Unstable amplitude and noisy image induced by tip contamination in dynamic force mode atomic force microscopy

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Liquid 1-decanethiol was confined on an atomic force microscope (AFM) tip apex and the effect was investigated by measuring amplitude-distance curves in dynamic force mode. Within the working distance in the dynamic force mode AFM, the thiol showed strong interactions bridging between a gold-coated probe tip and a gold-coated Si substrate, resulting in unstable amplitude and noisy AFM images. We show that under such a situation, the amplitude change is dominated by the extra forces induced by the active material loaded on the tip apex, overwhelming the amplitude change caused by the geometry of the sample surface, thus resulting in noise in the image the tip collects. We also show that such a contaminant may be removed from the apex by pushing the tip into a material soft enough to avoid damage to the tip. © *2007 American Institute of Physics.*
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I. INTRODUCTION

There are several modes of interaction in atomic force microscope (AFM) between the probe tip and the sample surface that can be used to image surface features. Dynamic force mode AFM operates by oscillating the cantilever at or around its resonance frequency and monitoring the amplitude change when the tip is brought close to the sample surface.[1–4] In this mode, the tip taps the sample or is in an intermittent contact with the sample. This mode is widely used in mapping surface morphology for a wide variety of materials. One of the advantages in dynamic force mode AFM is that the lateral forces occurring in the course of scan are reduced compared with the contact mode AFM. In this latter mode in which the tip mechanically contacts the sample and the lateral shearing force caused by scanning of the tip on the sample surface may easily degrade the surface of a sample.[3]

Because AFM is a mechanical probe microscope, an AFM image is a convolution between the shape of the tip apex and the shapes of the surface features. Thus, to obtain an image reflecting the "true" surface features, the tip apex should be kept as small as possible. In everyday AFM practice, this means that one should keep the tip free from contamination and/or degradation. We have proposed a simple method to check the contamination of the tip using a biaxially oriented polypropylene film that is characterized with a nanometer-scale fiber like network structure.[5,6] This method emphasizes verifying the tip performance rather than characterizing the overall tip shape. What matters most is the "effective" tip apex that dominates the interaction with the sample surface features. Sometimes an apparently blunt tip could actually result in an image having good spatial resolution unmatched by the overall shape of the tip, as clearly demonstrated by Skårman *et al.*[7] This could result from the presence of a tiny particle on the tip apex, which acts as the effective tip. Of course, in most cases a contaminated tip would most likely degrade the performance of the original tip.

On the other hand, if the material contaminating the tip apex is active in producing extra forces, the contaminated tip is capable of causing noise in the AFM imaging. Therefore, it is important to know how such an active contaminant confined on a tip apex behaves when the tip is in proximity with the sample surface. This is particularly true for materials considered to be "sticky."

The amplitude-distance curve (ADC), i.e., the change of the oscillation amplitude of the cantilever as a function of the tip-sample distance, provides useful information on interaction between the tip and surface, such as the attractive and repulsive forces exerted.[8–15] We have reported that the ADCs measured in retraction cycle for a contaminated tip provide useful information on the materials confined on the tip apex.[5] Most contaminants result in poor imaging quality either by causing tip effects[16–19] and/or noise. Tip effects reflect the increase in tip size as the contaminants add to the tip apex.[5,6] A noisy AFM image can be a result of uncontrollable interaction (such as sudden bridging or breaking) between the tip and the sample surface mediated by interspersed sticky contaminants. In this article, we demonstrate that such a contaminant confined on the tip apex displays an uncontrollable variation in the oscillation amplitude of the cantilever, causing noise in the AFM images the contaminated tip collects.

