is quite different than the pitting that initiated during AFM scratching of Al in flowing chloride solutions.⁵

Two observations help prove that the trench in Fig. 1 was created by a synergistic effect of the mechanical abrasion and the environment, *i.e.*, CMP. The fact that a trench formed in the rastered area indicates that the region of the sample next to the rastered area dissolved at a much lower rate, and dissolution alone was not responsible for the trench. The trench was not formed by pure mechanical wear because a sample that was rastered in the exact same fashion as that in Fig. 1, except in air instead of in solution, exhibited no material removal (see Fig. 2). Note that the range for the gray scale values, representing the height of the topography, is only 20 nm for Fig. 2a compared to 200 nm for Fig. 1a.

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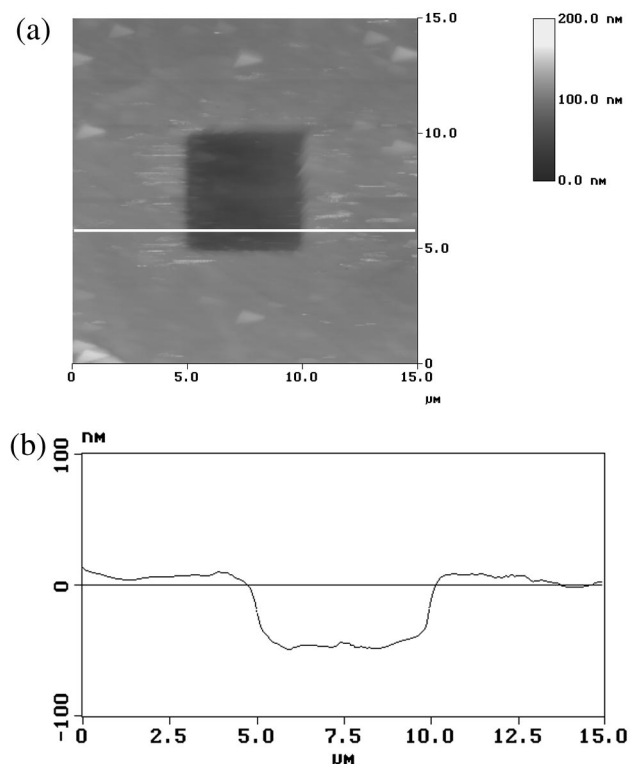


Figure 1. *In situ* contact mode AFM image of area of pure Al rastered for 1 h in 0.5 M Na₂SO₄ + 0.01 M Na₂B₄O₇ (pH 9.2) at open circuit (approximately -1.9 V MSE) at a set point of 3 V. (a) Expanded view of rastered area with z range of 200 nm and (b) cross-sectional profile at location of line in part a.

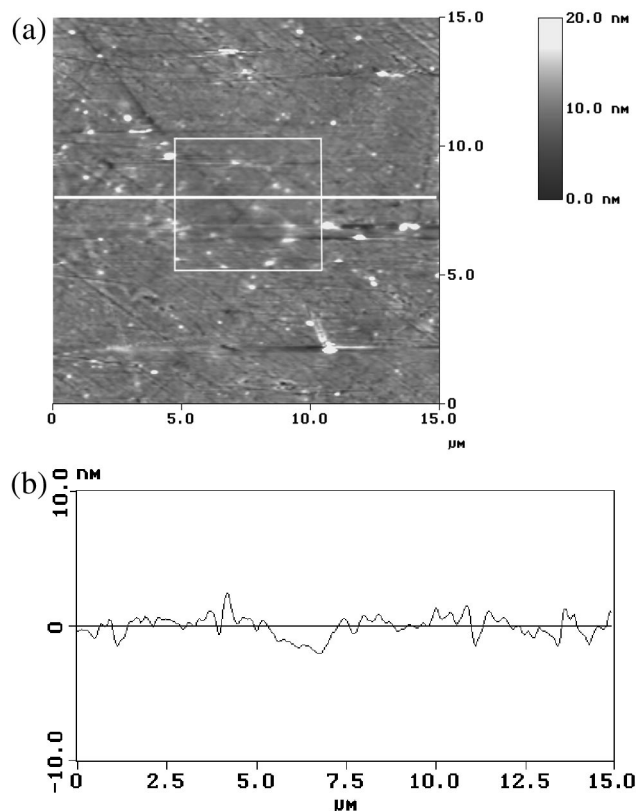


Figure 2. AFM image of area of pure Al rastered for 1 h in air at a set point of 3 V. (a) Expanded view of rastered area with z range of 20 nm; the box indicates the location of the area rastered with the high set point, (b) cross-sectional profile at location of line in part a.

