

Locally Enhanced Relative Humidity for Scanning Probe Nanolithography

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The formation of a water meniscus between a sharp tip and a solid surface is one of the prevailing requirements for scanning probe microscope (SPM)-based lithographies, such as dip-pen nanolithography (DPN) and conductive tip induced oxidation. The water meniscus functions as a medium for the oxidation or mass transfer to the solid surface. Here we report a simple, efficient, and effective approach to enhance the local relative humidity and thus increase the size of the water meniscus by bringing a water-containing capillary tube to the proximity of the tip–surface contact area. The enhancement in local relative humidity is confirmed via an increase in the measured tip–surface adhesion forces and the widths of DPN generated parallel lines. Compared to the global control of relative humidity for the whole lithography system, the short distance between the “water reservoir” and the tip–surface contact area enables rapid increase in the local vapor pressure of water, less perturbation, and minimal erosion to the state-of-the-art electronics. As a result, most scanning probe lithography experiments at high relative humidity can now be performed in a reasonable time frame.

The water condensation on solid surface in a humid environment is a fundamental issue in surface science and strongly related to many macroscopic natural and artificial processes including fog formation, moisture retention, chemical distillation, among many others.^{1,2} This omnipresent phenomenon at the micro- and nanometer scale has been highlighted in diverse fields such as local surface hydrophilicity, nanotribology, lubrication of two sliding surfaces, and most recently, the scanning probe microscope (SPM)-based imaging and lithography techniques.^{3–12} The SPM-based lithography in ambient condition strongly depends on the formation of water meniscus to produce nanoscale features on a substrate through the current/field-induced local oxidation of surfaces, organic monolayers and polymer films or the delivery of molecules or molecular assemblies from an “inked” tip of an atomic force microscope (AFM) in dip-pen nanolithography (DPN).^{13–22} Although the detailed lithographic mecha-

nisms may vary, the conductive AFM-based oxidative lithography and DPN share the common feature in the formation of a tiny water meniscus between the tip and the surface.

In this regard, many experiments have confirmed the effects of the water meniscus by revealing the relation between the pattern size and the relative humidity of environment.^{21,22} The adjustment of humidity has become a major and sometime indispensable way to control the formation of nanostructures. For instance some molecules can be patterned only when the relative humidity of the environment reaches a threshold value.²⁰ The humidity increase is usually achieved by introducing water vapor (bubbling nitrogen through water) into a chamber which hosts the SPM, and the relative rate of change of this “system humidity” is typically about 10% per hour in an optimized system.²² Although it has been successful in forming many surface structures, the system humidity method inevitably incurs significant problems such as long equilibration time, perturbation to surface properties over whole sample area, undesirable or even catastrophic water condensation on the state-of-the-art instrument, and subsequent erosion to electronic circuits, especially at high relative humidity. It should be noted that the intrinsically highly localized SPM techniques do not need much water to generate the water meniscus or to enhance local humidity. Thus, an ideal method would be a localized approach with less water that consequently leads to short response time and less erosion, among other advantages.

Herein we describe a simple yet efficient method to enhance the local relative humidity around the tip–surface

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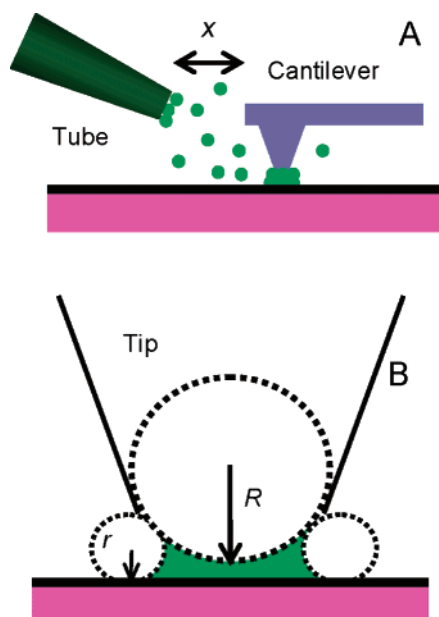
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Scheme 1. (A) Scheme of the approach to enhance local relative humidity for scanning probe lithography; (B) the contact between an AFM tip (effective radius R) and a flat surface, and the size of water meniscus (r_1 and r_2).



contact area. We demonstrate the efficacy of our approach with successful and controlled DPN patterning. Here, instead of introducing water vapor into the whole chamber system, a water-containing capillary tube is brought at the proximity to the contact area, to locally increase the water vapor pressure via three sequential processes: (i) spontaneous evaporation of water from the capillary tube, (ii) diffusion of water vapor, and (iii) condensation of water molecules in the tip–surface gap (Scheme 1). The resultant increase in the volume or the size of the water meniscus is reflected in the measurement of the tip–surface adhesion forces and the size of DPN patterned alkylthiol nanostructures on gold substrate. Although we demonstrate the local humidity enhancement only for DPN nanolithography, it is clearly viable to reasonably extend the method to other similar experiments where the local control of certain property or material delivery, which depends on humidity, is warranted.

