

Effects of Surface Functionality and Humidity on the Adhesion Force And Chemical Contrast Measured with AFM

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Introduction

The ability to probe chemical heterogeneity with nanometer scale resolution is essential for developing a molecular-level understanding of a variety of phenomena occurring at surfaces of materials. One area that could benefit greatly from nanoscale chemical measurement is an understanding of the degradation mechanisms of polymeric materials exposed to the environment. For example, the degradation (photo and hydrolytic) of polymers and polymeric materials has been observed to occur non-uniformly in which nanometer pits form locally, which deepen and enlarge with exposure (1,2). The pitting has been postulated to initiate in the hydrophilic degradation-susceptible regions of the films (3). However, due to the lack of spatial resolution of the most current surface analytical techniques, the chemical nature of the degradation-initiated locations has not been identified. The use of a chemically-functionalized probe in an AFM (chemical force microscopy CFM) (4) has been shown to be capable of discriminating chemically-different domains of self-assembled monolayer (SAM) surfaces at the nanoscale spatial resolution. This study provides data to demonstrate that, by using proper RH at the tip-sample environment, the contrast between the hydrophilic and hydrophobic domains in SAM and polymer samples can be discerned, and presents results on the effects of RH on tip-sample adhesion forces for different substrates.

Materials and Experimental Procedures

Samples used included non-gradient and gradient-patterned SAMs, homogeneous hydrophilic and hydrophobic SAMs, SiO₂-covered Si (SiO₂-Si), Au-coated Si, and hydrophilic/hydrophobic block copolymer. Except for one patterned SAM where silane on Si was used, other SAM samples were prepared using thiol chemistry on Au-coated Si substrates. The gradient patterned SAM samples consisted of alternating hydrophilic (COOH) and hydrophobic (CH₃) stripes with gradient surface free energy along the perpendicular direction of the stripes. The preparation of this sample has been described elsewhere (5). The SiO₂/hydrophobic patterned SAM was fabricated using the vapor-mediated soft lithography technique. In this approach, a polydimethylsiloxane stamp having raised and recessed pattern was applied onto a SiO₂-Si substrate. The stamp/substrate was exposed to saturated vapor of n-octyldimethylchlorosilane (ODS). In this way, the substrate areas that were under the stamp recessed domains reacted with ODS to form a CH₃-terminated SAM, while the areas under the raised domains were masked by the stamp, leaving the hydrophilic SiO₂ layer on the substrate unreacted. After two hours of exposure, the stamp was removed and the treated substrates were washed thoroughly with toluene to remove excess ODS. COOH, OH, and CH₃-terminated SAMs were prepared using the usual procedure for thiol chemistry. Accordingly, after cleaning thoroughly with piranha/distilled water and dried with N₂, 100 nm thick Au-coated Si wafers

were immersed in 1 mmol/L in ethanol solutions of 16-mercaptohexadecanoic acid, 11-hydroxy-1-undecanethiol, and 1-octadecanethiol for 24 h at room temperature. The treated substrates were rinsed thoroughly with ethanol and immersed in ethanol again for another 24 h to remove any of the weakly adsorbed molecules in the SAMs. All samples were measured within one day after preparation. The chemically-heterogeneous polymer sample was a block copolymer of polystyrene and polyethylene oxide (PS-*b*-PEO). The bulk specimen of PS-*b*-PEO was annealed at 180 °C and then fractured under liquid nitrogen.

