Robust Self-Assembled Octadecylphosphonic Acid Monolayers on a Mica Substrate

H.-Y. Nie,* D. J. Miller, J. T. Francis, M. J. Walzak, and N. S. McIntyre

Surface Science Western, Room G-1, Western Science Centre, University of Western Ontario, London, Ontario N6A 5B7, Canada

As determined by scratch tests, self-assembled monolayers (SAMs) of octadecylphosphonic acid (OPA) on a muscovite mica substrate were found to be mechanically robust and to serve as a lubricant to protect the underlying mica substrate. For comparison purposes, three polymer films were subjected to scratch tests under the same conditions. The scratch tests were conducted using a diamond-tipped stylus, and the resultant scratches were examined using atomic force microscopy. The excellent mechanical strength of OPA SAMs is supported by analysis with time-of-flight secondary ion mass spectrometry, which suggests that the headgroup of the OPA is strongly bonded to the substrate atoms. The molecular lubrication provided by OPA SAMs suggests that the interaction between the headgroup and the substrate is sufficiently strong to endure significant shear force and that the hydrocarbon chains are able to dissipate shear energy.

Introduction

Organic molecular self-assembled monolayers (SAMs)[1,2] on a solid surface provide a simple path to fabricate ordered molecular structures.[3] They possess the potential to serve as nanolubricants for advanced micro-electromechanical systems[4] and magnetic hard disk storage units.[5] A SAM prepared on a solid substrate has proved to have an excellent friction coefficient under different temperature and relative humidity conditions.[6] Friction coefficient measurements of organic molecular SAMs prepared on a solid surface showed a superior lubricity of the films.[7] SAMs have demonstrated promise as ultrathin barriers preventing a number of processes, such as Cu diffusion between a Cu electrode and SiO_2 dielectrics in nanometer-scale semiconductor devices.[8] These examples involve the use of various silanes[4,5,8] and thiols[6,7] to form SAMs.

The formation of SAMs of octadecylphosphonic acid (OPA) on a mica substrate has been recently investigated using atomic force microscopy (AFM).[9−14] There are two SAM model systems: alkanethiols on a gold[1] surface and silanes on an oxide surface.[2] Thiol molecules form SAMs on gold by a specific interaction between the sulfur atom and gold atom. Silanes form SAMs on an oxide surface on the basis of a mechanism linked to their ability to polymerize.[9] On the other hand, for OPA SAMs on a mica

substrate, the attachment chemistry is believed to be fairly general.[9] Therefore, the system of OPA on mica appears to serve as a more general model system for investigating the fundamentals of SAM formation on surfaces such as mica.[9,11] AFM studies on the mechanism of SAM formation of OPA[10] and its thermal stability[12] have been reported. It has been found that an OPA SAM layer on a mica substrate shows a self-healing behavior when scratched by a sharp silicon tip (radius ∼20 nm).[13]

There are a number of articles reviewing the full range of issues in SAM systems.[11,15,16] The mechanical properties of thiol SAMs have been investigated using nanoindentation, revealing that the molecules compress under the indentation.[17,18] Experiments on molecular-scale tribology showed decreases in the thickness of alkylsilane SAMs as imaging pressures increase.[19] In this study, we report on experiments that aimed to probe the strength of OPA SAMs as a lubricant on a mica substrate. We conducted AFM investigation on OPA SAMs on a mica substrate as well as on bare mica substrates exposed to calibrated mechanical scratching performed with a 2-μm-radius diamond tip using a mechanical profiler. Our experimental results on scratch tests clearly suggest that the OPA SAMs protect the underlying mica substrate, which is otherwise scratched under the same conditions. We used time-of-flight secondary ion mass spectrometry (ToF-SIMS) to investigate the ion fragments from the OPA SAM samples upon the primary ion bombardment. The ToF-SIMS results suggested strong interactions between the OPA headgroup and the mica substrate. Our experimental results of both the scratch tests and ToF-SIMS analysis demonstrate that OPA SAMs serve as a good lubricant on a mica substrate.