DPN experiments were performed with ultrasharp silicon nitride microcantilevers with a spring constant of 0.05 N/m, purchased from Veeco Inc. The tips were thoroughly cleaned using ethanol and deionized water and radiated with UV light for 30 min prior to use. The cleaning procedure makes the tip surface hydrophilic which is favorable for the water condensation. The measurement of the adhesion force, the formation of DPN nanopatterns, and the determination of pattern size were performed under ambient conditions using either a Digital Instrument IIIa AFM (Veeco, Inc.) or a Nanoink dedicated DPN instrument, NScriptor. The substrate for the force measurement was bare native silicon dioxide on silicon surface that was cleaned thoroughly. The gold substrate was prepared by depositing a 40 nm gold layer on 600 nm silicon dioxide with 10 nm chromium as an adhesive layer. A saturated mecaptohexadecanoic acid (MHA, Aldrich) in ethanol solution was used as ink for DPN. The ink-coating was performed by dipping a cleaned tip into the ink-well for 30 s, followed by blow-drying using a gentle flow of air. A glass tube with an inner diameter of 1 mm was filled with deionized water and controlled by a three-dimensional micro-manipulator to approach the contact

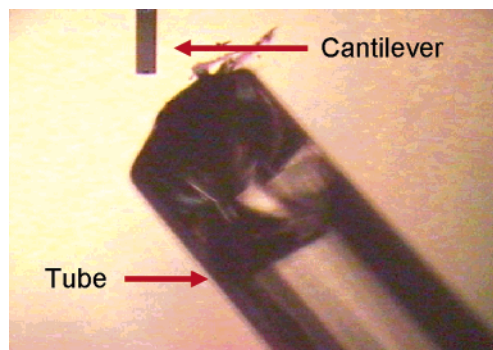


Figure 1. Optical micrograph shows a capillary tube approaching an AFM/DPN microcantilever.

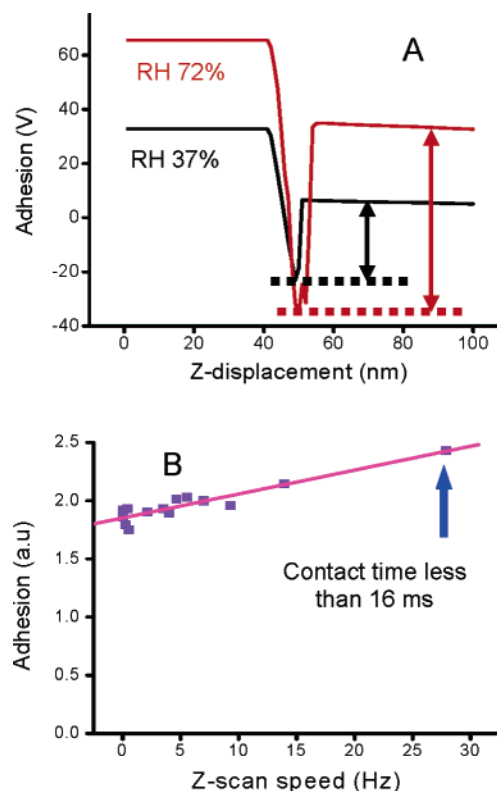


Figure 2. (a) Typical force–distance curves collected at different system controlled relative humidity, and (b) the magnitude of adhesion forces measured at different Z-scan speed.

area. The tube–tip distance was determined using an optical microscope, and the lower edge of the glass tube was kept at a similar height as the cantilever, as shown in Figure 1.

