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# Enhancing Sensitivity of Atomic Force Microscopy for Characterizing Surface Chemical Heterogeneity

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## Introduction

Over the last 10 years, atomic force microscopy (AFM) has played an increasingly important role in characterizing surface morphology and surface properties (such as elasticity, friction and adhesion, etc.) of materials. However, the ability to identify and map the surface chemical heterogeneity has remained an unfulfilled opportunity in the field of AFM. Chemical force microscopy (CFM) [1, 2] is a successful approach for enhancing the chemical sensitivity of AFM. In this method, AFM probes with controlled surface chemistry (usually modified with a self-assembled monolayer or SAM) are used to measure the tip-sample adhesion or the frictional contrast between different regions of the sample. The key to the success of these measurements is ensuring that interactions between the modified tip and the sample surface are dominated by the chemical species on the surface of the tip and the sample surface studied. Because capillary forces are usually 1-2 orders of magnitude higher than specific chemical interactions, CFM has usually been conducted in liquid instead of air to eliminate capillary effects.

In this study, a well-controlled humidity system is used to enhance the sensitivity of AFM in characterizing surface chemical heterogeneity. The relative humidity of the tip-sample environment is controlled using a humidity generator and a novel small-volume environmental chamber designed and fabricated at the National Institute of Standards and Technology. The relative humidity in the chamber can be controlled from nearly 0 % relative humidity (RH) up to 95 % RH at room temperature. The effects of relative humidity on AFM image contrast are studied using a patterned SAM sample and polymers with alternating regions of hydrophobic and hydrophilic materials. The results clearly demonstrate that the image contrast between hydrophilic and hydrophobic regions of a surface is substantially increased in elevated relative humidity environments.

## Experimental\*

**Environmental Chamber.** An environmental chamber has been designed (patent has been amended) for use with a scanning stylus AFM system [3]. The chamber encloses the AFM scanner, tip assembly, optical cantilever detection system, sample, and the side-mounted optical microscope. It is comprised of two major components; a main chamber within which the AFM scanning head assembly is



Figure 1. Environment chamber attached to a scanning stylus AFM

placed; and an integrated sample platform and spring-loaded base plate that allows samples to be loaded and unloaded without removal of the main chamber. It also contains an inlet and an outlet ports to allow air of desired RH to be pumped into and out of the chamber. Humidity in the chamber is measured by a humidity sensor placed at the outlet. The RH of the air pumped from the humidity generator into the humidity chamber is controlled and maintained to  $\pm 3\%$  of the preset values of between 0% RH and 95% RH.

**Materials and Specimen Preparation.** Patterned SAM samples with alternating regions of hydrophobic and hydrophilic materials were prepared by microcontact printing ( $\mu$ CP) [4]. The silicon wafers were coated with a 15 Å thick adhesion layer of Cr followed by a 100 Å thick of Au layer via magnetron sputtering. An elastomeric stamp bearing a pattern of raised and recessed areas was inked with a 1mM solution of 11-mercaptoundecanoic acid ( $\text{HOOC}(\text{CH}_2)_{10}\text{SH}$ ) in ethanol, and then pressed on the gold coated silicon wafer to transfer the pattern. Subsequently the unprinted regions of the substrate were filled with 1-octadecanethiol ( $\text{CH}_3(\text{CH}_2)_{17}\text{SH}$ ) from ethanol solution.

Two types of chemically heterogeneous polymer surfaces were prepared. One was a block polymer of polystyrene-b-polyethylene (PS-b-PEO). The bulk specimen of PS-b-PEO was annealed at 180 °C and then fractured under liquid nitrogen. The fractured surface was examined with the AFM in tapping mode under different RH levels. A second polymer specimen was a bilayer of PS and poly (acrylic acid) (PAA). The PS-PAA sample was prepared by spin casting a PS solution in toluene on to the silicon substrate, and then a solution of PAA in water was spun cast on to the PS layer. Due to the low surface energy of PS, the PAA dewetted over the PS layer forming viscous fingering patterns [5].

**Atomic Force Microscopy.** Except where specifically noted, a Dimension 3100 scanning probe microscope and Nanoscope IIIa controller

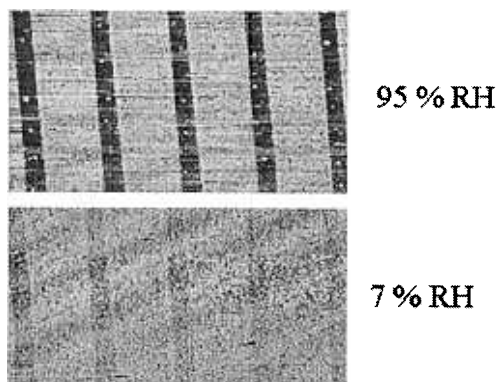
from Digital Instruments was operated in tapping mode to characterize the sample surfaces at different RH levels. Commercial silicon probes were used in tapping mode. Topographic and phase images were obtained simultaneously using a resonance frequency of approximately 300 kHz for the probe oscillation and a free-oscillation amplitude of  $62\text{ nm} \pm 2\text{ nm}$ . The set-point ratios ranged from 0.80 to 0.90.