Materials and Methods

Crystalline powder of OPA [$CH_3(CH_2)_{17}PO_3H_2$, molecular weight $M_w = 334.47$] was purchased from Alfa Aesar (Ward Hill,

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MA). A 0.25 mM OPA solution in ethanol was used to prepare the OPA monolayers on a mica substrate. The OPA solution was spread on a freshly cleaved mica substrate for ~10 s, after which the excess was removed in a stream of compressed gas. This simple process is able to produce homogeneous OPA SAMs on a mica substrate, as examined by imaging the surface morphology using AFM. The OPA layer thickness reported ranges between 1.6 and 2.0 nm, as determined using AFM by different research groups.[9,12,14]

Scratch tests were carried out using a diamond-tipped stylus profiler (P-10, Tencor). The radius of the diamond was ~2 μm. The scratch tests were conducted by scanning the surface of interest at a scan speed of 50 μm/s and at an applied force of 0.5 mN, the maximum force available for the profiler.

Contact mode AFM (Explorer, TopoMetrix) was used to evaluate the results of the scratch tests conducted on OPA SAMs deposited on a cleaved mica substrate. A rectangular silicon cantilever with a nominal spring constant of 0.05 N/m was used. The cantilever was 300 μm long, 35 μm wide, and 1.0 μm thick. The imaging force was on the order of several nanonewtons. For the reference polymer samples, which are described later, dynamic force mode AFM was used. For dynamic force mode AFM, rectangular silicon cantilevers with a spring constant of ~40 N/m were used. The cantilever was 125 μm long, 35 μm wide, and 4.0 μm thick. The tip integrated on both types of cantilevers had an apex radius of ~10 nm. The experiments involving sample preparations, scratch tests, and AFM imaging were conducted in air under a relative humidity of 35−40%.

ToF-SIMS (ION TOF ToF-SIMS IV, Cameca) was used to study the SAMs prepared on a mica substrate. A 25-keV, 10-kHz pulsed primary Ga^+ ion beam was used to bombard the sample surface. The ion beam had a measured current of 2.5 pA, and a dose of ~$10^{13}/cm^{-2}$ was used. The negative secondary ion fragments introduced by the primary ion bombardment were collected and analyzed from an area of 500 μm × 500 μm.

Three polymer materials were also used for the same scratch tests for comparison purposes. Poly(ethylene oxide) (PEO) films were deposited on mica and a Si(100) substrates by covering the substrate with a 0.5 wt % PEO (M_w = 300 000) solution in deionized water for ~30 s and subsequently spinning the sample at 9000 rpm to remove the excess solution. PEO films prepared in this manner showed a monolayer of nanometer-scale fibers.

A thermally extruded, biaxially oriented isotactic polypropylene (PP) film (0.03 mm thick) was also used in this study. The PP film was produced from a homopolymer resin (M_w = 1.9 × 10^5, polydispersity 6.0). The base resin contains 500−1000 ppm each of an inorganic acid scavenger and a high-molecular-weight phenolic antioxidant. The PP was produced on a tenter-frame film line and quenched at 45 °C prior to orientation. The PP film was formed with machine-direction (MD) and transverse-direction (TD) draw ratios of 5.2:1 and 9:1, respectively.

The 0.1-mm-thick poly(ethylene terephthalate) (PET) film was fabricated from a homopolymer resin with a degree of polymerization of 100 (M_w = 2.5 × 10^4). The PET base resin contained ~300 ppm of residual metal catalyst and 50 ppm of an organometallic thermal stabilizer. Biaxially oriented PET film was produced from this resin on a tenter-frame film line. The MD draw ratio was 3.4:1, and the TD draw ratio 4.6:1. For the two biaxially oriented PP and PET films, the scratches were created in the MD.