It has been recognized that ADC is governed by the second order differential equation of motion,[11–13]

$$mdz^2/d^2t + k_c z + \alpha dz/dt = F_{ts}(z_t, z) + F_0 \cos \omega t,$$

where m is the mass of the tip/cantilever ensemble, k_c the spring constant of the cantilever, α the damping factor, F_{ts} the interaction force between the tip apex and the sample

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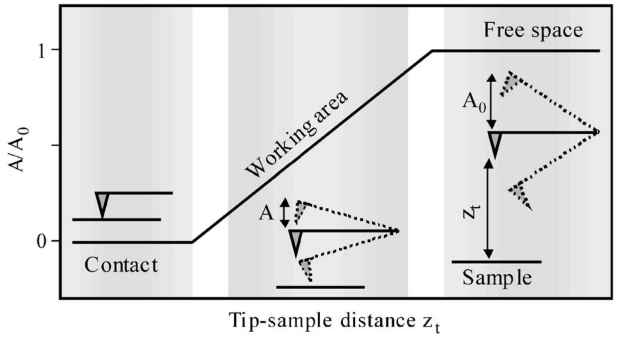

FIG. 1. Schematic illustration for amplitude vs tip-sample distance z_t of an oscillating cantilever in free space (far away from the sample surface) and in the working area where the oscillation amplitude A is damped to 20%–80% of that in free space A_0. The rest position of the cantilever is z_t, which is the tip-sample distance. When z_t becomes zero or less, the cantilever stops oscillating and mechanical contact is established, capable of manipulating contaminants if they are present on the tip apex.

surface, z_t the rest position of the tip, z the position of the tip during oscillation, F_0 the amplitude, and ω the angular frequency of the driving force used to oscillate the cantilever. Assuming that F_{ts} is due to van der Waals and contact forces, Garcia and co-worker have conducted simulations as well as experiments and found that for samples having Young's modulus larger than 100 MPa, the amplitude decreases almost linearly with the decreasing tip-sample distance.[11–13]

An ADC is schematically illustrated in Fig. 1 to depict the three characteristic areas in terms of tip-sample interaction: free space, working area, and contact. When the tip is far away from the sample surface, there is no interaction between them so that this regime is called free space. The insert of Fig. 1 schematically shows the amplitude of the oscillating cantilever in free space (A_0) where the distance between the tip and the sample surface z_t is much larger than the amplitude. When the tip is positioned at a distance that is smaller than A_0, the oscillation amplitude is damped to a certain value, denoted in the insert as A. This is the working area of the dynamic force mode AFM since a change of the tip-sample distance will cause a change in the resultant amplitude A. When the tip scans the sample surface, the system adjusts the cantilever up or down in accordance with the contour of the sample surface so as to keep a preset damped amplitude, which constructs the topography of the sample surface. This preset damped amplitude is commonly called set point, which is expressed as A/A_0 and is the feedback parameter in dynamic force mode AFM. If the tip is mechanically contacted with the sample surface, the cantilever no longer oscillates; this is the regime called contact, which can be used to remove contaminants from the tip apex.

Zitzler *et al.* have clarified that the formation and rupture of a capillary neck during the oscillation cycle give rise to a capillary force added to F_{ts}, which can be detected in ADCs.[14] Those forces (i.e., van der Waals, contact, and capillary forces) are apparently more or less intrinsic to the tip-sample interaction. If the tip apex is contaminated by materials which cause additional, unpredictable forces to F_{ts}, the ADC should deviate from its behavior in the working area when these extrinsic forces are absent. We demonstrate in this article such a case caused by the presence of a liquidlike contaminant on the AFM probe tip apex. A sudden appearance of such forces when the tip is in the working area causes unpredictable changes in oscillation amplitude of the cantilever, which shall be reflected as noise in an AFM image obtained using such a contaminated tip. This situation is usually seen as noisy AFM images when imaging samples on which the tip is prone to contamination by sticky materials. We demonstrate by using a thiol-contaminated AFM tip in this article that the extra forces induced by the contaminant are responsible for the noise seen in an AFM image collected using the tip.