The magnitude of the adhesion force in the force–distance curve of AFM has widely been used as a measure of the attraction between the tip and the surface which contains the contribution from capillary interaction.²³ Given identical other conditions, the change in the adhesion can reflect the size of water meniscus formed between the tip and the surface. Figure 2a shows two typical force–distance curves that were collected at different relative humidity. The adhesion force measured at the relative humidity of 72% is almost double as that at the relative humidity of 37%, suggesting an increase in the size of the water meniscus formed between the tip and the surface. We then investigated the dynamics of

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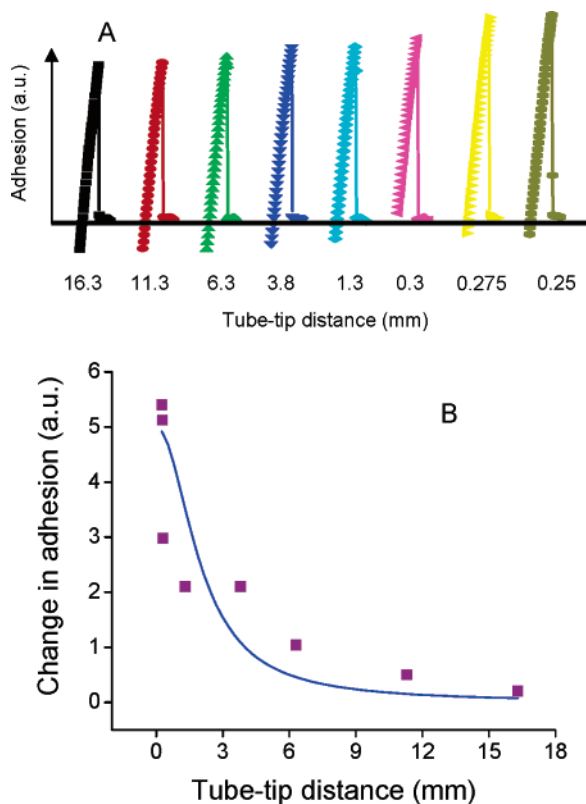


Figure 3. (a) Force–distance curves collected using the same pair of tip and surface at different tube–tip distance, the force curves are inverted to highlight the difference in adhesion; (b) the relation between the tube–tip distance and the change of adhesion force.

meniscus formation by changing the Z-scanning speed during the collection of force–distance curves. Figure 2b shows that, when the scanning speed is increased from 0 to 27.8 Hz, the adhesion force shows a slight increase that is probably induced by the hydrodynamic dragging of water. This suggests instantaneous formation of the water meniscus even at the scanning speed of 27.8 Hz. Considering the Z-ramp distance of $2.5 \mu\text{m}$, the tip–surface contact time (16 ms) at the scan speed of 27.8 Hz is probably the upper limit for the formation time of the water meniscus. Thus, we conclude that the rate controlling step for humidity increase is not the formation of the water meniscus but the diffusion of water vapor from the source to the tip–surface contact area.

The first evidence of locally enhanced relative humidity is from the measurement of the adhesion forces at different tube–tip distance using the force–distance curve. In a typical experiment, a clean AFM tip was brought into contact with the silicon dioxide substrate at a frequency of 5 Hz, which corresponds to the tip–surface contact time of less than 0.1 s when the ramp distance in the Z direction is $3.92 \mu\text{m}$. Figure 3a shows a series of force–distance curves collected at the different tube–tip distances, in which the Z positions of the cantilever after retracting from the surface are reset to compare the adhesion force. Each curve is inverted in order to highlight the difference in the magnitudes of adhesion forces. The changes in adhesion forces are derived by subtracting the adhesion force measured at the largest distance (16.3 mm). Figure 3b shows the changes in adhesion forces as a function of tube–tip distances, where a sharp increase is evident when the capillary tube is brought to the tip–surface contact area. Since all other conditions are identical, the difference in adhesion reflects the change in the size of the meniscus.

The use of the same pair of tip and surface means there should be no appreciable contribution from surface chemistry, contact area, roughness, or contamination. Meanwhile as the measurements were usually completed in 10 min, any other contribution should be minimal.

The mechanically controlled approach of water containing tube can reduce the equilibration time to reach certain level of humidity. The equilibration time includes two parts: (a) the diffusion time for molecules traveling to the contact area, and (b) the accumulation time to build-up the meniscus. From the force measurement, we know that the adhesion force increases immediately upon the approaching of the capillary tube to a distance of several μm . The approach operation itself takes no more than 5 s to complete, suggesting the fast increase of the local humidity. Then the capillary tube was quickly removed far away, and the adhesion force was monitored continuously by collecting a serial of force–distance curves. It took about 10 min for the dissipation of water and the recovery of adhesion force to its original value in the ambient condition (data not shown). Therefore the response time especially the time for the humidity increase is much shorter than the time for the system humidity method that usually needs tens of minutes or even several hours.