The process of scratching at high loads causes the initially sharp but fragile Si tips to dull significantly with time. The triangles seen in Fig. 1a, which are images of the tip caused by small particles on the surface, are evidence of this dulling. The tip used to raster the sample shown in Fig. 2 was one that had been used previously in an *in situ* experiment that went to high setpoint voltages and was somewhat dulled as a result. Therefore, the effective pressure (force/tip-area) applied to the sample shown in Fig. 2 was similar to that in Fig. 1. It should be noted that it was possible to create a wear mark in Al in air by scratching with a fresh Si tip. For example, after scratching for 1 h in air with a new tip, a 4 nm deep wear mark was formed. Regardless of the exact tip condition, the material removal rates by scratching in the pH 9.2 solution were much higher than those observed in air.

The nominal removal rate of Al during *in situ* AFM rastering in the pH 9.2 borate/sulfate solution is shown in Fig. 3 as a function of applied potential and tip setpoint voltage, or force. It should be noted that the dissolution rate of the unscratched area was high in the pH 9.2 solution relative to the other solutions studied. As was found for AFM scratching of Al in stagnant NaCl solution,⁵ the material removal rate in the scratched area increased with increasing setpoint voltage, or higher tip/sample force. The rate also increased with increasing applied potential. The removal rate at about -1.4 V MSE was slightly higher than that at open circuit, which varied from -1.7 to -1.9 V MSE during the time of the experiment. However, at a controlled potential of about -0.9 V, the removal rate increased by more than an order of magnitude.

The material removal rate was a sensitive function of pH, which is expected based on the stability of Al oxide. The nominal removal rate during *in situ* AFM scratching of Al in 0.5 M Na₂SO₄ containing sufficient H₂SO₄ to form a pH 5 was much lower than that in the pH 9.2 solution, Fig. 4. The removal rate in a 0.5 M Na₂SO₄ solu-

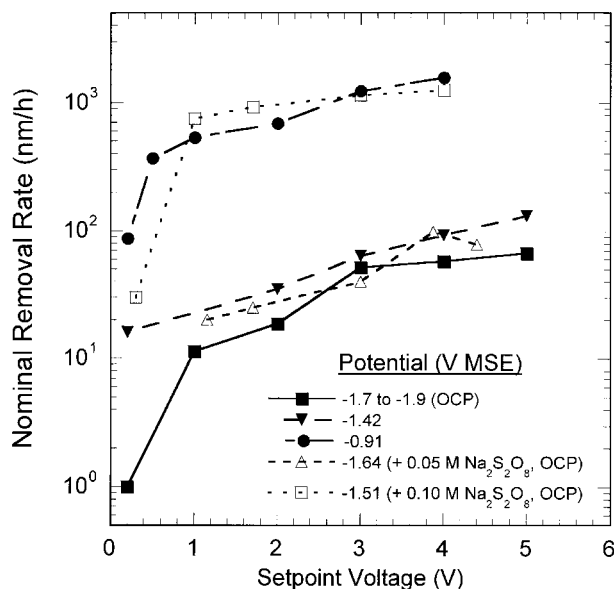


Figure 3. Nominal removal rate of pure Al during *in situ* AFM scratching in 0.5 M Na₂SO₄ + 0.01 M Na₂B₄O₇ (pH 9.2) as a function of setpoint voltage on the AFM photodiode. Measurements at the open-circuit potential (OCP) and two applied potentials are shown. Also shown is the removal rate at open circuit in solutions containing Na₂S₂O₈.

