

Single asperity tribochemical wear of silicon nitride studied by atomic force microscopy

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Nanometer scale single asperity tribochemical wear of silicon nitride was examined by measuring the wear of atomic force microscope tips translated against a variety of substrates in aqueous solutions. We show that the chemical nature of the substrate plays an important role: significant wear was observed only when the substrate surface is populated with appropriate metal-hydroxide bonds. Mica and calcite substrates, whose water-exposed cleavage surfaces lack these bonds, produced little if any tip wear. As a function of contact force F_N and scan duration t , the length of the tips in this work decreases approximately as $(F_N t)^{0.5}$. We propose that pressure-induced intermediate states involving hydroxyl groups form on both the tip and the substrate; chemical reactions subsequently form transient bridging chemical bonds that are responsible for tip wear. © 2002 American Institute of Physics. [DOI: 10.1063/1.1510595]

I. INTRODUCTION

Silicon nitride ceramics are hard, inert, and stable at high temperatures, making them attractive for use in extreme environments. However, conventional polishing and grinding operations often produce surface defects and cracks that lead to premature component failure. Tribochemical or chemical-mechanical polishing¹ can produce very smooth, defect-free, silicon nitride surfaces, but this process is not well understood. Hydrodynamic lubrication, which results in low friction and almost no wear, has been observed on sufficiently smooth silicon nitride surfaces²⁻⁴ and has potential applications in high performance ceramic bearings. Wear of silicon nitride and silicon oxide is also of great interest in chemical-mechanical polishing of semiconductors for integrated circuits.

Atomic force microscopy (AFM) uses a sharpened tip to probe a surface with high spatial resolution. Typically, low contact forces are used to minimize damage to the tip and the substrate. However, by monitoring tip wear, an AFM can be used to measure the effect of high-force scanning on the tip and the substrate. Silicon nitride AFM tips made by chemical vapor deposition (CVD) are commercially available. By observing how these tips wear as a function of substrate material, solution chemistry, and contact force, we can characterize the tribochemical wear of CVD silicon nitride over a wide range of conditions. In the AFM geometry, the tip serves as an idealized single asperity interacting with a nearly flat substrate with a precisely controlled normal force, sliding speed and direction.

Geometrically, AFM wear experiments are analogous to the traditional pin-on-disk or ball-on-disk wear experiments,⁵⁻⁷ where a pin of silicon nitride is pressed against a rotating disk of silicon nitride or other material. In dry air, silicon nitride typically wears abrasively in micro-

scopic pin-on-disk experiments, producing significant debris and leaving a rough wear track. However, in moist air or water, silicon nitride can wear to produce a very smooth surface, with no detectable wear debris.⁷ Subsequently, the friction coefficient can drop to very low values (<0.005) and wear nearly stops. Apart from the low friction, this is of interest because water is an inexpensive and environmentally friendly lubricant; in principle, self aligning bearings could wear to form smooth mating surfaces, then stop wearing. Surface smoothing is believed to be tribio-chemical—worn material passes directly into solution a few molecules at a time. When the surface is sufficiently smooth, asperity contact is eliminated and the pin rides on a thin film of water (hydrodynamic lubrication). Subsequent wear rates are quite low.

Wear of silicon nitride AFM tips has been previously studied by Khurshudov and Kato⁸ using silicon substrates in air at normal forces of ~ 20 nN. The worn tips showed rough surfaces, consistent with more macroscopic observations of silicon nitride in dry air. Wear was attributed to fatigue of the AFM tip surface. Bloo *et al.*⁹ continuously scanned a grating for 1 h using a silicon nitride tip in air at a normal force of 100 nN. They observed small changes in tip shape which they attributed to adhesive wear, plastic deformation, and low cycle fatigue.

The wear of sharp, silicon AFM tips on oxidized silicon surfaces has been characterized at relatively high contact forces. Katsuki *et al.*¹⁰ scanned SiO₂ samples in KOH solution at normal forces of 1–6 μ N and found nearly equal amounts of material were removed from the tip and the substrate. The wear rate showed a weak maximum at a solution pH between 10 and 12. They attributed the initial tip wear to fracture, but later tip wear to tribochemical effects. (In the later stages of wear, the applied stress was believed to be insufficient for fracture.) Seta *et al.*¹¹ scanned SiO₂ in KOH solution with silicon tips and pure water for 1 h at normal forces of 1–8 μ N. Although they did not quantify tip wear, they observed less tip wear in water than in KOH solution.