II. TECHNIQUES AND MATERIALS

A stiff silicon cantilever (spring constant: ~30 N/m) with geometric dimensions of 130 μm long, 29 μm wide, and 3.7 μm thick was used in this study. The tip attached to the free end of the cantilever was about 10 μm long and the nominal tip apex radius was 20 nm. The dynamic force mode of a TopoMetrix's Explorer was employed, in which the cantilever is oscillated at its resonant frequency (~260 kHz as measured using the AFM system) with an oscillation amplitude around ~25 nm in free space. The oscillation amplitude decreases when the tip is brought close to the surface so that the tip "feels" the attractive and repulsive forces between them. For AFM imaging, the cantilever is scanned across the sample surface at a certain distance from the sample surface where the oscillation amplitude is damped 50% from that in free space, i.e., a set point at $A/A_0=50\%$.

A 50-nm-thick gold film was sputter coated on AFM tips and a silicon substrate. The thiol used in this study was 1-decanethiol ($C_{10}H_{22}S$) purchased from Sigma-Aldrich Canada Ltd. The thiol was loaded onto the gold-coated tip by approaching the cantilever into the liquid thiol placed on a gold film coated on a Si substrate. The feedback mechanism of the AFM protected the tip from crashing into the gold film. Then the tip was retracted from the thiol and used to conduct amplitude versus tip-sample distance measurements and/or imaging on another fresh gold film prepared on a Si substrate.

The resonance frequency of the gold-coated cantilever was determined by measuring the oscillation amplitude of the cantilever as a function of the frequency of the driving force. The amplitude of the cantilever oscillated at the resonance frequency was monitored when the tip was brought to and then retracted from the surface at a speed of 100 nm/s. The amplitude A was plotted as the ratio to that in free space A_0. The origin for the distance between the tip and sample surface was arbitrarily chosen as distance in the approaching ADC where the damped amplitude A is half of A_0 (i.e., $A/A_0=50\%$). The oscillation of the cantilever would stop when the tip is in mechanical contact with the sample surface and $A/A_0=0$ is used to describe this state. AFM images consisting of 300 lines with 300 pixel points per line were obtained with a scan rate of 5 μm/s. The experiments were performed in air under a relative humidity of ~40%.

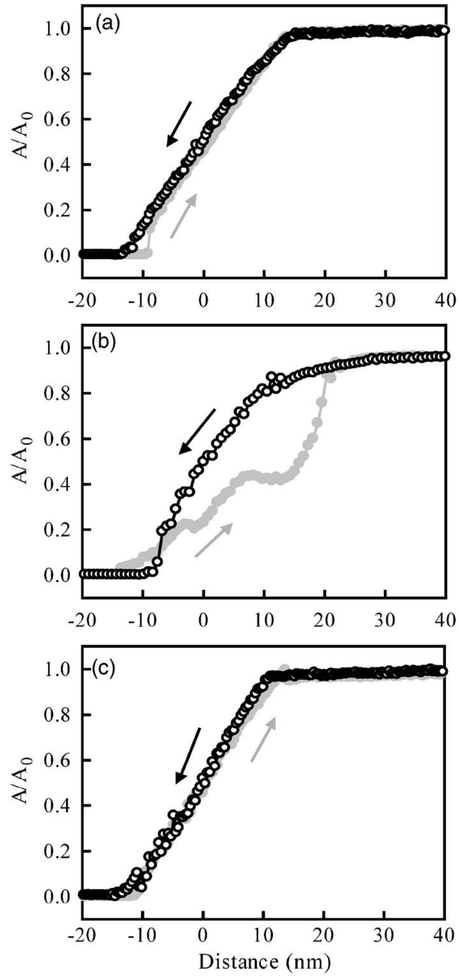

FIG. 2. Amplitude-distance curves obtained on a gold film by a clean gold-coated tip (a) and by the same tip after being immersed in the thiol for the first (b) and the second (c) cycle of measurements, respectively. The change of the amplitude with respect to tip-sample distance is represented by open circles and filled gray circles when the tip is brought to (indicated by the black arrow) and retracted from (indicated by the gray arrow) the sample surface, respectively. The speed of the tip approaching to and retracting from the sample surface was 100 nm/s.