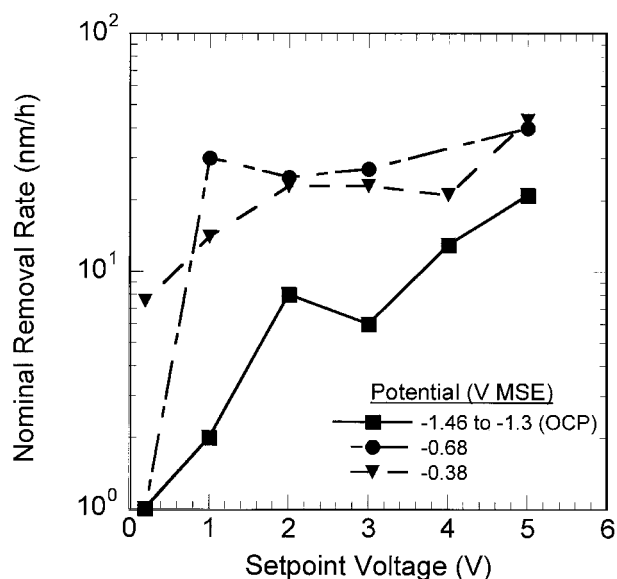


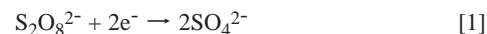
Figure 4. Nominal removal rate of pure Al during *in situ* AFM scratching in 0.5 M Na₂SO₄ + 0.0001 M H₂SO₄ (pH 5) as a function of setpoint voltage on the AFM photodiode and electrode potential.

tion buffered at pH 7 (by adding 0.09 M H₃BO₃ and 0.0005 M Na₂B₄O₇) was almost identical to that in the pH 5 solution. Applied potential had an accelerating influence in the pH 5 and pH 7 solutions, but much less than for the pH 9.2 solution. The higher potential drives dissolution, but also anodization, which would tend to make a more robust film.

CMP slurries typically contain an oxidizing agent to accelerate the dissolution. The *in situ* AFM scratching approach can be used with the potential increased by the presence of an oxidizing agent instead of using an applied anodic potential. The results of scratching Al in 0.5 M Na₂SO₄ + 0.01 M Na₂B₄O₇ containing 0.05 M or 0.1 M Na₂S₂O₈ are shown in Fig. 3. The pH decreased slightly as a result of the addition of persulfate; it was 9.1 and 9.0 for solutions containing 0.05 and 0.1 M persulfate, respectively. The open circuit potentials for Al in these solutions were -1.64 and -1.51 V MSE, respectively. Note that the nominal removal rate at the open circuit potential of -1.51 V in the presence of 0.1 M persulfate was much higher than at a controlled potential of -1.42 V in the absence of persulfate, and equivalent to that at -0.91 V in the absence of persulfate. In other words, to achieve a removal rate measured under open circuit conditions in the presence of an oxidizing agent, it was necessary to use a much higher applied potential.

When an anodic potential is applied by a potentiostat, the cathodic reaction is primarily located at the remote counter electrode. In contrast, when the potential is achieved by the presence of an oxidizing agent, the cathodic reaction occurs in close proximity to the anodic reaction. The scratched area is a very small fraction of the

total exposed area, suggesting that the cathodic reaction could occur at a relatively distant location on the same electrode. However, the reactivity of the fresh Al surface is much greater than that of the nearby passive surface, as evidenced by the copious hydrogen evolution observed in pits in Al. Therefore, it is likely that a large fraction of the cathodic reaction occurs very close to the scratching tip. The borate in the solution makes it rather well buffered, and the reduction of persulfate to sulfate should not affect the pH



However, small changes in pH are likely as a result of the cathodic reaction. Dissolved oxygen is present even in the presence of persulfate, and oxygen reduction will also take place, which would tend to increase the pH locally. Furthermore, the addition of persulfate to the sulfate/borate solution decreased the pH slightly, so the consumption of persulfate by Reaction 1 would result in a local increase in pH. The pH of 9-9.2 is in the range where the stability of Al₂O₃ is a sensitive function of pH. So it is possible that the higher rate of material removal at open circuit in the presence of an oxidizing agent relative to that at a similar applied potential was a result of small local pH increases associated with the cathodic reaction.

The nominal removal rates shown in Fig. 3 and 4 should scale with the CMP rate, but should not be compared directly. The tip was in contact with a given spot on the rastered area only a small fraction the total raster time. The nominal removal rate was limited by this contact time. The correlation to CMP must account for the average number of contact points per unit area between the abrasive particles and the substrate at any given time.

Conclusions

It has been shown that *in situ* AFM scratching of pure Al can result in accelerated removal of material within the rastered area by a process similar to CMP. The removal rate depended strongly on solution pH, electrode potential, and the applied tip/sample force, as indicated by the AFM setpoint voltage. It is suggested that this approach will be useful for clarifying the mechanisms of CMP and for rapidly screening CMP solutions during process development.

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