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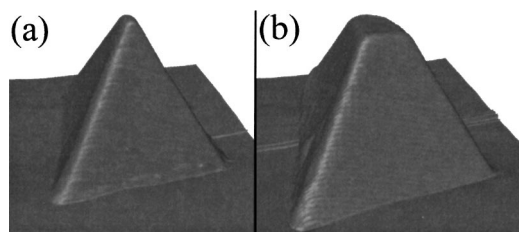


FIG. 1. AFM images of: (a) a fresh AFM tip and (b) the same tip after wear. The AFM tip was scanned 45 scans times across a sodium trisilicate glass substrate in ammonium hydroxide solution ($pH \sim 11$) at an applied force of 125 nN. Each image has been slightly cropped from the original $1500 \times 1500 \text{ nm}^2$ image. The vertical (z) axis has the same scale as x and y axes.

Tip wear in water also yielded rougher surfaces and wear debris, while tip wear in KOH solution did not produce wear debris. This would suggest that mechanical wear of silicon is more important in water, and that tribochemical wear dominates in KOH at these contact forces.

In this work, we monitor tip wear on silicon nitride tips in aqueous solutions as a function of scanning time and applied force using a variety of substrates. These results provide insight into the wear process under conditions where tribochemical wear predominates.

II. EXPERIMENT

Atomic force microscopy images were acquired with a Molecular Imaging PicoScan AFM with fluid cell. Commercial CVD silicon nitride cantilevers were obtained from Digital Instruments. These cantilevers have a nominal force constant of 0.58 N m^{-1} . Cantilever analysis using the thermal noise method on tips used in this work yielded typical force constants of $0.41 \pm 0.01 \text{ N m}^{-1}$. Wear was induced by scanning $3 \times 3 \text{ }\mu\text{m}^2$ patterns in raster mode at a tip velocity of $16 \text{ }\mu\text{m/s}$. This corresponds to a sliding distance of 1.5 mm per scan; the largest sliding distance reported here is 67.5 mm. Due to the important role of the substrate in tip wear, and because it is nearly impossible to reposition a tip on exactly the same portion of the surface after a wear measurement, each wear measurement required a new AFM tip and a previously unscanned portion of the substrate.

The tip shape before and after each wear experiment was characterized by scanning a silicon substrate which had been etched to form sharp spikes $\sim 600 \text{ nm}$ tall with a tip radius of curvature of $< 10 \text{ nm}$ (MikroMasch, TGT01). Because the spikes are significantly sharper than the AFM tip, imaging the spikes produces an image of the AFM tip. Typical images before and after a wear experiment are shown in Fig. 1. Tip images were analyzed by first flattening the image and then counting the number of pixels at a series of height increments above the baseline, producing a plot of the cross-sectional area of the tip as a function of height above the baseline. After the tip was worn, this procedure was used to determine the area of the end of the worn tip. By comparing the area of the worn end of the tip to tip shape measurements made on the same tip before wear, the total change in tip length H due to wear was readily determined.

The noncontact voltage baseline was measured by acquiring a force curve before and after each scan. For long

sequences of scans, the baseline was measured and reset periodically, typically every five scans. The contact force was determined from the difference between the voltage setpoint and the average baseline, the known cantilever force constant, the instrument setpoint gain (4.3), and the measured AFM sensitivity. AFM sensitivity (determined from slope of the contact region of the force curve) was measured for each sample.

Most of the wear experiments reported in this work employed sodium trisilicate glass ($\text{Na}_2\text{O} \cdot 3\text{SiO}_2$) substrates, which were cut from boules provided by Larry Pedersen, Pacific Northwest National Laboratories. Each substrate was polished with $0.25 \text{ }\mu\text{m}$ diamond powder immediately before use. Relative to silicon nitride (typical Vicker hardness $> 17 \text{ GPa}$), this glass is very soft (Vicker hardness $< 3 \text{ GPa}$). To probe the role of tip-substrate chemistry on the tip wear rates, a variety of other substrates were also employed, including soda lime glass (commercial Gold Seal plain microscope slides). Microscope slides were used either right out of the box with no treatment, or after polishing with $0.25 \text{ }\mu\text{m}$ diamond paste. Flat cleavage surfaces of calcite (Iceland spar, Chihuahua, Mexico) were employed as an example of a surface with minimal hydroxide formation. Mineral FeO_4 (magnetite) was polished with silicon carbide and then with $0.25 \text{ }\mu\text{m}$ diamond paste to produce a smooth surface. Mica (single crystal muscovite) was freshly cleaved before imaging. Polycrystalline silicon nitride was cut from a sintered bar and polished with diamond paste. Sapphire (single crystal), titanium dioxide, and zirconium dioxide were polished with $0.25 \text{ }\mu\text{m}$ diamond paste before scanning. Single crystal quartz and fused silica (previously polished surfaces) were washed before scanning.

