True-molecular resolution imaging by frequency modulation atomic force microscopy in various environments

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In this study, we discuss the relationship between Q factor of the cantilever in various environments and frequency noise in frequency modulation atomic force microscopy (FM-AFM). We first present true-molecular resolution FM-AFM images of alkanethiol self-assembled monolayers taken in a moderate vacuum environment (vacuum pressure: 6 Pa) and in air (cantilever Q factor: 390) using FM-AFM with a low noise cantilever deflection sensor. The results reveal that the minimum Q factor to obtain true-molecular resolution in FM-AFM can be less than a few hundred. © *2005 American Institute of Physics.* [DOI: 10.1063/1.1852721]

Imaging of molecular-scale structures is becoming more and more important as the global interest in organic electronic devices is growing rapidly. Scanning tunneling microscopy (STM)[1] has been the most common technique to visualize molecular-scale structures so far because of its high spatial resolution and simple experimental setup. However, STM cannot be applied to the imaging of insulating materials because it utilizes tunneling current flowing between a tip and a sample as a feedback signal for the tip–sample distance regulation.

In contrast, frequency modulation atomic force microscopy (FM-AFM)[2] is capable of imaging organic materials with true molecular resolution even on insulators[3,4] as well as on conductive surfaces.[5–7] Nevertheless, all of the molecular-scale FM-AFM images presented so far were taken in ultrahigh vacuum (UHV) environments, which has significantly limited possible FM-AFM applications, especially in biology and organic molecular science. On the other hand, AFM apparatus working in various environments such as moderate vacuum, ambient and liquid are now commercially available. Although these AFMs are relatively compact and easy-to-use compared to UHV-AFMs, there have been no reports on molecular-resolution FM-AFM images with such a simple AFM.

With increasing attention to the field of biological science, strong demands for high-resolution imaging tools in liquid environments have emerged. The major problem in FM-AFM operation in a liquid environment is that Q factor of the cantilever is extremely low. For a standard microfabricated silicon cantilever, the Q factor is 10 000–30 000 in vacuum, 300–600 in air, and 1–20 in liquid. Since the force sensitivity in FM-AFM improves with increasing Q factor,[2] there must be a lower limit of Q factor that allows us to achieve a true-molecular resolution. In that sense, it is essential to know the performance of FM-AFM in air as a first step

to explore the possible FM-AFM applications in low-Q environments.

This letter reports on a relatively compact and easy-to-use FM-AFM that can achieve a true-molecular resolution even in moderate vacuum and ambient conditions. True-molecular resolution FM-AFM images of alkanethiol self-assembled monolayers (SAMs) on Au(111) surfaces are demonstrated in those environments.

The molecule used in this experiment was 1-dodecanethiol $(CH_3(CH_2)_{11}SH, C_{12})$ purchased from Sigma-Aldrich Co., Ltd. The Au(111) surface was prepared by the evaporation of gold onto a freshly cleaved mica substrate which was heated at 420 °C. The Au(111) surface was immersed in 1 mM ethanol solution of C_{12} for 15 min so that it was covered with a self-assembled thiol monolayer. Then the sample was rinsed in pure ethanol and dried in N_2 flow. The monolayer formed with this procedure consists of closely packed thiol molecules with their molecular axes tilted about 30° from the surface normal.[8–10] Since true-molecular resolution has been demonstrated on the same system by UHV-FM-AFM,[11,12] the monolayer is suitable for our experiments.

FM-AFM imaging was performed in constant frequency shift mode, where the negative shift of the cantilever resonance frequency (Δf) induced by the tip–sample interaction was kept constant for the tip–sample distance regulation. The cantilever was vibrated in constant amplitude mode, where the vibration amplitude of the cantilever (A) was kept constant by adjusting the amplitude of a cantilever excitation signal. A highly doped n-Si cantilever (Nanosensors: NCH) with a resonance frequency (f_0) of about 300 kHz and a nominal spring constant (k) of 40 N/m was used for the imaging. The tip and the sample were grounded during the imaging.