Results and Discussion

Shown in parts a and b of Figure 1 are topographic and friction force images, respectively, for a sample of OPA SAMs prepared on a mica substrate after being subjected to a scratch test using a diamond tip (~2 μm radius) at an applied force of 0.5 mN. The images are presented in gray scale, where bright areas correspond to those that are higher (Figure 1a) or have a larger friction force (Figure 1b). Figure 1a shows that the OPA SAMs on the mica substrate are characterized by closely packed islandlike monolayers. The coverage of the SAMs was greater than 80%. The black areas between the OPA islands in the topographic image (Figure 1a) represent the exposed mica
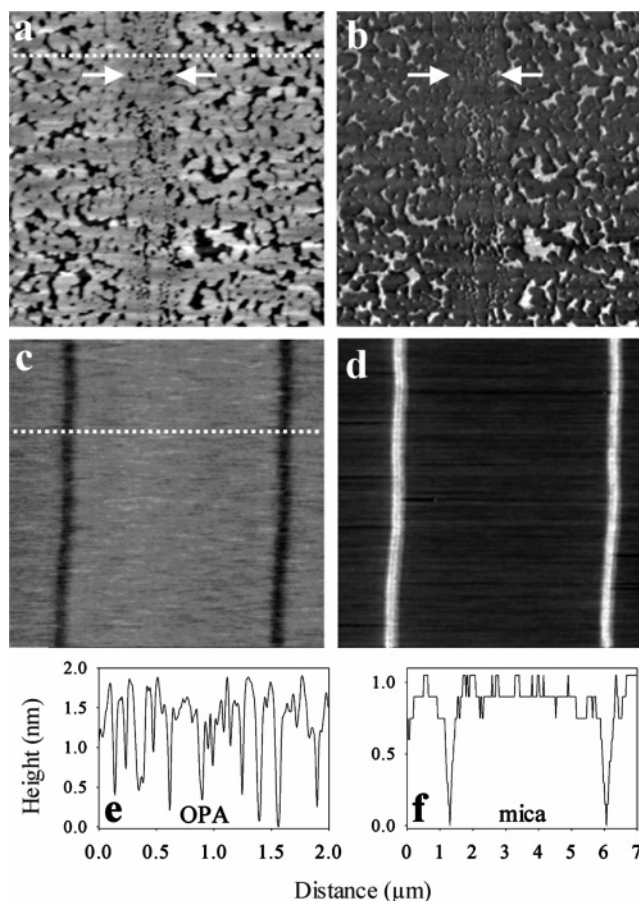

Figure 1. Topographic (a) and friction force (b) images (scan area 2 μm × 2 μm) for OPA SAMs prepared on a mica substrate. The inserted arrows guide the eye to the merely recognizable scratch created using a diamond tip (~2-μm radius) under an applied force of 0.5 mN at a speed of 50 μm/s. The same scratch test was conducted on a bare mica substrate, and the topographic (c) and friction force (d) images (scan area 7 μm × 7 μm) clearly show the scratches created. Shown in parts e and f are profiles isolated from the dotted lines in parts a and c, respectively. The gray scale for both parts a and b is 2.5 nm. The gray scales for the friction force images in parts b and d are 3.8−4.1 and 3.4−5.2 nA, respectively, with the unit of measure, nanoamperes, corresponding to the output of the photodetector which responds to the torsion on the cantilever.

surface. Figure 1e shows a profile isolated from the topographic image for the OPA SAMs shown in Figure 1a. OPA SAMs prepared on mica substrates appeared to have a thickness of ~1.8 nm, as determined from the contact mode AFM measurements (a dynamic force mode or tapping mode AFM measurement usually resulted in a lower value of ~1.6 nm).

As shown in Figure 1a, the morphological difference between the scratched area and the pristine area is merely recognizable by the difference in the density of the monolayer in the scratched area guided by the inserted arrows, as compared to that in the pristine area. This indicates that the shear deformation rearranged the OPA molecules in such a way that they were able to diffuse to a proximate, unoccupied mica surface. If local heating were also possible during scratching, then both temperature and pressures[17,18] would contribute to making OPA molecules movable on a nanometer scale, as observed in Figure 1a. In fact, it has been shown that molecules of OPA SAMs on a mica substrate start to diffuse at a temperature of 90 °C.[12] The image in Figure 1a shows in fact the most significant change caused by scratching we ever observed in our OPA SAM samples. We have found

that, for OPA SAMs with a higher coverage, there was no apparent change on the scratched area, indicating that diffusion of the molecules requires proximate open space. We also noticed that there was a depression of only a couple of angstroms on the scratched OPA area from evaluating a number of scratch tests conducted on our OPA SAM samples. In other words, the scratch test only depressed the monolayers to an extent of a couple of angstroms without a significant change in the OPA SAMs.