Both contact mode and tapping mode AFM were performed using a Dimension 3100 scanning probe microscope and Nanoscope IIIa controller (Digital Instruments)*. Commercial unmodified Si₃N₄, Si, and oxygen plasma-treated carbon nanotube (CNT) tips were used (tip radius of all three types was <10 nm). Si₃N₄ and Si tips were cleaned by UV/ozone for 30 min before use. The CNT tips were made from multiwall CNT (MWCNT) and fabricated using a method described in Reference (6). This method attaches the MWCNT tip to the cantilever of an AFM probe through covalent bonding. The oxygen-plasma treatment of CNT tips was performed using an O₂ pressure of 66.5 kPa and a power of 50 w for 2 min. For tapping mode, images were obtained using an AFM probe at a resonance frequency of 270 kHz and with a free-oscillation amplitude of 62 nm ± 2 nm. The set-point ratios ranged from 0.80 to 0.90. Force-versus-distance curves were obtained in contact mode at constant load. Each data point of the adhesion force was the average of 30 measurements. Relative humidity (RH) of the tip-sample environment was controlled using a NIST-patented environmental chamber described previously (7). RH in the chamber was continuously monitored by a humidity sensor.

Results and Discussion

Figure 1 shows AFM phase images of the gradient patterned SAM sample taken at 7 % RH and 95 % RH. A schematic of the gradient SAM is included for clarity (center illustration). The thin stripes are the hydrophilic regions and the matrix (thick stripes) is the chemical gradient material. These images were obtained using an unmodified Si tip. It should be noted Si wafers are generally covered with a thin layer of SiO₂, which, under normal ambient conditions, is fully hydroxylated, with approximately 5 OH/nm² (8). Therefore, Si tips should be regarded as OH-terminated probes. At 7 % RH, the phase contrast between the stripes and the matrix is poor, even for the regions that have the highest surface free energy differences (far left of the schematic). However, the contrast between the same two regions is greatly increased at 95 % RH (top image). At high RH, the contrast even in the regions having small surface free energy difference can also be observed (bottom). Because the chain length and chemical structure of the stripes and the matrix are similar, the contrast observed is believed to be due mainly to the hydrophilicity difference between the two regions, rather than to their mechanical property difference. RH has no effect on the height image contrast (not shown).

Figure 2 displays AFM phase images for a SiO₂/ODS pattern SAM sample using oxygen plasma-treated CNT tip (a) and conventional unmodified Si tip (b) taken at four different RHs. In this figure, the bright stripes are the hydrophilic SiO₂ and the dark matrix is the hydrophobic

* Certain commercial product or equipment is described in this paper in order to specify adequately the experimental procedure. In no case does such identification imply recommendation or endorsement by the National Institute of Standards and Technology, nor does it imply that it is necessarily the best available for the purpose.

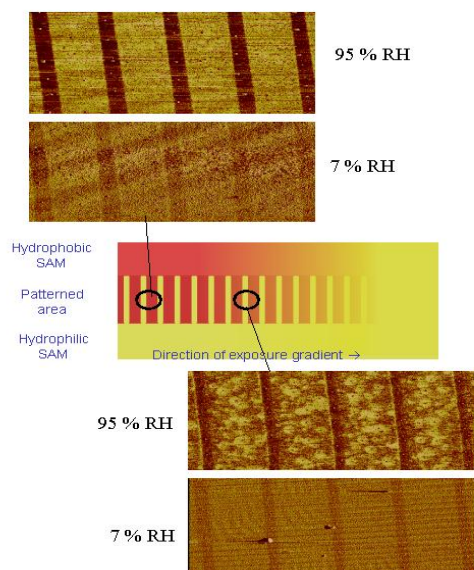


Figure 1. Effect of RH on phase image contrast for different hydrophilic/hydrophobic gradients; (unmodified Si tip; stripe: hydrophilic; matrix: hydrophobic)

CH_3 , and all images were taken at the same location. Clearly, the contrast obtained by the plasma-treated CNT tip is greatly enhanced at 50% RH but drastically decreases at 73 % or 95 %RH. For the Si tip, the RH-enhanced contrast remains high even at high RHs. One example to demonstrate the effect of RH on contrast image taken using the contact mode AFM is illustrated in Figure 3. The sample was the SiO_2 /ODS patterned SAM and the probe was an unmodified Si_3N_4 tip. Data on the adhesion force as a function of RH for the SiO_2 substrate and CH_3 -terminated SAM are included for comparison. The contrast is greatly enhanced at 53 % RH and decreases slightly at 90 % RH, consistent with adhesion force data.