III. RESULTS

A. Effect of scan time (sliding distance) and contact (normal) force

The effects of scan duration (which determines the sliding distance) and contact or normal force (F_N) were explored using sodium trisilicate glass ($\text{Na}_2\text{O} \cdot 3\text{SiO}_2$) substrates and ammonium hydroxide solution ($pH \sim 11$). The progression of wear was observed by measuring the amount of material removed from a series of AFM tips, where each tip was treated with a different number of scans at the same contact force ($\sim 120 \text{ nN}$). The scan size and tip velocity were chosen so that each scan involved 1.5 mm of total tip travel along the substrate in 50 s. The total change in tip length for each new tip is plotted as a function of the number of scans in Fig. 2(a). In terms of instantaneous depth of wear, tip wear is initially rapid and gradually slows. Because of the pyramidal tip shape, the area of the tip is increasing with time as wear occurs. The dark line shows a simultaneous least squares fit of a power law expression (described below).

Another set of measurements were undertaken as a function of contact force. Again using a fresh tip for each measurement, 15 scans were performed on a sodium trisilicate glass substrate at the contact force of interest, followed by depth of wear characterization. The resulting change in tip height as a function of normal force is displayed in Fig. 2(b).

Height Change vs Number of Scans and Contact Force

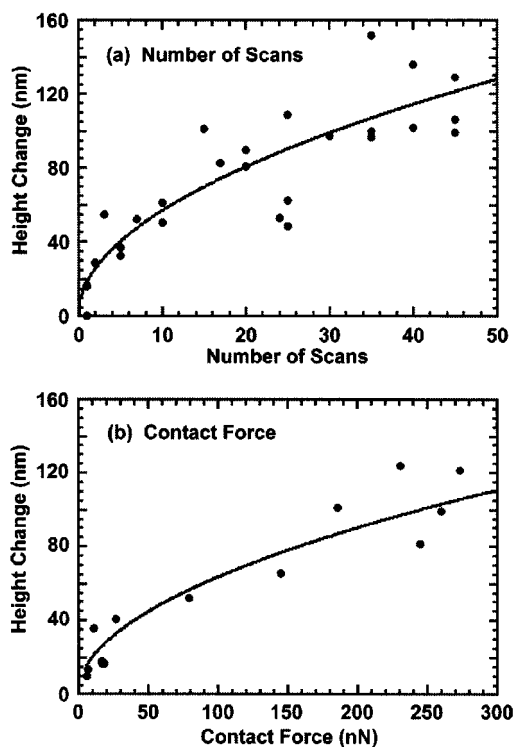


FIG. 2. Height change in AFM tip: (a) as a function of the number of scans on trisilicate glass in ammonium hydroxide ($pH \sim 11$) at a contact force of ~ 120 nN and (b) as a function of contact force over 15 scans. Each scan was 3000×3000 nm² at 5.2 Hz. Each tip wear measurement was undertaken with a fresh AFM tip: (circles) experimental data and (line) least squares fit of Eq. (1) to both sets of data simultaneously.

The dark lines in Figs. 2(a) and 2(b) show the result of a least squares fit of the form $(F_N \times \text{time})^M$ to both data sets simultaneously. The best fit yielded a functional dependence of $(F_N \times \text{time})^{0.51}$.

When compared to macroscopic pin-on-disk wear of silicon nitride in similar solutions, the volume removal rates represented in Fig. 2 are high. For comparison with conventional wear measurements, we convert the height data of Fig. 2(a) to a volume removal rate per unit normal force per unit sliding distance. The slope of the wear rate data in Fig. 2(a) between 5 and 20 scans corresponds to a volume removal rate of 1×10^{-13} m³/N·m. This is 1 order of magnitude higher than the highest volume removal rates observed by Chen *et al.*¹² and Jahanmir and Fischer¹³ and Muratov *et al.*¹⁴ This may in part be due to the exceptionally high stresses at the AFM tip contact (initially >1 GPa) and the single asperity nature of contact, as discussed below.

B. Effect of solution and substrate chemistry

The effect of solution pH was explored by performing a series of measurements involving 25 scans across a sodium trisilicate substrate at a contact force of ~ 120 nN in one of three media: ammonium hydroxide ($pH=11$), water ($pH=7$), and concentrated hydrochloric acid ($pH=1$). No significant changes in tip wear with pH were observed.

The tip wear produced during 25 scans across a variety of substrates in distilled water ($pH=7$) at a contact force of

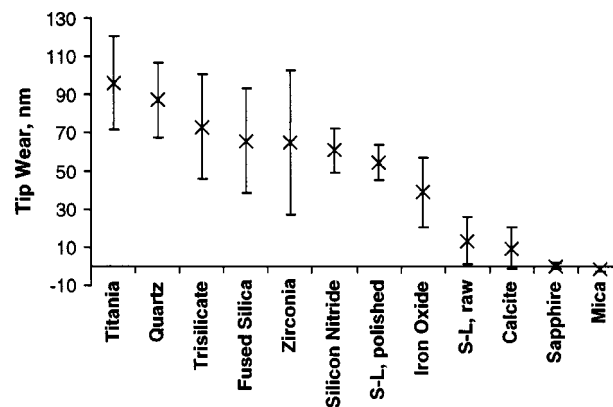


FIG. 3. Amount of tip wear on various substrates in water produced by 25, 3000×3000 nm² scans at 5.2 Hz and a contact force of ~ 120 nN. A fresh tip was employed for each set of scans. Plot shows average and standard deviation for three measurements on each substrate material. "S-L" refers to soda-lime glass.