It is clear from the friction force image in Figure 1b that the exposed mica surfaces have a higher friction force than the surrounding OPA islands. Contrasts in a friction force image, as shown in Figure 1b, serve to distinguish the hydrophilictiy of the surface features in the same image. This difference in friction force arises because the mica surface is hydrophilic, while the methyl-terminated OPA SAM surface is hydrophobic. As shown in Figure 1b, after the scratch test, however, there is no significant difference seen in the contrast in the friction force image between the scratched OPA surface and the surrounding pristine OPA surface, indicating that the chemistry of the monolayer is unchanged.

The barely detectable scratches serve to show where the diamond tip scratched the surface. The width of the scratches created on the OPA SAMs under an applied force of 0.5 mN is ~320 nm. The result of the scratch test conducted on the OPA SAMs showed that the molecular headgroups were not removed by the shear force applied to the film by the diamond tip. This suggests that a strong interaction exists between the headgroups of the OPA molecules and the mica substrate.

To illustrate the strength of the OPA SAMs in resisting shear deformation imposed by the diamond tip, we conducted similar scratch tests on bare mica substrates, on which clear scratches were created. Parts c and d of Figure 1 show topographic and friction force images, respectively, for scratches created on the bare mica substrate. Figure 1f is a cross-sectional profile isolated from Figure 1c, allowing us to estimate that the scratches are ~300 nm wide and ~1 nm deep. The friction force image in Figure 1d shows that the scratches have a higher friction force than the pristine surface.

Scratches created on bare mica substrates under a lower relative humidity were sometimes invisible in topographic images, but the friction force images always displayed a higher friction force on the scratches. This difference has been explained previously as arising from a rupture of only a single layer of Si−O bonds (0.2 nm) at the mica substrate, instead of the removal of one complete layer (~1 nm).[20]

It is thus clear that, under the scratching conditions that left scars of ~1 nm deep on a bare mica substrate (Figure 1c), the OPA SAMs were resilient to the shear deformation. Our experimental results thus show that the OPA SAMs actually protected the underlying mica substrate when subjected to the scratch tests. From the scratching results for the bare mica substrate, it is clear that the shear force imposed by the diamond tip was enough to remove one layer of mica. The organic molecules in SAMs would be desorbed if the applied pressure is high enough.[16,18] The diamond tip during the scratching compressed the OPA molecules but apparently not to the extent that would destroy the SAMs. This experimental fact indicates that OPA molecular headgroups interacted sufficiently strongly with the mica substrate. Because there is no significant deformation or morphological change in the scratched area, it is clear that the compressed

OPA molecules relaxed when the load was removed. The compression of the OPA molecules may be responsible for dissipating the deformation energy applied form the diamond tip during scratching.

To understand the significance of the lubrication provided by OPA SAMs, it is necessary to know the nature of the mechanical stress to which the monolayers have been exposed during scratching. The indentation of a tip into a surface results in a mutual elastic deformation, unless the force reaches the point where a plastic deformation occurs. Analysis of Hertzian contact establishes the relationship among the contact radius, the deformation depth, and the applied forces.[21,22] The formation of a scratch can be treated as an indentation that moves in a lateral direction. The width of the scratch is a measure of the contact radius of the diamond tip during the formation of a scratch. Assuming the width of the scratch records the contact diameter, we can estimate the applied pressure and the deformation depth into the sample surface.

According to Landau and Lifshitz,[21] the contact radius, a, between a sphere with radius R and a plane, under an applied force, F, is reduced to

$$a = (FDR)^{1/3}$$

The parameter D is related to the Young moduli, E, of the two bodies and their Poisson ratios, σ. In the case where the sphere has a much higher E value than the plane, as is true for our system of a diamond tip (~1000 GPa[23]) versus a mica substrate (150−200 GPa[24−26]), $D = 3(1 - \sigma^2)/(4E)$. Assuming a Poisson ratio of 0.3, a diamond tip with a 2-μm radius under an applied force of 0.5 mN will make a contact radius of 165−150 nm on a mica substrate with a Young modulus of 150−200 GPa. This calculation thus predicts a scratch width of 330−300 nm, which is close to the scratch width observed on the mica substrate. From the applied force and the contact radius, one can estimate the maximum pressure imposed by the diamond tip on the sample surface, which is $^3/_2$ times the mean pressure $F/(\pi a^2)$.[22]

The depth, d, to which the sphere deforms the (softer) plane is[21]

$$d = (FD)^{2/3}(R)^{-1/3}$$

The deformation depth is inaccessible in the case of an elastic deformation because the deformed body will recover upon the removal of the applied force. From the measurable scratch width, it is possible to estimate this deformation depth. From the above two equations for contact radius and deformation depth, one can eliminate the Young modulus and the applied force from the equations and relate them as $d = a^2/R$. The width of the scratches as determined from the AFM images is thus used for an estimation of the deformation process. In a system of a SAM on a mica substrate, the contact radius of the diamond tip is mainly limited by the Young modulus of the underlying substrate.