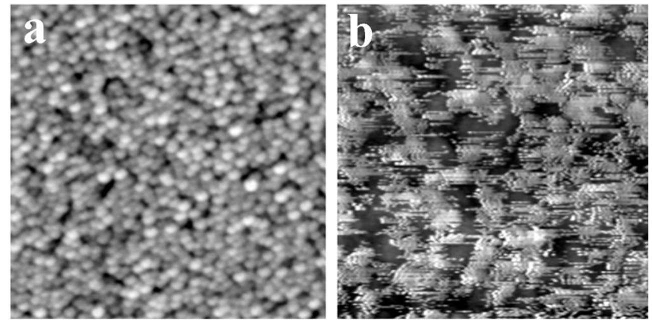

FIG. 3. A dynamic force microscopy image (scan area: $1 \times 1\ \mu m^2$) of a gold film obtained by the same tip that was (a) cleaned from thiol and (b) recontaminated by thiol. The set point for the two images was $A/A_0 = 50\%$. Gray-scale range is 7 nm for both images.

III. RESULTS AND DISCUSSION

The ADCs measured using clean gold-coated tips on a clean gold-coated Si substrate were reproducible; a typical one is shown in Fig. 2(a), where the frequency of the driving force was set at 261.2 kHz, the measured resonance frequency of the cantilever. The curve shows that when the tip is approaching the surface, the amplitude (black open circles) decreases. The decrease of amplitude with decreasing distance is due to the interactive forces exerted between the tip and the sample surface. The amplitude decreases almost linearly with decreasing tip-sample distance. This behavior results from the requirement for satisfying the equation of motion for the oscillating tip assuming that the tip-sample interactions be dominated by van der Waals and contact forces. This has been theoretically investigated by Garcia and co-worker.[11–13] The amplitude is finally damped to zero when the tip is brought to mechanical contact with the sample surface. When the tip is retracted from the surface, the amplitude increases (gray filled circles) and coincides with the approaching one (black open circles). In general, adhesion established due to the mechanical contact between the tip and the sample may produce a delay in the amplitude from recovery. For the gold-coated tip and the gold-coated Si substrate system, however, as shown in Fig. 2(a), such a hysteresis is insignificant.

In order to contaminate our gold-coated AFM tip with a liquidlike material, we used the AFM to bring the tip in contact with the liquid thiol film extended on the surface of a gold film prepared on a Si substrate. Then the tip was retracted from the liquid thiol and moved to another gold film coated on a Si substrate for ADC measurements. Shown in Fig. 2(b) is the first ADC obtained after the tip was contaminated by the thiol. There is a significant change in the amplitude when the tip is brought to the sample; that is, the amplitude starts to decrease earlier and deviates from linearity in the working area. Under such a situation, imaging was usually not possible, since there was apparently too much material loaded on the tip apex. When the tip is retracted from the sample the amplitude shows an even more significant change from that for the clean gold-coated tip. The hysteresis seen between the approaching and retracting ADCs is attributed to adhesion caused by the thiol loaded on the tip apex because of the mechanical contact between the tip and the sample surface. The steplike features seen in the retracting ADC [Fig. 2(b)] suggest additional forces contributed by stretching of the liquidlike material as the tip is being retracted from the sample surface.

One might be able to remove the thiol from the tip apex by repeatedly pushing the tip a certain distance into the surface of the gold film deposited on a Si substrate. Shown in Fig. 2(c) is the ADC obtained after the one shown in Fig. 2(b), where the tip has been pushed ~10 nm into the sample surface. Now, the ADC resembled the one obtained using the clean tip [Fig. 2(a)], indicating that the thiol was removed from the tip apex, regardless of whether it was deposited on the sample surface or moved to the sidewall of the tip. Therefore, pushing a contaminated tip into a soft material could be effective in cleaning the contaminated tip apex.

