Improved Imaging of Soft Materials with Modified AFM Tips

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Herein, we report a simple method for making silicon nitride tips hydrophobic without significantly changing their shape. Specifically, we show that atomic force microscope (AFM) tips coated with physisorbed multilayers of 1-dodecylamine, when used in air, offer enhanced resolution for both organic and inorganic materials. The reason for this is due to a significant reduction in the capillary effect associated with water condensation between the tip and substrate.

Introduction

Recently, we reported the experimental observation that when an atomic force microscope (AFM) is operated in air, water condenses between the tip and surface and then is transported via the capillary as the tip is scanned across the surface.[1] Notably, this filled capillary and the capillary force associated with it significantly impede the operation of the AFM, especially when run in lateral force mode (LFM).[2,3] In air, the capillary force can be 10 times larger than chemical adhesion force between tip and sample.[4] Therefore, the capillary force can substantially affect the structure of the sample and the imaging process. To make matters worse, the magnitude of this effect will depend on many variables, including the relative hydrophobicities of the tip and sample, the relative humidity, and the scan speed. For these reasons, many groups have chosen to work in solution cells where the effect can be made more uniform and reproducible.[5,6] This, however, imposes a large constraint on the use of an AFM, and the solvent can affect the structure of the material being imaged.[7] Therefore, other methods that allow one to image in air with the capillary effect reduced or eliminated are desirable. Herein, we report one such method, which involves the modification of silicon nitride AFM tips with a physisorbed layer of 1-dodecylamine, Figure 1. We find that such modified tips improve one's ability to do LFM in air by substantially decreasing the capillary force and offering higher resolution, especially with soft materials.

Experimental Section

All data presented in this paper were obtained with a Park Scientific model CP AFM with a combined AFM/LFM head. Cantilevers (model MLCT-AUNM, cantilever A with force constant = 0.05 N/m) were obtained from Park Scientific. The AFM is mounted in a Park vibration isolation chamber that has been modified with a dry nitrogen purge line. Also, an electronic hygrometer, placed inside the chamber, was used for humidity measurements (±5% with a range of 12−100%). Muscovite green mica was obtained from Ted Pella, Inc. Soda lime glass microscope slides were obtained from Fisher. Polystyrene spheres with 0.23 ± 0.002 μm diameter were purchased from Polysciences. 1-Dodecylamine (99+%) was purchased from Aldrich Chemical, Inc. and used without further purification. Acetonitrile (ACS grade) was purchased from Fisher Scientific Instruments.

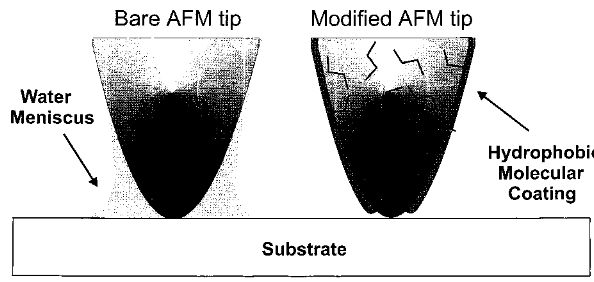

Figure 1. Diagrams depicting water condensation and meniscus formation between (left) a bare tip and surface and (right) a 1-dodecylamine-modified tip and surface.

Discussion

Our protocol for tip modification involves rinsing an AFM cantilever and tip with acetonitrile several times to remove any residual contaminants on the tip prior to soaking them in a ~5 mM 1-dodecylamine/acetonitrile solution for approximately 30 s. Next, the tip is blown dry with compressed Freon leaving a layer of 1-dodecylamine on the AFM tip and cantilever. Experience has shown that repeating the dipping procedure several times typically leads to the best results. The 1-dodecylamine is physisorbed rather than chemisorbed onto the silicon nitride tips. Indeed, the 1-dodecylamine can be rinsed off the tip with acetonitrile, as is the case with bulk silicon nitride. Modification of the tip in this manner significantly reduces the capillary effect due to atmospheric water condensation as evidenced by the experiments outlined below.