AFM was also operated in contact mode with friction force imaging using unmodified and a SAM-modified  $\text{Si}_3\text{N}_4$  tip. The effect of relative humidity on the contrast of friction force images was gauged.

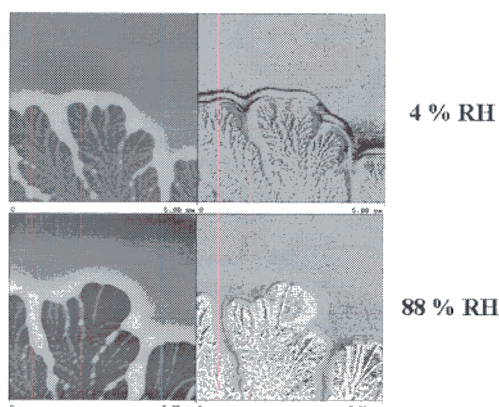
## Results and Discussion

In Figure 2, AFM phase images of the patterned SAM sample are shown for 7% RH and 95% RH. The thin stripes are hydrophilic regions and the matrix (thick stripes) is hydrophobic material. Very little phase contrast is observed between the stripes and the matrix at low humidity (bottom). However, the contrast is distinctly increased at high humidity (top). Because the chain length and structure of the strip and the matrix are similar, the difference in the hydrophilicity between the different regions is assumed to be the major factor in the change of the phase contrast rather than mechanical interactions.

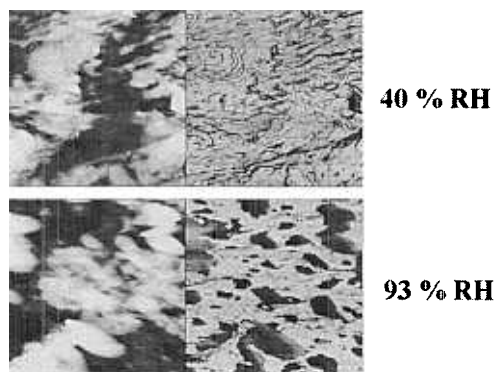
The effect of relative humidity on the contrast of AFM phase images has also been observed for the polymer samples with hydrophilic and hydrophobic regions. In Figure 3 and Figure 4, AFM images are shown of the dewetted PS-PAA bilayer and the fractured surface of the PS-b-PEO bulk specimen at low and high RH levels. The flat region outside the fingering pattern in Figure 3 is covered with the hydrophilic PAA layer, and the lower flat area inside the pattern was the hydrophobic PS-rich region [5]. Because the glass transition temperature of PS and PAA are similar ( $\sim 100\text{ }^\circ\text{C}$ ), the phase contrast between the PAA and PS-rich regions is weak at low humidity. High humidity clearly enhances the phase



**Figure 2.** AFM phase images of patterned SAM with hydrophilic strip and hydrophobic matrix at different RH levels. Color scale in phase images is  $60^\circ$ .



**Figure 3.** AFM images of PS-PAA dewetted patterns at different RH levels. Scale size is  $5\ \mu\text{m} \times 5\ \mu\text{m}$ ; color scale in height image (left) is 150 nm and in phase image (right) is  $90^\circ$ .



**Figure 4.** AFM images of the fractured surface of PS-b-PEO bulk specimen at different RHs. Scale size is  $3\ \mu\text{m} \times 3\ \mu\text{m}$ ; color scale in height image (left) is 150 nm and in phase image (right) is  $90^\circ$ .

contrast between the two regions. For the PS-b-PEO sample (Figure 4), the phase image at high humidity exhibits not only an increased phase contrast but also a larger area of dark-phased domains. The dark domains are believed to be the water-soluble PEO phase. It is reasonably suggested that, at high humidity, the PEO regions are swollen and rearrangement has taken place on the surface of the PS-PEO copolymer.

The above results have clearly demonstrated that, with increased RH environments, the chemically heterogeneous regions can be more effectively distinguished with the AFM. The increased phase contrast observed in our work is based on differences in interactions between the tip and different regions of the sample with the adsorbed moisture at the elevated humidity.

### Summary

The effects of relative humidity on AFM image contrasts of a patterned SAM and some heterogeneous polymers were studied. The results show that RH is a useful tool that can enhance the chemical sensitivity of AFM, making it more effective for nanoscale characterization of surface chemical heterogeneity in both model and real-world materials.

\* Certain commercial instruments and materials are identified in this paper to adequately describe the experimental procedure. In no case does such identification imply recommendation or endorsement by the National Institute of Standards and Technology.

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