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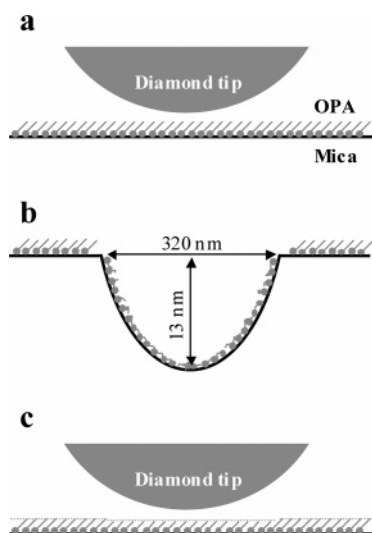(26) Kracke, B.; Damaschke, B. *Appl. Phys. Lett.* **2000**, *77*, 361.

Figure 2. Before (a), during (b), and after (c) the Hertzian contact between the diamond tip and an OPA SAM on a mica substrate. The molecule of OPA and the tip depicted are not to scale. Note that in part b the deformation depth is exaggerated with respect to the diameter of the contact area; the perimeter of the contact area is omitted. The dotted line in part c depicts the depression of the contacted area.

From Figure 1a, the width of the scratch for an OPA SAM is estimated to be ~320 nm under an applied force of 0.5 mN. The contact radius, a, between the diamond tip and the surface is therefore ~160 nm. Following the Hertzian contact model described above, this radius reveals the depth of the sample surface (OPA SAM plus mica substrate) deformed by the tip upon scratching as being ~13 nm. The maximum and mean pressures of the diamond tip on the OPA SAM are 9.3 and 6.2 GPa, respectively. Therefore, despite the fact that the surface was temporarily deformed 13 nm inward during the formation of the scratch, the OPA SAMs endured this deformation without being destroyed or removed from the substrate—a reflection of the strong interaction between the OPA molecular headgroups and the mica substrate.

The deformation of an OPA SAM on a mica substrate by the diamond tip is illustrated in Figure 2. The system of a diamond tip approaching a surface of an OPA SAM is shown in Figure 2a. The deformation under the conditions of an applied force of 0.5 mN is shown in Figure 2b. Upon removal of the diamond tip, the recovery of the monolayer is shown in Figure 2c, although the OPA molecules may be compressed to some extent.[17-19] To emphasize the relationship between the length of the molecules and the deformation, the diameter of the contact area is not to scale.

As shown in Figure 2b, when the diamond tip scratches an OPA SAM prepared on a mica substrate, the surface is deformed 13 nm, under a maximum or a mean pressure of 9.3 or 6.2 GPa (calculated from the observed contact radius of 160 nm). Under such "harsh" conditions, the monolayer should have been deformed. The monolayer is apparently not destroyed and the OPA molecules recover upon the removal of the load. As depicted in Figure 2c by the dotted line, however, the monolayer could be depressed a couple of angstroms as measured by AFM for our samples. We believe that the OPA chains also play an important role in the dissipation of the shear energy through their flexibility (compression and relaxation responding to loading and unloading of pressures, respectively); thus, they are functioning as a lubricant. This is supported by experimental[17] and theoretical[18] inves-
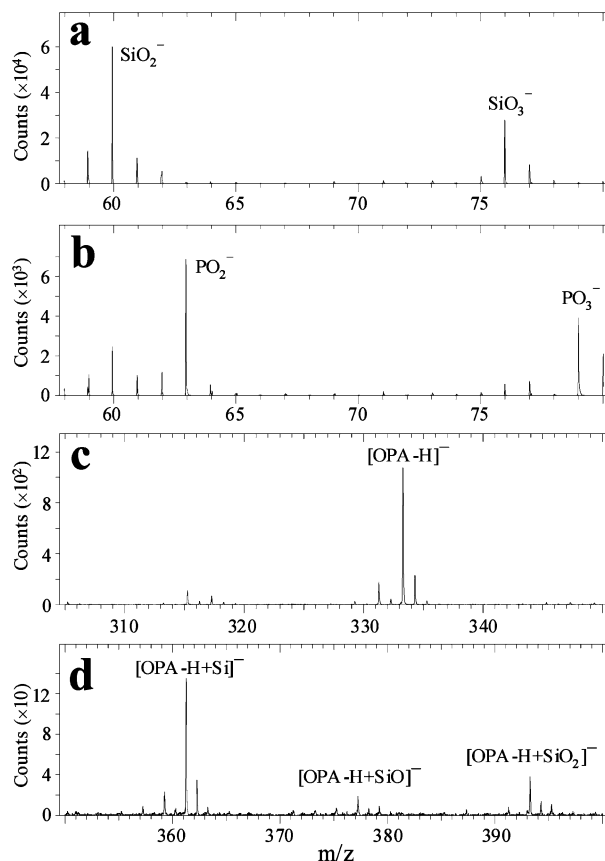