The local enhanced relative humidity was further confirmed from the increase in the size of DPN-generated MHA patterns. It is known that both the transfer of ink molecules from the tip to the surface and the ink diffusion on the surface are facilitated by the presence of water meniscus. Increasing the size of the water meniscus leads to an increased size of the pattern. Figure 4a shows a series of friction force images ($10 \times 10 \mu\text{m}^2$) of parallel lines formed by moving an MHA coated AFM tip on different areas of a gold surface at the speed of 0.1, 0.2, and $0.4 \mu\text{m/s}$, respectively. These lines are produced using the same tip, and the distances between the end of capillary tube and the tip–surface contact area are changed from several mm to $50 \mu\text{m}$. The line widths at different tip moving speed are used to calculate the line diffusion coefficient, which is dependent on the size of water meniscus.²⁴ An evident tube–tip distance dependence is shown in Figure 4, panels b and c, for the diffusion coefficients calculated from the line widths at the moving speed of 0.1, 0.2, and $0.4 \mu\text{m/s}$, and the normalized line widths at the moving speed of $0.2 \mu\text{m/s}$, strongly suggesting the size increase of water meniscus at short tube–tip distance. The normalization of line widths involves subtracting the width of the line generated in the absence of capillary tube (48 nm), and dividing a factor of 100.

The water column in the capillary tube is much larger compared with the volume around the tip–surface contact area, and can be treated as an infinite water reservoir that lasts for a long time. Although water molecules leave the liquid-phase continuously, the small surrounding area close to the tube end is still saturated with water vapor. Therefore the vapor pressure $P(x, t)$ at a given distance x from the end of the tube and a give time t is governed by Fick's second law of diffusion

$$\frac{\partial}{\partial t}(P(x, t)) = D \frac{\partial^2}{\partial x^2}(P(x, t)) \quad (1)$$

where D is the diffusivity constant of the vapor molecules and is about $20 \text{ mm}^2/\text{s}$ for water vapor at 20°C in ambient condition. Two boundary conditions for the diffusion

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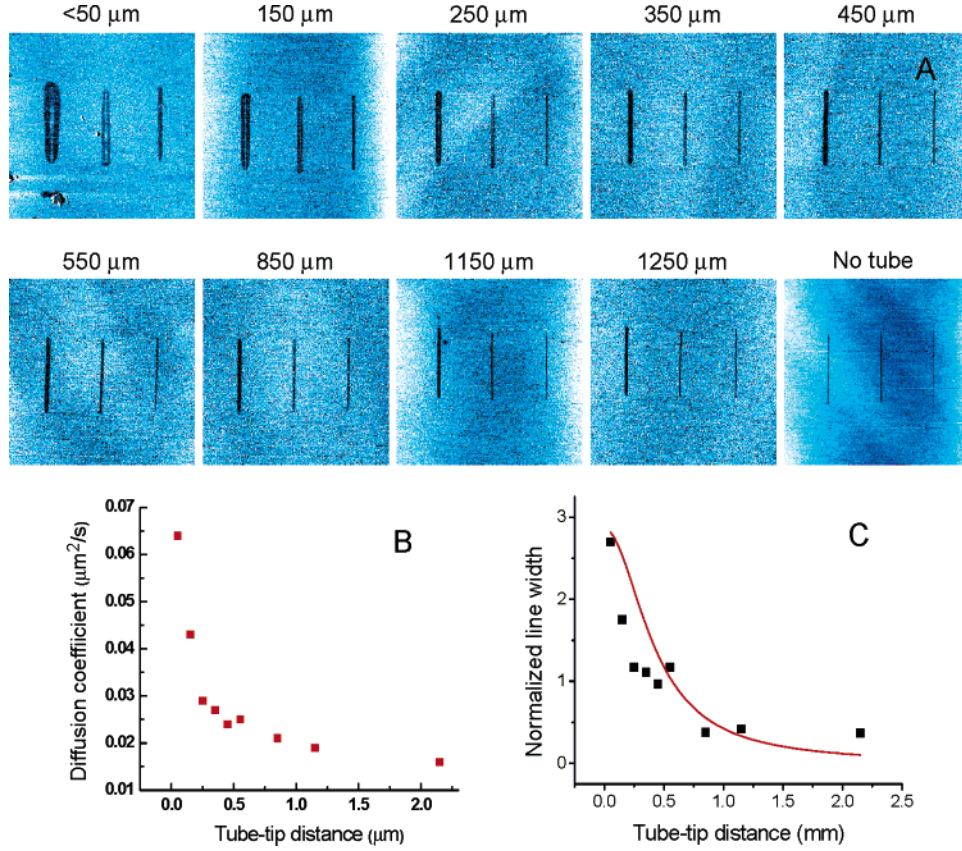