After removing the thiol from the tip apex as evidenced by the ADC shown in Fig. 2(c), the tip was used to collect AFM images of the gold film surface. Shown in Fig. 3(a) is an AFM image for the gold film using the cleaned tip, which resembles the image collected by the clean tip before it was contaminated by thiol (not shown). The particles seen in the image are actually larger than the real particles of the gold film since coating a gold film on the original tip increased the size of the tip apex. Other than tip effect caused by the enlargement of the tip apex,[5,6] Fig. 3(a) shows a good quality AFM image. On the other hand, Fig. 3(b) shows a noisy AFM image collected on the same gold film surface using the same tip after it was recontaminated with thiol during scanning. This was not easy to obtain by dipping a tip into the liquid thiol film directly; this usually resulted in too much liquid thiol on the tip apex prohibiting any AFM imaging.

The height in an AFM image is simply the tip position offset from the sample surface so as to keep the set point ($A/A_0=50\%$ in our case) during scanning the tip across the sample surface. Therefore, any change in the amplitude transforms to a change in the height of an AFM image, regardless of reasons for that change. When the tip-sample interaction is dominated by van der Waals and contact forces,[11–13] the tip-sample distance is solely determined by the surface topography for the set point on a homogeneous material. Therefore, the height of the surface features of the sample will be truthfully imaged by AFM [Fig. 3(a)] with a tip free from an active material. However, when the tip is contaminated by an active material giving rise to extra forces, the amplitude becomes highly unstable so that the AFM feedback system causes unstable tip-sample distance. The noisy features seen in Fig. 3(b) thus reflect unstable amplitudes caused by the thiol confined at the tip apex during scanning. The presence of the thiol on the tip apex could result in a bridge forming between the tip and the sample surface. As a result, additional forces arise, which result in unstable amplitudes, causing the noisy features seen in Fig. 3(b). To prove this hypothesis, we measured ADCs using the same tip immediately after collecting the noisy AFM image shown in Fig. 3(b).

Figure 4(a) shows the first ADC measured on the gold film using the tip after it collected the image shown in Fig. 3(b). The result clearly shows features related to very different interactions from the van der Waals and contact forces[11–13] between the tip and sample surface; this is an evidence for the existence of the thiol on the tip apex. These changes in amplitude indicate that there is an emergence of bridging of the thiol confined on the tip apex with the sample surface before the tip is mechanically contacted with the sample surface, resulting in a stretching force; this stretching force disappears when the tip becomes closer to the sample, probably because the thiol strands bridging the tip and the sample are relaxed. When this stretching force vanishes, the amplitude reverts to that with no thiol on the tip apex. Then the tip is brought to be in mechanical contact with the sample so that the amplitude is damped to zero.

When the tip is at the distance where the amplitude is damped 50% (the set point for imaging), one can see the abrupt changes in the amplitude (open circles) from the magnification of this region shown in Fig. 4(b). Also shown is an ADC for the cleaned tip from Fig. 2(c), which shows a linear decrease in amplitude with decreasing tip-sample distance. Because of the unstable oscillation amplitude around the set

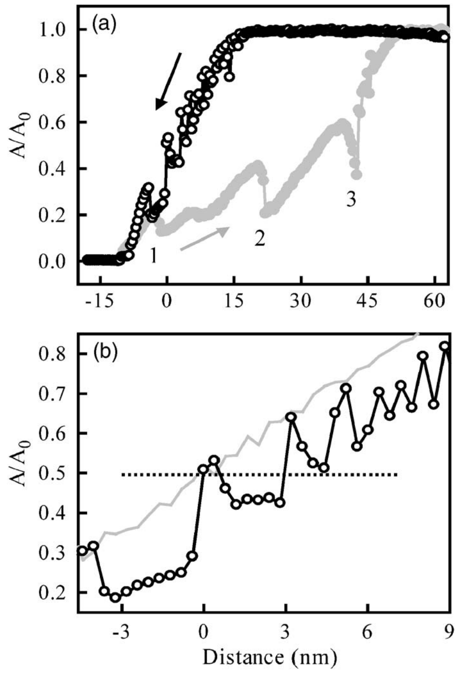

FIG. 4. The amplitude-distance curve (a) obtained using the tip that had collected the image shown in Fig. 3(b). The tip is first brought in contact with the sample followed by retraction. The black and gray arrows indicate tip approach and tip retraction, respectively. The three main peaklike features in the first amplitude-distance curve (a) when the tip is retracted from (filled circle) the sample are marked 1, 2, and 3. Magnification of the approaching amplitude-distance curve within the range of $A/A_0=80\%$ to $A/A_0=20\%$ is shown in (b). Also shown in (b) is a gray line showing the counterpart from a cleaned tip [Fig. 2(c)] and a broken line showing the set point of $A/A_0=50\%$ for imaging. The speed of the tip approaching to and retracting from the sample surface was 100 nm/s.