~ 120 nN is shown in Fig. 3. Three tip wear measurements were made for each sample, starting with a fresh tip each time. Tip wear for five of the substrates was also measured in NH_4OH solution ($pH=11$, data not shown); in all cases tip wear at $pH=11$ was almost identical to tip wear at $pH=7$.

All of the substrates producing significant tip wear (i.e., quartz, fused silica, zirconia, titania, sodium trisilicate glass, polished soda lime glass, and silicon nitride) form modified hydroxide layers in aqueous solution. Twenty-five scans on these materials at a contact force of 120 nN typically removed 50–100 nm of material from the tip. This wear is sufficient to produce a flat area of about 120×120 nm² at the end of the tip. Images of these tips showed that for all of these substrates this flat area was quite smooth, as in Fig. 1(b), with no detectable signs of roughening.

Conversely, substrates which do not form significant hydroxide layers in aqueous solution (calcite, sapphire, and mica) produced little tip wear. Typical wear during 25 scans of these substrates was 0–15 nm, with typical uncertainties less than ± 2 nm. Although the mica structure possesses Si–OH bonds, these bonds are not exposed to the surface by cleavage. The Si–OH bonds on adjacent layers are linked by polyvalent cations, and cleavage occurs between surfaces lacking these bonds.^{15,16} The lack of significant tip wear during scanning on these surfaces is evidence that hydroxide bonds are needed. Note that hardness of the substrate has no influence on tip wear.

Given the role of water in hydroxide formation, the effect of surface hydroxide formation was confirmed by performing wear measurements under ethyl acetate, which eliminates the presence of water. Neither the tip nor the sodium trisilicate glass substrates were given any special treatment to eliminate hydroxyl groups. The resulting tip wear was insignificant (10 ± 8 nm—not shown on plot) at $F_N = 120$ nN; this wear is similar to the (lack of) tip wear produced by scanning calcite in water. Similarly, no tip wear is seen under ethyl acetate on a fused silica substrate. The exclusion of water prevents the replacement of hydroxide bonds consumed in initial wear-related reactions with the AFM tip. It is well known that glass substrate wear rates

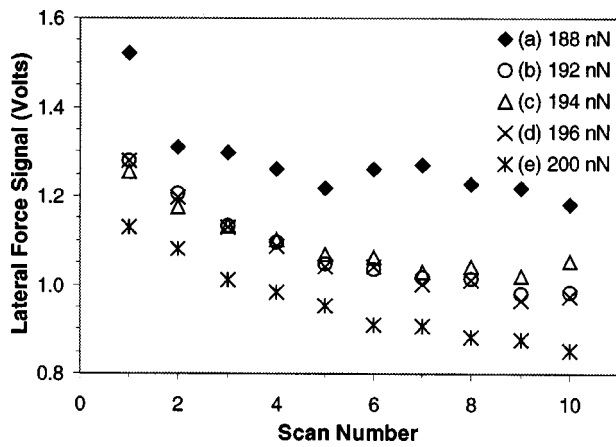


FIG. 4. Lateral force signal during sequential scanning at five different locations on sodium trisilicate glass in ammonium hydroxide solution ($pH \sim 11$). Ten $750 \times 750 \text{ nm}^2$ scans at 7.8 Hz were taken at the first location with a new tip (a), then the tip was moved to an unscanned area and another ten scans were taken (b), then (c) etc.

during polishing operations drop dramatically when water is excluded, presumably for similar reasons.^{17,18}

C. Relation between tip wear and friction

In macroscopic wear experiments involving Si_3N_4 on Si_3N_4 , chemical–mechanical planarization often reduces the coefficient of friction between the tip and the substrate. Macroscopic wear rates have been attributed to a mechanism depending directly on friction. Thus, as the slider and substrate become sufficiently smooth, hydrodynamic lubrication prevails and wear drops to very low levels.

In our case, we note that lateral force measurements (relative values only) such as those shown in Fig. 4, indicate only a small reduction in friction ($<10\%$) during the course of a typical wear experiment. Unlike some nanoscale systems^{19,20} probed at a fixed normal force, friction here is definitely not proportional to the nominal tip–substrate contact area, i.e., friction *decreases* in Fig. 4 as the area *increases*. Furthermore, the small size of the decrease and the significant wear rates that prevail throughout the duration of scanning in this work argue strongly against any transition to hydrodynamic lubrication. The high stresses under the tip, even at our largest contact areas ($\sim 2.5 \times 10^{-14} \text{ m}^2$), prevent the formation of a continuous fluid film between the tip and the substrate.