Figure 4. (a) AFM images of DPN generated MHA patterns on Au surface using the tip moving speed of 0.1, 0.2, and 0.4 $\mu\text{m/s}$ at different tube-tip distances; the line diffusion coefficients (b) and the normalized line widths (c) increase as the results of larger water meniscus.

equation are: at the initial conditions ($t = 0, x = 0$) the vapor pressure is P_{sat} and the vapor pressure at infinite is essentially zero. The solution to the diffusion equation is

$$P(x,t) = \frac{P_{\text{sat}}}{\sqrt{\pi Dt}} \exp\left(-\frac{x^2}{4Dt}\right) \quad (2)$$

On the other hand, the water vapor will spontaneously condense from vapor phase into the tip–surface gap. The equilibrium curvature $(1/r_1 + 1/r_2)^{-1}$ is related to the relative vapor pressure (relative humidity) p/p_{sat} as shown in the Kelvin equation

$$r_k = \left(\frac{1}{r_1} + \frac{1}{r_2}\right)^{-1} = \frac{\gamma V}{RT \log(p/p_0)} \quad (3)$$

where r_k is the Kelvin radius and V is the molar volume of water ($\gamma V/RT = 0.54$ nm for water at 20 °C).

For a distance of 1 mm, it usually takes a water molecule 0.05 s to diffuse, if the water diffusion coefficient is 20 mm^2/s . The equilibrium between the condensed water and the surrounding vapor can be established immediately. Therefore, the vapor pressure $P(x, t)$ in eq 2 is equal to the pressure P_{sat} in eq 3, and the following equation is obtained where the size of the water meniscus (r_k) is related to the tube-tip distance (x) and diffusion time (t)

$$r_k = -\frac{\gamma V}{RT} \frac{9.2Dt}{x^2 + 2.3Dt + 4.6Dt \log(Dt)} = \frac{1}{a + bx^2} \quad (4)$$

If $\gamma V/RT$ is 0.54 nm, t is 5 s, and D is 20 mm^2/s for water vapor at 20 °C in ambient condition, and the unit of water

meniscus size is in nm, the a and b values in the equation are calculated to be 2.32 and 0.002, respectively. From the equation, the local relative humidity can be adjusted by changing the distance from the capillary tube to tip–surface contact area (x), changing the diameter of the capillary tube, increasing the temperature of water (T), and adding certain surfactant or salt into water containing in the capillary tube (γ), etc.¹

The water meniscus forms a contact line on the surface of conical shaped tip, and the measured adhesion change is proportional to the length of the contact line, which is proportional to the size of water meniscus (r_k). Thus the measured adhesion change should be proportional to the size of water meniscus (r_k). Figure 3b suggests that the equilibrium size of the water meniscus depends on the tube-tip distance: when the distance is reduced, the size of water meniscus increases. Fitting the adhesion data to eq 4 gives a value of 0.2, and b value of 0.05; as a comparison, fitting the normalized line width data to the same equation gives a value of 0.35 and b value of 2 (Figure 4c). The discrepancies between these values and those obtained from the theoretical analysis may be the results of decreased MHA concentration in meniscus that changes the surface tension and fluid property of DPN ink, the oversimplified analysis that ignores nanoscale geometry features of AFM tip, the subtle links between local humidity, adhesion force and ink-diffusion, and the arbitrary data normalization. However what is more important here is that both the adhesion force and line width data have the same trends of change as the functions of tube-tip distance that is predicted in eq 4. This fact unambiguously supports our initial idea on the enhancement of local humidity using a water-containing capillary tube. Again, since there is no such thing as a small

hydrometer that can be placed in the vicinity of AFM tip, the adhesion data or the size of nanopatterns has to be used in order to quantify the local humidity through the comparison between a system-controlled humidity and a locally controlled one.

In summary, a method to locally enhance the water vapor pressure and relative humidity close to the contact area of a scanning probe microscope tip and a surface has been introduced, demonstrated, and validated with force-distance curves and DPN experiments. The fast response in relative humidity and less perturbation to the system enable a useful control over the relative humidity for DPN lithography. The adjustment range can be reasonably expanded below 30% relative humidity by operating in a low background environment. Further optimization on the tube diameter and the tube-tip distance will make

the method more versatile and general for scanning probe-based lithography and related techniques.

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