A digital oscilloscope, directly connected to the lateral force detector of the AFM, can be used to record the lateral force output as a function of time. In this experiment, the force of friction changes direction when the tip scans left to right as compared with that of right-to-left scans. Therefore, the output of the LFM detector switches polarity each time the tip scan direction changes. If we record this output during one or more AFM raster scans, it is in the form of a square wave; see Figure 2. The height of the

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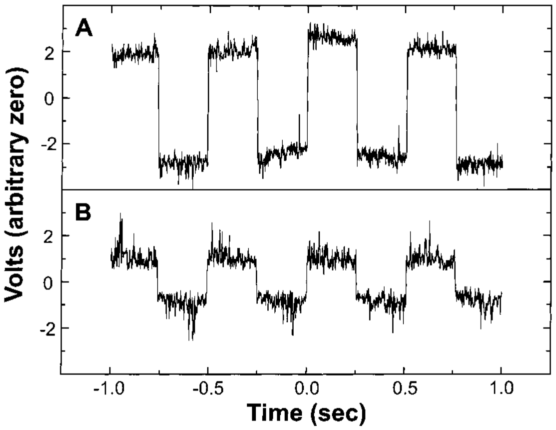

Figure 2. Oscilloscope recording of lateral force detector output. The time of the recording spans four scan lines. Since the signal is recorded during both left and right scans, the heights of the square waves are directly proportional to the friction. The *Y*-axis zero has been shifted for clarity. (A) Before 1-dodecylamine is placed on the tip. (B) After the tip has been coated with 1-dodecylamine.

square wave is directly proportional to the sliding friction of the tip on the sample, and therefore, one can compare the forces of friction between that of an unmodified tip and glass sample and that of a modified tip and sample simply by comparing the height of the square waves under nearly identical scanning and environmental conditions. The tip/glass sample frictional force is at least a factor of 3 less for the modified tip than that for the unmodified tip. When this experiment was done on a mica substrate, a similar reduction in friction was observed ($\sim 3\times$). In general, reductions in friction measured in this way and under these conditions range from a factor of 3 to more than a factor of 10 depending upon substrate and environmental conditions such as relative humidity.

While this experiment shows that 1-dodecylamine treatment of an AFM tip can lower friction, it does not prove that water and the capillary force are the key factors. In a second experiment, we examined the effects of the 1-dodecylamine coating on the capillary transport of water. Details of water transport involving unmodified tips were discussed elsewhere.[1] When an AFM tip is scanned across a sample, it will transport water to the sample via capillary action; see Figure 3A. After scanning a $4 \times 5\ \mu m^2$ area of a soda glass sample for several minutes, one can deposit contiguous adlayers of water onto the substrate that can be imaged by LFM by increasing the scan size. Areas of lower friction, where water has been deposited, appear darker than nonpainted areas; see Figure 3A. The same experiment conducted with a tip coated with 1-dodecylamine does not show evidence of substantial water transport; see Figure 3B. Indeed, only random variations in friction were observed.

While these two experiments show that friction can be reduced and that the transport of water from the tip to the substrate by capillary action can be inhibited by coating the tip with 1-dodecylamine, they do not provide information about the resolving power of the modified tip. Mica is an excellent substrate to evaluate this issue, and indeed, lattice-resolved images of mica could routinely be obtained with the modified tips demonstrating that this modification procedure reduces the force of friction without blunting the tip; see Figure 4A. It is impossible to determine whether the portion of the tip that is involved in the imaging is bare (Figure 1) or has a layer of 1-dodecylamine on it. In fact, it is quite possible that the 1-dodecylamine layer has been mechanically removed from

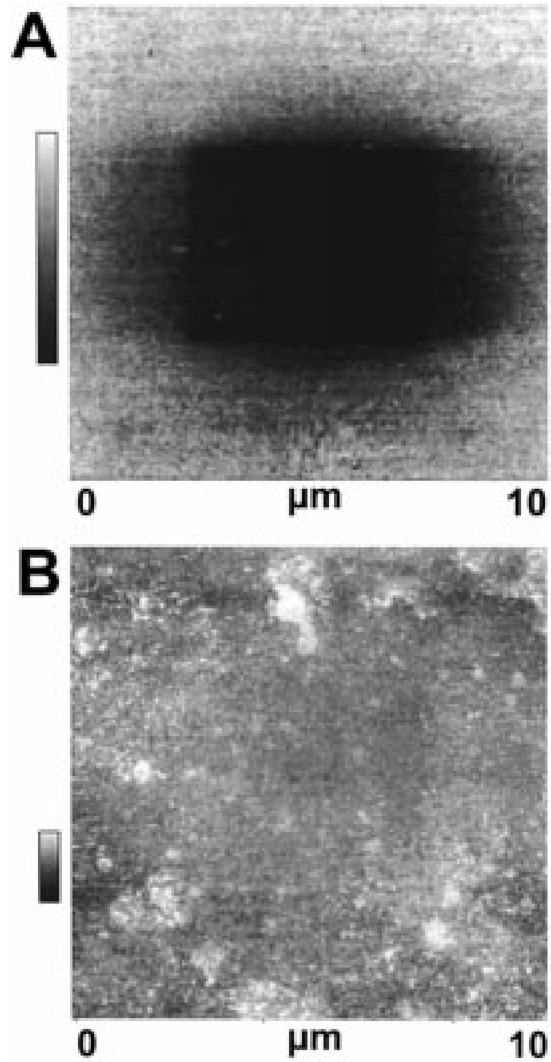

Figure 3. LFM images showing (A) water transported to a glass substrate (dark area) by an unmodified tip and (B) the result of the same experiment performed with a 1-dodecylamine-coated tip. Height bars are in arbitrary units.

this part of the tip, thereby exposing the bare Si_3N_4. In any event, the remainder of the tip must have a hydrophobic layer of 1-dodecylamine on it since water is inhibited from filling the capillary surrounding the point of contact, thereby reducing the capillary effect.