point [indicated by the insert broken line in Fig. 4(b)], the tip-sample distance becomes highly unstable as the feedback system tries to follow the set point of $A/A_0=50\%$. This results in noisy height distributions in the AFM image [Fig. 3(b)] reflecting this unstable ADC in the working area around the set point of $A/A_0=50\%$. Without the contamination, as the gray line in Fig. 4(b) suggests, the amplitude decreases linearly with decreasing tip-sample distances, which assures that the AFM image it collects is a reflection of the topographic features of the sample surface [Fig. 3(a)]. On the other hand, the unstable amplitude induced by the thiol-loaded tip dominates the amplitude change and could jump to different tip-sample distances in order to follow the fine gold particles that only require a small change in amplitude. Therefore, the noisy features seen in the AFM image [Fig. 3(b)] are simply a reflection of the unstable amplitude, which is induced by extra forces mediated by the presence of an active material, thiol, on the tip apex.

The retracting ADC shall provide additional information on the thiol after it is squeezed between the tip and the sample surface. As shown in Fig. 4(a), upon retracting the tip from the sample surface after tip-sample contact, striking features appear in the amplitude. There are three main peaks (marked as 1, 2, and 3) characterized by an abrupt decrease in the amplitude while the tip is being retracted from the sample surface. This abrupt decrease in amplitude at the three peaks can be explained by a sudden emergence of extra forces exerted to the tip caused most likely by stretching the thiol strands when the tip is departing from the sample. The cycle of loading and removing thiol on the tip apex was reproducible when the experimental procedures were followed. The first retraction ADC would show step- or peak-like features as seen in Figs. 2(b) and 4(a), though the detailed shape of these features might be affected by the amount of the thiol confined on the tip apex.

Peaks 1 and 2 show a similar behavior, i.e., after the abrupt decrease in amplitude, there is a gradual increase in amplitude. On the other hand, peak 3 shows an abrupt increase in amplitude after the amplitude reaches the valley. We believe that this corresponds to the end of the interaction between the tip apex and the sample surface mediated by the thiol, since the tip is now sufficiently removed apart from the sample surface ($\sim$55 nm) so that the bridge made by the thiol must break. The experimental facts we observed in Figs. 3(b) and 4(a) suggest that the existence of the thiol on the tip apex must be responsible to the noisy features in the AFM image, the unstable amplitude in the approaching ADC, and the peaklike features in amplitude in the retracting ADC.

IV. SUMMARY

In conclusion, by confining 1-decanethiol on a gold-coated AFM tip apex and measuring the amplitude of the oscillating cantilever as a function of tip-sample distance on a gold film, we demonstrated that such an active material gives rise to extra forces to the interaction between the tip and the sample surface. These extra forces appear to arise from the bridging and breaking between the contaminated tip and the sample surface mediated by the active material, with the tip approaching to and retracting from the sample surface, respectively. We have observed that the amplitude changes abruptly when approaching the contaminated tip to the sample surface so that there appears the same amplitude at multiple, adjacent, tip-sample distances around the working distance corresponding to the set point. This unstable amplitude induced by the contaminant confined on the tip apex is responsible for the noisy features in the AFM image the contaminated tip collects. Therefore, the measurement of amplitude versus tip-sample distance is useful in revealing the state of an active material confined on a tip apex; it can be used to estimate when the confined active material starts to exert forces on the tip in the tip approach process and whether the active material is removed in the tip retraction process following the tip being pushed a certain distance into the sample surface.

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