The advantage of using elevated RH to enhance the contrast between the hydrophilic and hydrophobic domains in a chemically-heterogeneous polymer is shown in Figure 4. This sample is a cryo-fractured surface of the PS-PEO block copolymer. The images were taken with an unmodified Si tip in tapping mode. The dark domains are believed to be the water-sensitive, hydrophilic PEO material and the bright areas are the hard, hydrophobic PS. The phase images of Figure 4 clearly shows that high RH not only enhances the contrast between the hydrophilic and hydrophobic regions but also enlarges the hydrophilic areas, suggesting that a marked surface rearrangement has occurred in this copolymer sample. In general, the effect of RH in polymeric materials is more complex than that for ultra thin SAM since water not only is adsorbed onto the hydrophilic polymer surface, but also diffuses into the bulk material resulting in swelling and plasticization, which directly affects the phase image contrast.

Figure 5 presents the relationship between the adhesion force (pull-off force) and RH for different substrate surfaces. Water contact angle (θ), total surface free energy (γ_s) and its components (dispersion force, γ_s^d , and polar force, γ_s^p), and surface polarity, ($P = \gamma_s^p/\gamma_s$) of these surfaces are given in Table 1. The surface free energy components were determined using the harmonic mean method (9) and water and methylene iodine as the liquids. Contact angles were the average of six droplets. All results in Figure 5 were obtained using only one unmodified Si_3N_4 tip, except that the tip was cleaned with UV/Ozone for 30 min before the measurement of each substrate. The results shown in Figure 5, which are the average of 30 different measurements, are highly reproducible.

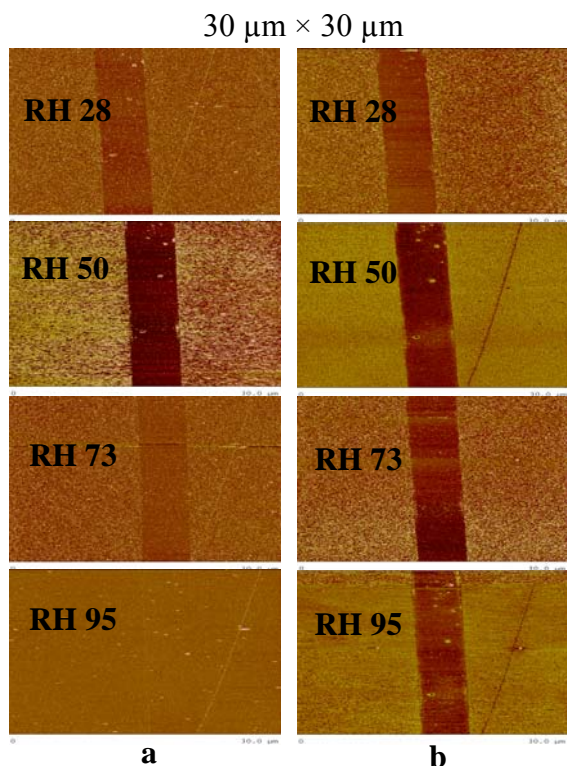


Figure 2. AFM phase image contrast as a function of RH for plasma-treated CNT tip (a) and Si tip (b) on a SiO₂-Si/CH₃-terminated patterned SAM; stripe is Si-SiO₂ substrate and matrix is CH₃-terminated SAM.