While the atomic-scale imaging ability of the AFM is not adversely affected by the 1-dodecylamine coating on the tip, the above experiment does not provide useful information about the suitability of the tip for obtaining morphology data on a larger scale. To obtain such information, we imaged a sample of monodisperse 0.23 mm diameter latex spheres with both modified and unmodified tips. Since the topography recorded by an AFM is a convolution of the shape of the tip and the shape of the sample, any change in the shape of the tip will be reflected in a change in the imaged topography of the latex spheres.[8] We find that there is no detectable difference in images taken with unmodified and modified tips (see Supporting Information). This shows that the shape of the tip is not significantly changed as it would be if a metallic coating had been evaporated onto it. Moreover, it suggests that the 1-dodecylamine coating is

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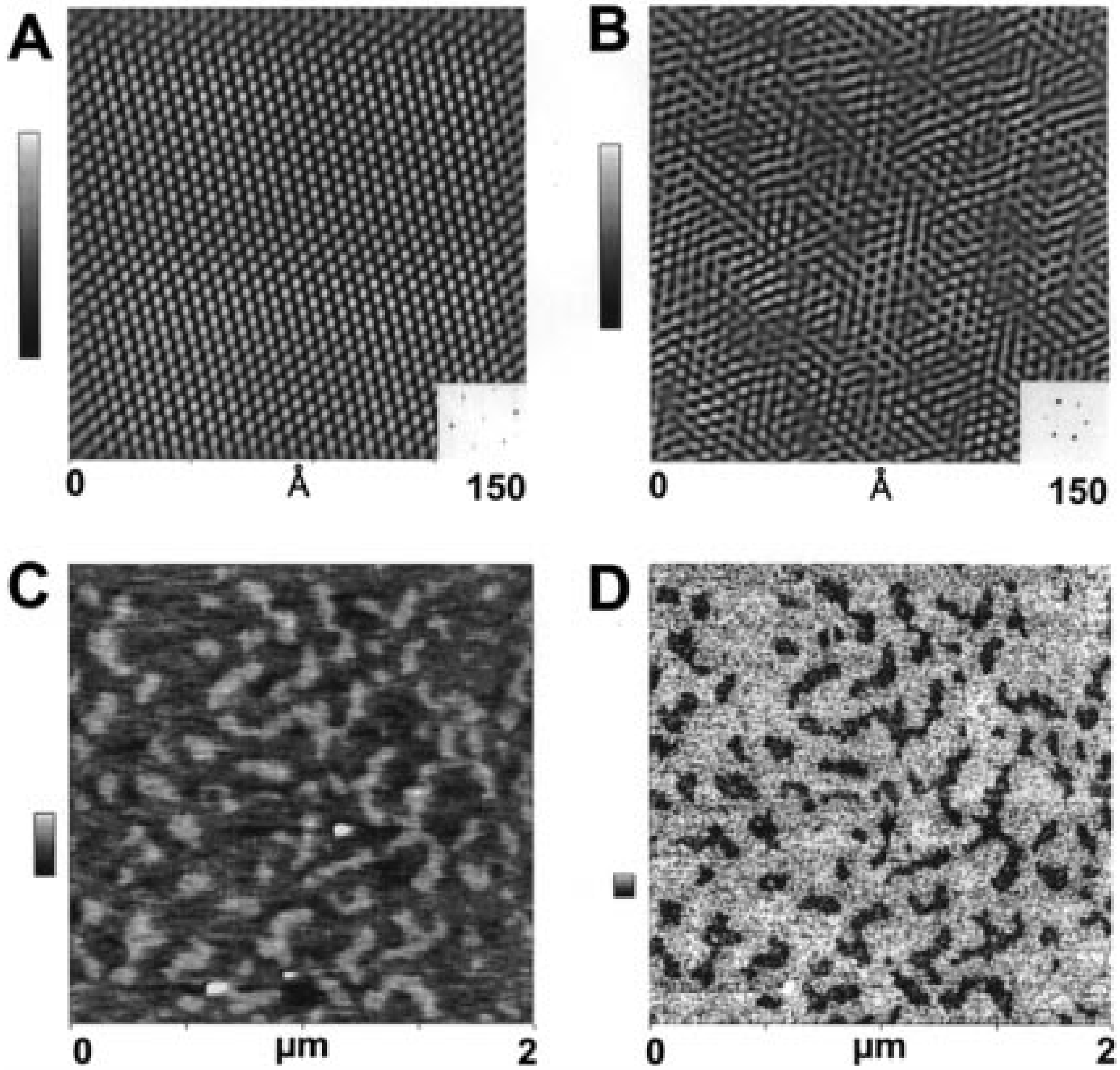