Figure 3. ToF-SIMS mass/charge spectra of a cleaved mica substrate (a) and an OPA SAM (b−d) prepared on a mica substrate. Other ion fragments of the muscovite mica substrate, such as O, OH, Si, and AlO, were also detected.

tigations on the mechanical relaxation of thiol SAMs on a gold surface, which suggest that molecular compression provides a mechanism for energy dissipation.

AFM examination and the elastic deformation analysis described above clearly show that an OPA SAM is mechanically robust and serves as an excellent lubricant on the mica substrate. The strong interaction between the OPA headgroup and the mica substrate was confirmed by ToF-SIMS analysis. Shown in parts a and b of Figure 3 are ToF-SIMS spectra of negative secondary ions for a freshly cleaved mica surface and an OPA SAM on a mica substrate, respectively. Muscovite mica has a layered structure where every two tetrahedral silicate layers sandwich an octahedral alumina layer.[27-29] The mica surface is terminated by the basal oxygen atoms of the silicate tetrahedron. Each such basal oxygen atom is shared by two tetrahedral silicate units to form a hexagonly linked plane. The apical oxygen atoms of the silicate tetrahedra are shared by the underlying AlO_4-$(OH)_2$ octahedra. The tetrahedral silicate ion layers are connected by a rather weak potassium ion (K^+), so that mica is cleavable in this layer. The thickness of the structure between the two layers of K^+ is ~1 nm. It is clear from Figure 3a that the ion fragments of SiO_2^- and SiO_3^- are characteristic of the mica substrate. They are due to the decomposition of the tetrahedral silicate layer of the mica surface upon the primary ion bombardment.

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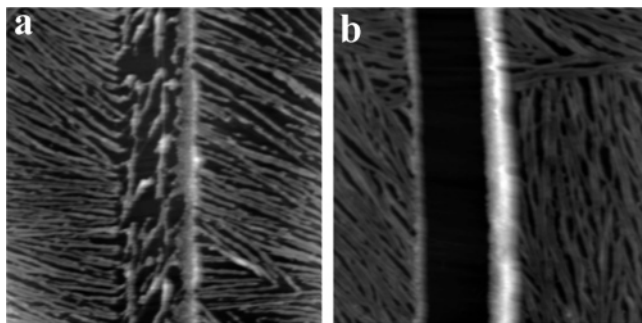
Figure 4. AFM images (scan area 2 μm × 2 μm) of scratched PEO films spin-coated onto a mica substrate (a) and a Si substrate (b), respectively. The gray scales are 17 and 37 nm for parts a and b, respectively.

Figure 5. AFM images (scan area 10 μm × 10 μm) of scratched biaxially oriented PP (a) and PET (b) films. The gray scales are 113 and 177 nm for parts and b, respectively.

For the sample of an OPA SAM prepared on a mica substrate, as shown in Figure 3b, ion fragments of PO_2^- and PO_3^- were detected. These ion fragments are used to identify the OPA molecule. The appearance of the SiO_2^- signal in Figure 3b is believed to arise from the incomplete coverage of the OPA SAM on the mica substrate.