As noted above, the wear rate versus time (as area increases) is higher than expected if the wear rate were simply proportional to the normal stress, i.e., the increasing tip area reduces the normal stress more than it reduces the wear rate. In contrast, the frictional force decreases even as the tip area increases. Our results are inconsistent with the hypothesis that the wear rate is proportional to friction. Friction and wear in this system involve different chemical or mechanical processes.

IV. DISCUSSION

A. Numerical model of tip wear

The stresses contributing to chemical–mechanical tip wear depend strongly on tip area. Thus, for a given contact force, the resulting stress will decrease as wear progresses and the tip area increases. For a given tip and normal force, one expects that the rate of tip wear decreases as wear proceeds—as observed in Fig. 2. The dark lines in Fig. 2 represent a least squares fit of the form:

$$H(F_N, t_F) = k(F_N t_F)^M, \quad (1)$$

where $H(t_F)$ is the total change in height during a scan experiment of duration t_F (the duration of the wear experiment) and F_N is the contact force. (Applying the same power to F_N and t_F is equivalent to assuming that the instantaneous change in tip height dh/dt is proportional to F_N .) A least squares fit of both sets of data in Fig. 2 simultaneously to Eq. (1) yields $M = 0.51 \pm 0.05$. Both sets of data are described quite adequately.

To interpret these results, we wish to infer the instantaneous wear rate from measurements of total wear $[H(F_N, t_F)]$. The relationship between $h(t)$ and $H(F_N, t_F)$ is given by

$$H(F_N, t_F) = \int_0^{t_F} \left. \frac{dh}{dt} \right|_{F_N} dt, \quad (2)$$

where $h(t)$ is the instantaneous wear rates as a function of time.

The data of Fig. 2 clearly indicate that the wear rate is not simply proportional to the applied stress. For a square pyramid with a tip angle of 70° , the basal area $A = \alpha h^2$, where $\alpha = 1.99$. If the tip wear rate (dh/dt) were simply proportional to stress,

$$\frac{dh}{dt} = \frac{kF_N}{A} = \frac{kF_N}{\alpha h^2}. \quad (3)$$

Integrating this expression yields $H(F_N, t_F) \sim (F_N t_F)^{1/3}$, i.e., $M = 0.33$, in contrast to the observed time and normal force dependence ($M = 0.51 \pm 0.05$). Equation (3) predicts that the rate of tip wear decreases much more slowly with time than is actually observed.

The data are better described by an instantaneous wear rate proportional to the product of applied stress and the length of the worn area $l = \sqrt{\alpha h}$

$$\frac{dh}{dt} = \frac{kF_N l}{A} = \frac{kF_N \sqrt{\alpha h}}{\alpha h^2} = \frac{k' F_N}{h}, \quad (4)$$

where $k' = k/\sqrt{\alpha}$. When integrated, this yields $H(F_N, t_F) \sim (F_N t_F)^{0.5}$, in good agreement with the observed dependent $[(F_N t_F)^{0.51}]$.

The extra factor of h in the numerator of Eq. (4) has the effect of increasing dh/dt at long times (large h) relative to Eq. (3). One possible source of this increase is the gradual, stress-activated production of a chemical precursor state on the substrate as the tip passes over. If the time constant for

precursor formation is small relative to the duration of the applied stress, the precursor concentration will be approximately uniform and constant under the AFM tip. However, if the time constant for precursor formation is long relative to the duration of applied stress, the concentration of states under the tip will increase in a linear fashion from the leading edge of the tip to the trailing edge. Further, the maximum concentration will be proportional to the time required for the tip to pass over any given point on the surface. This time is proportional to the length of the flat portion of the tip, $l = \sqrt{ah}$. The stress at a given substrate location under tips with large flat areas is sustained for longer times than tips with small flat areas, producing higher concentrations of precursor states and yielding faster wear. Given the scan speeds and tip dimensions involved in this work, the relevant time scale for this effect is on the order of milliseconds.

B. Role of chemical processes

Numerous studies have shown that on exposure to moist air or water, the silicon nitride surface rapidly oxidizes to form a thin layer of silicon oxides. Angle resolved x-ray photoelectron spectroscopy (XPS) measurements by Hah et al.²¹ show 2 nm thick oxide layers on silicon nitride surfaces formed by cleaving in air. Tribochemically polished surfaces showed a similar oxide layer, with approximate composition corresponding to 0.2–0.5 nm SiO_2 and 1.0–1.5 nm SiO_xN_y . Abrasively polished surfaces showed thicker oxide layers. Adhesion between silicon nitride AFM tips and a variety of substrates in water was inconsistent with predictions assuming that the tip was composed of Si_3N_4 , but did match predictions for tips composed of SiO_2 .²² In a separate study, XPS of Si_3N_4 AFM tips found considerable amounts of oxygen on the surface, which was attributed to an oxide layer.²³ Traces of surface oxide are also found in wear tracks on silicon nitride.¹³ The ubiquity of oxide films on silicon nitride suggests that the wear of silicon nitride AFM tips is dominated by removal of the oxide, which is subsequently regenerated by further oxidation.