Figure 4. (A) Lattice-resolved image of a mica surface with a 1-dodecylamine-modified tip. The 2D Fourier transform is in the insert. (B) Lattice-resolved, LFM image of a self-assembled monolayer of 11-mercapto-1-undecanol. This image has been Fourier transform-filtered, and the FFT of the raw data is shown in lower right insert. Scale bars are arbitrary. (C) Topographic image of water condensation on mica at 30% relative humidity. The height bar is 5 Å. (D) LFM image of water condensate on mica at 30% relative humidity (same spot as in C).

fairly uniform over the surface of the tip, and it is sharp enough that it does not adversely affect atomic-scale imaging.

A significant issue pertains to the performance of the modified tips in the imaging of soft materials. Typically, it is difficult to determine whether a chemically modified tip exhibits improved performance as compared with a bare tip. This is because chemical modification is often an irreversible process, which sometimes requires the deposition of an intermediary layer. However, since the modification process reported herein is based upon physisorbed layers of 1-dodecylamine, it is possible to compare the performance of a tip before modification, after modification, and after the tip has been rinsed and the 1-dodecylamine has been removed. Qualitatively, the 1-dodecylamine modified tips always provide significant improvements in the imaging of monolayers based upon alkanethiols and organic crystals deposited onto a variety of substrates. For example, a lattice-resolved image of a hydrophilic self-assembled monolayer of 11-mercapto-1-undecanol on a Au(111) surface can routinely be obtained with a modified tip; see Figure 4B. The lattice could not be resolved with the same unmodified AFM tip. On this surface, the coated tip showed a reduction in friction of at least a factor of 5 via the square-wave analysis. It should be noted that the OH-terminated self-assembled monolayer (SAM) is hydrophilic and hence has a strong capillary attraction to an unmodified tip. Reducing the capillary force via the modified tip allows one to image the lattice. A second example of improved resolution involves imaging free-standing liquid surfaces such as water condensed on mica. It is well-known that at humidities between 30 and 40%, water has two distinct phases on mica.[9,10] In previous work by Salmeron, a noncontact mode scanning polarization force microscope (SPFM) was used to image these phases. Salmeron found that when a probe tip comes in contact with mica, strong capillary forces cause water to wet the tip and strongly disturb the water condensate on the mica. To reduce the capillary effect so that two phases of water could be imaged, the tip in Salmeron's experiment was kept ~20 nm away from the surface. Indeed, because of this constraint, Salmeron found that one cannot image such phases with a contact mode scanning probe technique. In Figure 4, we show an image of the two phases of water

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on mica recorded at 30% humidity with a 1-dodecylamine modified tip in contact mode. The heights of the features (Figure 4C) correspond with the frictional map (Figure 4D) with higher features having lower friction. The quality of the modified tip, which we believe correlates with the uniformity of the 1-dodecylamine layer on the tip, is important. Only well-modified tips make it possible to image the two phases of water, whereas less well-modified tips result in poorer quality images. In fact, this is such a sensitive test that it can be used as a diagnostic indicator of the quality of the 1-dodecylamine-modified tips before proceeding to other samples.

Conclusions

In conclusion, we have reported a very simple but extremely useful method for making Si_3N_4 AFM tips hydrophobic. This modification procedure lowers the capillary force and improves the performance of the AFM in air. Significantly, it does not adversely affect the shape of the AFM tip and allows one to obtain lattice-resolved images of hydrophilic substrates including soft materials such as SAMs and even free-standing water on a solid support. The development of methodology that allows one to get such information in air is extremely important because, although solution cells can reduce the effect of the capillary force, the structures of soft materials can be significantly affected by solvent.[7] Finally, although it might be possible to make an AFM tip more hydrophobic by first coating it with a metal layer and then derivatizing that metal layer with a hydrophobic chemisorbed organic monolayer, it is difficult to do so without concomitantly blunting the AFM tip.

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Supporting Information Available: Topographic images of latex spheres with an unmodified tip and a tip coated with 1-dodecylamine. This material is available free of charge via the Internet at http://pubs.acs.org.

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