As shown in Figure 3c, deprotonated OPA molecules, denoted as $[OPA - H]^-$, were detected on the OPA SAMs. This indicates that an entire OPA molecule is removed upon the primary ion bombardment. However, we also observed in Figure 3d ion fragments of deprotonated OPA attached to the mica constituent Si, SiO, or SiO_2 fragments denoted as $[OPA - H + Si]^-$, $[OPA - H + SiO]^-$, and $[OPA - H + SiO_2]^-$, respectively. A recombination of these complex ion fragments is unlikely in the secondary ion formation if they are originally apart from each other.[30] Therefore, the ion fragments of Si, SiO, or SiO_2 attached to the deprotonated OPA molecule shown in Figure 3d arose most likely from the breaking of Si–O bonds within the silicate tetrahedra. It appears from this result that the headgroup–mica surface interaction may be comparable to or stronger than the covalent bonds within the silicate unit. The ToF-SIMS spectra shown in Figure 3d suggest a possible chemical bond formation between the OPA headgroup and the mica substrate, which is normally terminated by the basal oxygen groups of the tetrahedral silicate ions. However, more data on ToF-SIMS and other analytical techniques[30,31] are apparently required for identifying the nature and strength of the interaction between the OPA molecular headgroup and the mica substrate. On the basis of the scratching results and ToF-SIMS results, it is fair to state that a strong interaction between the headgroup of the molecule and the substrate provides the observed robustness of the OPA SAMs in the presence of shear deformation.

To compare the robustness of an OPA SAM on a mica substrate, we conducted scratch tests on a PEO film spin-coated onto both a mica substrate and a silicon substrate. The conditions of the scratch test were the same as those for the OPA SAM sample. Shown in parts a and b of Figure 4 are the results of the scratch tests of the PEO films spin-coated on a mica substrate and a Si(100) substrate, respectively. The PEO film is characterized by nanometer-scale fibers with a thickness of 5 and 8 nm on the mica and Si substrates, respectively. These PEO films were made on a substrate as part of a project to fabricate polymer films suitable for evaluating the performance of AFM probes.[32,33]
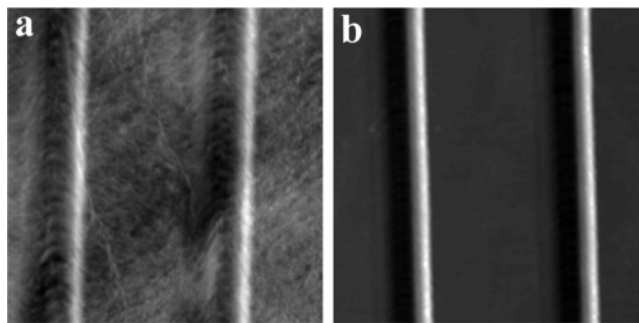
In contrast to the resilience of the OPA SAMs when subjected to the scratch test, the PEO fibers were destroyed and removed from the mica substrate (Figure 4a). Although the PEO was not completely removed from the scratched area, one can see from the AFM image that the remaining PEO strands have been totally modified in this area; that is, they are no longer in the form of the original fibers. The residual PEO materials are apparently rearranged under scratching and dragged along the shearing direction. PEO fibers may protect the mica substrate once at the cost of their removal upon scratching. Therefore, the physically adsorbed PEO fibers cannot compare with the OPA SAMs, which endure the scratching without a significant change in the SAMs (Figure 1a).

Figure 4b shows that the PEO fibers were completely removed from the Si substrate upon scratching. The ridge observed for the PEO film on the Si substrate is apparently the accumulation of PEO molecules as they were removed by the diamond tip. It is thus clear that the PEO fibers have a stronger interaction between a mica substrate than between a Si substrate. This can be explained by the fact that a freshly cleaved mica surface has a higher surface energy (more hydrophilic) than a Si substrate.

Although the modification and removal of PEO fibers on a mica substrate does not prove that the resilience of OPA SAMs on a mica substrate to scratching be due to a chemical bonding, comparison of their different scratching behaviors appears to show one that the OPA SAMs are hardly a physical adsorption on a mica surface. In other words, under a pressure as high as what we applied to the OPA SAMs (9.3 GPa), it is highly unlikely that a physically adsorbed molecular system remains undamaged.