Significantly, AFM tip wear in this work is strongly affected by the chemical, as opposed to mechanical, properties of the substrate. Relatively soft substrates, such as the sodium trisilicate glass, often produced much more tip wear than much harder substrates, such as sapphire. All of the substrates yielding extensive tip wear form surface metal hydroxide species. Quartz, fused silica, zirconia, titania, sodium trisilicate glass, polished soda lime glass, and silicon nitride substrates in aqueous solution all have high densities of surface $\text{M}-\text{OH}$ bonds, where M signifies metal or Si , and showed significant wear. Iron (II–III) oxide in aqueous solution is expected to display a high density of hydroxide bonds and produced intermediate levels of tip wear. Only one substrate with a potential for $\text{M}-\text{OH}$ bonds (alumina) failed to produce significant tip wear, possibly due to kinetic effects. In contrast, all substrates expected to lack surface $\text{M}-\text{OH}$ in aqueous solutions (calcite and mica) produced little if any tip wear. Therefore, we propose that tip wear results from reactions between hydroxide bonds on the tip with hydroxide bonds on the substrate.

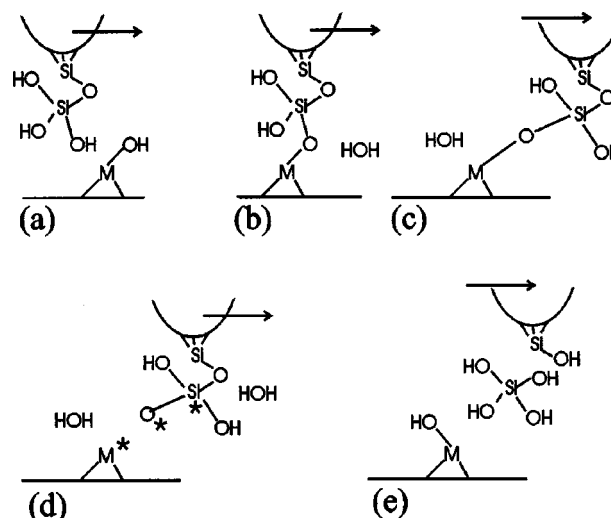


FIG. 5. Chemical reaction model for tribochemical tip wear. In water, the silicon nitride AFM tip is coated with a layer of silicon oxide. (a) During scanning, a hydroxyl group on the tip ($\text{Si}-\text{OH}$) encounters a hydroxyl group on the surface ($\text{M}-\text{OH}$). (b) The two groups react to form a bond, releasing water. (c) As the tip continues its motion across the surface, the bridging bond is stretched. (d) The bond breaks. Energy that was formerly stored in the stretched bridging bond is deposited in the atoms on either side (asterisks). (e) These “activated” atoms react with water, which may also break additional bonds. In this case, a bond between the silicon atom and the AFM tip breaks, releasing the silicon atom from the tip and producing aqueous $\text{Si}(\text{OH})_4$. Further tip motion yields additional reactions and more broken $\text{Si}-\text{O}$ bonds on the tip surface, as well as $\text{M}-\text{O}$ bonds on the substrate.

On close contact, silicon hydroxyls on the AFM tip can form chemical bonds to hydroxyl groups on the substrate surface.^{10,17,24} A schematic diagram of such tip–substrate bond formation is shown in Figs. 5(a) and 5(b). As the tip moves, these tip–surface bonds would be stretched [Fig. 5(c)], and eventually rebreak [Fig. 5(d)]. Simple bond breaking will not result in tip wear (requiring removal of Si). Breaking any connecting bond in Fig. 5(c) would leave the silicon atom attached to one of the surfaces, and breaking two bonds simultaneously is statistically unlikely. However, when a tip–surface bond breaks, the energy of the stretched bond may transfer to kinetic energy of the atoms on each side of the bond [Fig. 5(d)] which weakens the other $\text{Si}-\text{O}$ (or $\text{M}-\text{O}$) bonds toward reaction with water. We propose that this stretching and breaking process plays a critical role in tip wear.

Recoil energy as the stretched bonds break provides the mechanism to break the second bond after the first bond breaks, and it is the breaking of the second bond that leads to wear. The importance of this second step can also be observed in the lack of wear in the absence of water. As long as surface hydroxyls are present, tip–substrate bonds can form in the absence of water, and if bond breaking [Figs. 5(c)–5(d)] was all that was required for wear, then water would not be required for wear to occur. The fact that no wear occurs when ethyl acetate solution is used to exclude water strongly suggests that wear occurs not during bond breaking, but during subsequent reactions with water [Figs. 5(d)–5(e)].