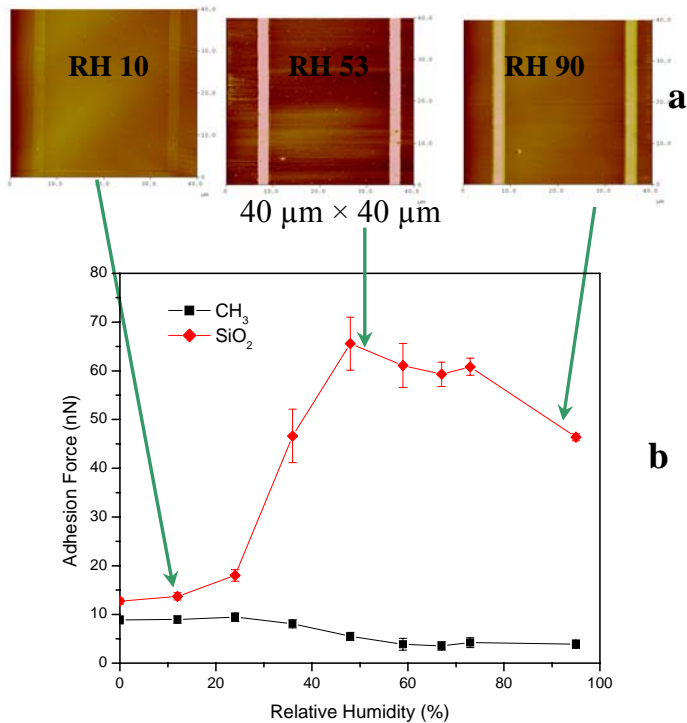


Figure 3. Effect of RH on image contrast (a) and adhesion force (b) obtained by contact mode for a SiO₂/OTS patterned SAM; stripe is the SiO₂ substrate and matrix is ODS.

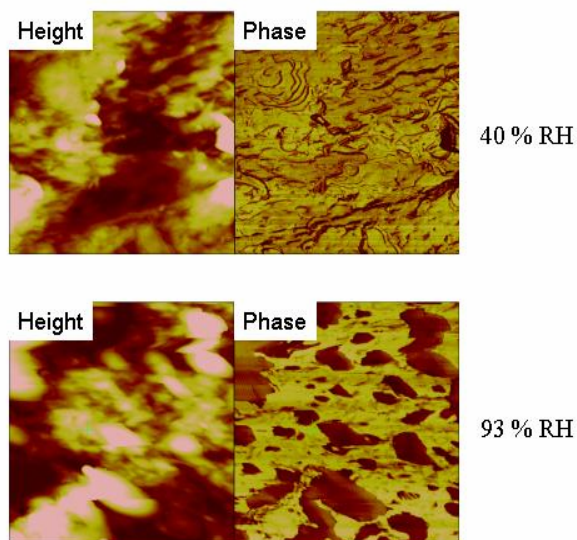


Figure 4. AFM images of PS/PEO block copolymer fractured surface at two RH levels.

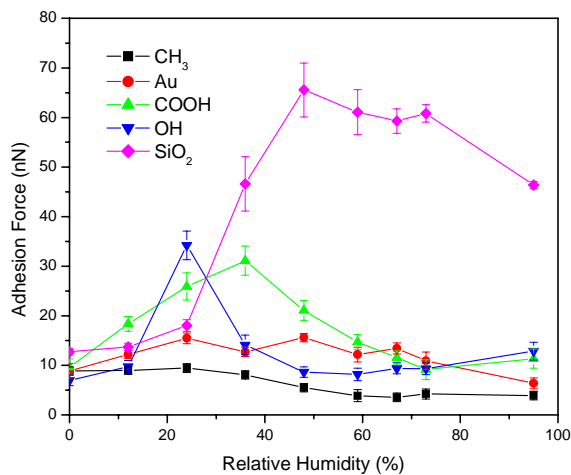


Figure 5. Adhesion force (pull-off adhesion) as a function of RH for an unmodified Si₃N₄ tip and different substrates. Each curve was the average of 30 measurements, and the error bars indicate one standard deviation.