We also conducted similar scratch tests on two industrially important biaxially oriented polymer films, PP and PET.[34] These polymer films are semicrystalline and have found a wide variety of applications from flexible packaging to use as electronic device substrates. Mechanical strength is thus expected for the polymer films from an application point of view. We show that the scratch tests resulted in a significant modification on PP and a clear removal of materials on PET. Shown in parts a and b of Figure 5 are results for the scratch tests conducted on a PP film and a PET film, respectively. The wide scratches created on the polymer films are due to their small Young moduli of 1–3 GPa.[35] The PP film is characterized by a

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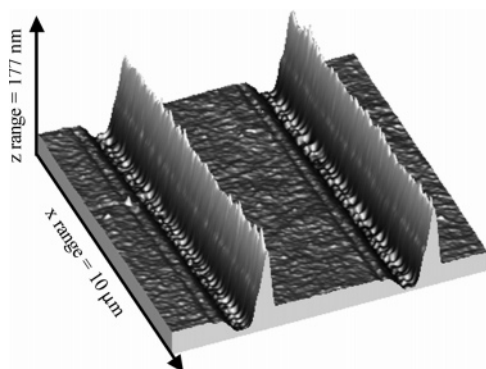
Figure 6. Three-dimensional image of Figure 5b which shows more clearly the scratches and ridges formed on the PET.

nanometer-scale fiberlike network structure.[32,33,36] We have observed an increase in surface energy in scratched areas on the PP surface as the scratching resulted in an increase in density and ordering of polymer strands on the surface.[36]

As shown in Figure 5b, material removal was observed for the PET film in the formation of a ridge beside the scratch. The scratch depth is ~15 and ~35 nm for the PP and PET films, respectively. The PET film is characterized by nanometer-sized particles (not visible at the magnification used) without the apparent fiberlike network structures that the PP film has. This structural difference explains the difference in their response to scratching, as shown in Figure 5. The scratch width for both of the polymers is 1.3−1.4 μm when measured from the top of the ridge. We use this value for the calculations of contact radius and pressure because the tip contact area would not reach beyond the top of the ridge. Thus, the maximum or the mean pressure applied to the polymer films was calculated to be ~0.5 GPa or ~0.3 GPa. To show how severely the PET film was scratched, a three-dimensional perspective of Figure 5b is shown in Figure 6, from which both the scratch and the ridge are more clearly seen.

We have demonstrated that an OPA SAM on a mica substrate is an excellent lubricant, as the diamond tip was able to depress the OPA SAM 13 nm inward on the rigid mica substrate without removing the OPA layer. The OPA molecules self-assembled on a mica substrate were able to endure this imposed shear deformation without significant changes, whereas the same (mica) substrate was seriously scratched under the same conditions without the OPA SAMs at the surface.

Our experimental results showed that a maximum pressure of 9.3 GPa did not damage the OPA SAMs. On the other hand, a maximum pressure of 0.5 GPa left permanent damages (scratches) on the PP and PEO polymer reference films. During the scratch test, the pressure of the diamond tip on the OPA SAMs was ~19 times larger than that imposed on the PP and PET surfaces. Such a comparison of the results of scratch tests for the OPA SAMs and the PP or PET films leads one to conclude that the interaction energy between the OPA headgroup and the mica substrate is much stronger than the adhesion energy of molecular chains in the polymer films. Intermolecular forces bonding polymer chains together in polymer materials are weaker forces than chemical bonds.[37]

Conclusions

Scratch tests using a diamond tip revealed that OPA SAMs were virtually undamaged under conditions that left 1-nm-deep scars on a bare mica substrate. This experimental fact demonstrated that an OPA SAM on a mica substrate is mechanically robust and serves as a molecular lubricant for the underlying mica substrate. ToF-SIMS detected ion fragments of mica constituents such as Si and SiO_2 attached to the deprotonated OPA molecules, suggesting strong interactions between the OPA molecular headgroup and the mica substrate. We believe that the OPA hydrocarbon chains are able to dissipate the shear energy, perhaps through the compression and relaxation of the hydrocarbon chains. The strength of OPA SAMs was compared with that of the three reference polymer films that were shown to be easily removed as in the case of the PEO film spin-coated on mica or Si, or highly modified for biaxially oriented PP and PET films.

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