Tip–substrate bond formation plays a critical role in the proposed model of tip wear. One might expect formation of such bonds would depend on the ratio of protonated ($\text{M}-$

OH) to deprotonated (M–O) hydroxyls on both surfaces, and thus vary with *pH*. Katuski *et al.*¹⁰ observed a weak dependence of silicon nitride AFM tip wear on *pH*, while Hah and Fischer⁶ observed no significant *pH* dependence of the macroscopic wear of silicon nitride in the presence of various chemicals. No significant *pH* dependence was observed in our work. A weak or absent *pH* dependence may reflect the heterogeneity of the surface. With SiO_xN_y and SiO₂ components, the tip surface may not have a well-defined isoelectric point. It is also possible that the local *pH* at the tip–substrate interface becomes nearly independent of the solution *pH* when the two surfaces are pressed tightly together and most of the solution is excluded.

C. Comparison with millimeter-scale wear experiments

AFM tip wear in this work appears to be predominately tribochemical, as opposed to mechanical (no abrasive or adhesive wear). For example, alumina is harder than quartz and is frequently used as a polishing abrasive.²⁵ Conversely, in the absence of tribochemical effects, silica generally makes a poor abrasive.¹⁸ Nevertheless, alumina (sapphire) produced little if any tip wear, while the relatively soft sodium trisilicate glass produced as much wear as crystalline quartz or silicon nitride. At the normal forces used (5–300 nN), fracture and deformation are strongly hindered, minimizing the abrasive effectiveness of hard materials like alumina. Given an appropriate chemical environment, tribochemical effects appear to dominate at the nanometer scale.

Tribochemical effects can dominate the friction and wear of macroscopic silicon nitride sliders in aqueous solutions under appropriate conditions. These tribochemical effects are of considerable interest, in part because tribochemical wear can produce smooth, precisely matted surfaces that subsequently display extremely low friction and wear rates under hydrodynamic lubrication.^{5,7} We found no evidence for hydrodynamic lubrication at the tip–substrate interface in this work. Lateral force estimates made using the tip geometry and typical Si₃N₄ moduli are consistent with an in-liquid coefficient of friction of ~0.6 between the tip and the sodium trisilicate glass substrate. Throughout our wear experiments, the estimated coefficient of friction remained much greater than those characteristic of hydrodynamic lubrication (<0.005); similarly, we observed no dramatic reduction in tip wear as wear progressed. We attribute the lack of hydrodynamic lubrication to the small size and relatively slow speed of the AFM tip, which does not allow formation of a continuous liquid film between the two surfaces.

Macroscopic sliding surfaces in solution that are too rough or are moving too slowly are supported in part by hydrodynamic forces and in part by asperity contact. Using silicon nitride spheres worn to produce a 300 μm diameter contact area, Muratov *et al.* studied a mixed hydrodynamic and asperity contact were regime dominated by chemical–mechanical processes.¹⁴ They found that the specific wear rate (volume removed per unit load per unit distance—m³/N m) was proportional to the frictional force over a wide range of slider velocities (1–100 mm/s). A most surprising and unexplained observation was that the specific wear rate

decreased with increasing load. Muratov *et al.* attributed wear under these conditions to a direct mechanical stimulation of the surface, which induced a chemical reaction resulting in wear. After accounting for the portion of the load supported by hydrodynamic forces, a simple model of simple asperity wear showed no velocity dependence on asperity wear.

At still lower slider velocities (<1 mm/s), Muratov *et al.* observed a different wear mechanism, where the specific wear rate increased markedly with decreasing slider velocity. This wear was attributed to the spontaneous formation of a chemically modified layer on the slider, which was subsequently removed by frictional forces. Similar modified layers are believed to be important in chemical-mechanical wear. Our tip velocity (16 μm/s) falls squarely in the range of slider velocities where such chemically modified layers are expected, but the AFM tip wear in this work shows no significant velocity dependence.

The results of macroscopic wear experiments can be rationalized with our single asperity measurements if this modified layer forms *between* asperities. As the asperities wear, the softer material between them is also removed, resulting in much higher specific wear rates than would be expected in the case of asperity wear alone. Soft material between asperities could also bear a portion of the total applied load. This wear mechanism would not apply to the single-asperity wear of AFM tips, where good asperity–substrate contact minimizes solution–asperity contact and prevents the formation of a soft modified layer.