Table 1. Water contact angle, total surface free energy and its components for various substrates (the uncertainty of water contact angle represents one standard deviation)

Substrate	θ H ₂ O, degree	γ_s^d , mJ/m ²	γ_s^p , mJ/m ²	γ_s , mJ/m ²	P= γ_s^p/γ_s
Si-Au-CH ₃	108.0 ±0.32	29.8	0	29.8	0
Si-Au	71.0 ±0.55	29.3	14.9	44.2	.38
Si-Au-COOH	45.8 ±0.34	26.6	29.9	56.5	.53
Si-Au-OH	37.8 ±0.35	28.9	33.2	62.0	.53
Si-SiO ₂	4.0 ±0.1	29.4	44.6	74.0	.60

For the CH₃-terminated SAM, little effect of RH on the adhesion force is observed, consistent with previous experimental results and theoretical prediction (10). The adhesion force of Au substrate increases slightly at low RH, remains essentially constant up to 70 % RH, and decreases. For SiO₂/Si substrate, the adhesion force increases slightly between approximately 0 % RH and 22 % RH, rises sharply afterward reaching a maximum at 50 % RH, and decreases afterward. The adhesion force curve for the SiO₂ substrate is similar to those reported by Xiao and Qian (10) and Salmeron et al. (11) for SiO₂/Si substrate and mica, respectively. That is, the adhesion force/RH curve consists of three regions: low adhesion force at low RHs, rising sharply and reaching a maximum at some RH, and decreasing at high RH. Sedin and Rowen (12) and Thundat et al. (13) also observed similar behavior for the low and intermediate RH ranges but did not observe a decrease with RH up to 75%.

Except for a difference in the magnitude and the RHs at which the adhesion force rises and falls, the adhesion force/RH curves for the OH- and COOH-terminated SAMs have similar behavior to that for the Si-SiO₂ substrate. The early rapid rise of adhesion force for OH and COOH is probably due to the ability of these groups to form multiple water layer at low RHs. Experiments to measure water sorption isotherms of these materials are being carried out to verify this postulation. On the other hand, the rapid fall at the intermediate RHs of the two organic SAMs may be due to leaching of the organic molecules from the SAM layer into the tip-sample water meniscus during exposure and measurement in humid environment. A small amount of the dissolved organic material can greatly decrease the surface tension of water. Surface tension of the meniscus liquid is directly proportional to the capillary force. The results shown above clearly indicate that the effects of RH on the adhesion force between an AFM tip and a sample is strongly dependent on the surface functionality of the substrate. Further, the image contrast between chemically-different domains at different RHs is closely related to the tip-sample adhesion force.

The adhesion force between an AFM tip and a sample measured in air has been known to consist of two main contributions: specific tip-sample interactions (van der Waals forces) and capillary forces resulting from condensation of water (10-12). At low RHs where only a monolayer of water exists, the adhesion force is mainly due to tip-sample interactions. In the region where the adhesion force increases sharply and reaches a maximum and where multiple monolayers of water has formed, the adhesion force is the sum of the tip-sample interactions and the capillary forces. The decrease of adhesion force at high RH has been explained due to the nanoscale tip geometry (10,11). Sedin and Rowen (12) have developed a model to account for the specific interactions, and Xiao and Qian (10) have quantitatively separated different contributions, at different RH levels.

Conclusions

The effects of relative humidity on AFM image contrast and adhesion force for different chemically-heterogeneous samples have been investigated. The results show that RH is a useful parameter to enhance the chemical sensitivity of AFM measurement. This approach is suitable for nanoscale characterization of chemical heterogeneity in model thin films and complex polymeric materials using AFM in air. Further research is needed to quantify the relationship between image contrast, surface free energy of the substrates, and tip-sample adhesion force as a function of relative humidity.

Acknowledgements

This research is supported by NIST Advanced Technology Program. We also thank Dr. Cattien Nguyen of Convergent Science and Technology for the plasma treatment of the CNT tips.

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