To compare our data more directly with macroscopic measurements, it is convenient to convert our measurements to specific wear rates (m³/N m), *K*. For our AFM tip geometry, *K* can be expressed in terms of *h*(*t*) as

$$K = \frac{\alpha h^2}{F_N \nu} \frac{dh}{dt}, \quad (5)$$

where ν is the tip velocity. Using the functional expressions for *h*(*t*) and *dh*/*dt* derived from the data [from Eq. (1)], the experimental value of *K* is proportional to (*F_Nt*)^{0.53}. If tip wear were simply proportional to stress, as in Eq. (3), the specific wear rate would be independent of contact force and time—typical of many tribological systems. As noted above, one possible explanation for the unusual load dependence of wear rates is a time- (under the contact) and stress-dependent formation of wear precursor states.

The resulting specific volume removal rate in this work is a function of time due to the combination of pyramidal tip geometry and unusual dependence of *dh*/*dt* on *h*(*t*). Experimental estimates of *K* during the first five scans are difficult due to the scatter in the data. However, between 5 and 15 scans, a meaningful value of *dh*/*dt* ~ 7 × 10⁻¹¹ m s⁻¹ can be determined from the data; during this interval, the average *h* is about 55 nm. At this stage of tip wear, the tip area is about $\alpha h^2 = 6 \times 10^{-15}$ m², the average stress applied to the tip is about 20 MPa, and therefore the specific material removal rate is about 1 × 10⁻¹³ m³/N m. By way of comparison, Muratov *et al.*¹⁴ measured a specific wear rate of 4 × 10⁻¹⁴ m³/N m for a macroscopic slider in aqueous CrO₃ at a tip velocity of 40 μm/s (the lowest speed for which data is re-

ported) and an average slider stress of 28 MPa. Thus the rate of material removal from the AFM is high relative to macroscopic silicon nitride systems under roughly comparable conditions.

The average rate of tip wear between 5 and 15 scans corresponds to the removal of approximately 1 monolayer of silicon ions every 4 s. During this time, the AFM tip travels about 60 μm (20 linear scans); due to the two-dimensional (2D) scanning action, the AFM tip is displaced 250 nm along an axis perpendicular to the linear scan direction during this time. Given the small size of the AFM tip, it is unlikely that this wear involves multiple monolayers of a soft reaction product—in contrast to wear at similar tip velocities on macroscopic silicon nitride sliders. The rate limiting step in the wear of AFM tips apparently involves only a surface monolayer.

D. Relation to chemical mechanical polishing

In some models of chemical mechanical polishing, material removal is attributed to the mechanical abrasion of a soft surface reaction layer. If, as we propose, this layer is formed between asperities, material removal will involve competition between the rate of the chemical reaction (to form the modified layer) and the rate of asperity wear (which limits the time for surface modification). In the context of commercial chemical mechanical polishing operations, asperity contact is ideally confined to colloidal particles on the polishing pad, while chemical surface modification is largely confined to the substrate being polished. However, it is difficult to account for the effectiveness of certain abrasive materials, such as cerium oxide, in terms of mechanical effects alone. The effectiveness of some polishing materials has been attributed to a poorly defined property sometimes called “chemical tooth.” In the present work, it is clear that the chemical reactivity of the substrate plays a key role in tip wear, which we feel is due to the formation of bridging oxide bonds between the tip and the substrate. The effectiveness of colloidal silica particles in chemical mechanical polishing (although not as effective as some other oxides) suggests that bridging oxide bonds may play a similar role in many chemical–mechanical polishing systems.

V. CONCLUSIONS

Silicon nitride AFM tips are a useful surrogate for the study of nanoscale single asperity wear in more macroscopic systems. Over a large range of contact forces and tip velocities, the wear of silicon nitride AFM tips is dominated by chemical-mechanical effects involving not only the solution but also the chemical nature of the substrate. In the present work, the only substrates that yield significant tip wear are characterized by high densities of metal–hydroxide bonds. Wear also requires an aqueous environment. Solution *pH* has little influence on tip wear rates. The role of water is assumed to replenish hydroxide bonds on the substrate surface that are consumed in mechanically mediated reactions with the tip.

AFM tip wear rates in water are not simply proportional to stress. The data are well accounted for if the wear rate is

also proportional to the linear dimension of the worn area of the tip. We propose that the resulting force- and time-dependent wear reflects the relatively slow, stress-activated formation of a reaction precursor under the tip—where larger tip areas maintain high stresses for longer times, and thus produce higher precursor concentrations than smaller tip areas.

Measurements of AFM tip wear provide a powerful probe of single asperity wear. By comparing the results of single asperity wear with macroscopic slider wear, wear mechanisms which affect primarily asperities can be isolated and studied apart from other wear mechanisms. Ultimately, we hope to understand macroscopic wear dominated by asperity contacts in terms of the wear of individual asperities from a given initial size distribution. Because silicon nitride tip hydrolyzes to silica on contact with water, these results also relate to the polishing of silicon dioxide in the manufacture of integrated circuits. Surface chemistry may also play an important role in promoting or limiting wear of silicon nitride and similar materials in micromechanical devices.

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