There are two major sources of the frequency noise in FM-AFM, i.e., noise due to the cantilever Brownian motion (δf_{th}) and noise from the deflection sensor (δf_{ds}). These noises are described by[13]
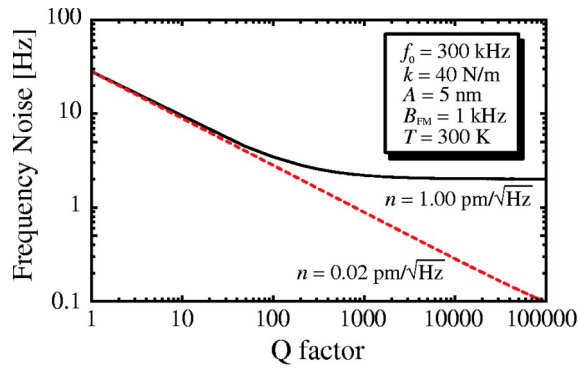
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FIG. 1. (Color online). Calculated frequency noise using Eqs. (1)–(3) plotted as a function of Q factor. The relevant parameters used in the calculation are shown in the inset.

FIG. 2. (Color) FM-AFM images of C_{12} SAM on Au(111) surface obtained in a moderate vacuum environment (vacuum pressure: 6 Pa). A tilt compensation and a low pass filtering were applied to the images. The AFM head was placed in a small vacuum chamber pumped only with a RP. The Q factor measured in the vacuum was about 19 000. (a) 10 nm×10 nm, Δf =−120 Hz, A=5 nm, v_{tip}=168 nm/s. (b) 6 nm×6 nm, Δf=−125 Hz, A =5 nm, v_{tip}=224 nm/s.

$$\delta f_{th} = \sqrt{\frac{2k_B T B_{FM} f_0}{\pi k Q A^2}}, \tag{1}$$

$$\delta f_{ds} = \frac{n}{\pi A} B_{FM}^{3/2}, \tag{2}$$

$$\delta f = \sqrt{\delta f_{th}^2 + \delta f_{ds}^2}, \tag{3}$$

where k_B, T, B_{FM}, and n denote Boltzmann constant, temperature, bandwidth of the FM detector, and the spectral density of cantilever deflection noise from a deflection sensor, respectively.

For commercially available AFMs, the typical value for n is about 1 pm/$\sqrt{Hz}$,[13] which is dominated by the photodiode shot noise. The solid line indicated in Fig. 1 shows the Q dependence of δf values calculated with Eqs. (1)–(3) and n =1 pm/$\sqrt{Hz}$. The relevant parameters used in the calculation are given in the inset of this figure. The plot reveals that the decrease of δf with increasing Q factor is suppressed after the Q factor exceeds a few hundred due to the influence of δf_{ds}. Thus, the frequency noise is not determined by Q factor depending on environments but by the performance of the deflection sensor in this case.

In order to investigate "Q-limited" performance of FM-AFM, the δf_{ds} has to be sufficiently suppressed. Thus, we have developed a low noise deflection sensor with an n value of about 0.02 pm/$\sqrt{Hz}$ by optimizing the electronic and optical components used in the optical beam deflection sensor, which will be described in detail elsewhere. Consequently, δf continuously decreases with increasing Q factor as indicated by the dotted line shown in Fig. 1. Therefore, our AFM can exhibit "Q-limited" performance both in air and vacuum environments.

For this study, we modified a commercially available AFM (JEOL: JSPM-4200) that can work in moderate vacuum and ambient conditions. We replaced the original deflection sensor with the above-mentioned optical beam deflection sensor. The original FM detector was replaced with our homebuilt FM demodulator using a PLL circuit.[14] Only the sample scanning stage with a scan range of 20 μm was used without any modifications. The AFM head is installed in a cylindrical chamber with a diameter of 15 cm and height of 30 cm. The chamber can be pumped with a turbomolecular pump and a rotary pump (RP). The AFM is much more compact and easy-to-use than an UHV-FM-AFM which requires sputter-ion pumps and chamber baking systems.
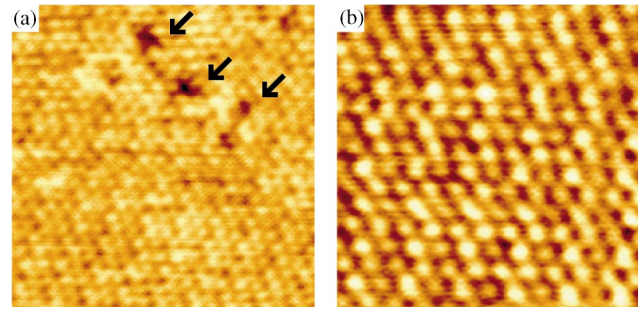
Figure 2 shows FM-AFM images of C_{12} SAM taken in a moderate vacuum environment (vacuum pressure: 6 Pa). Figure 2(a) shows individual molecules hexagonally packed with an intermolecular distance of about 0.5 nm. In this image, some molecular-scale defects are also resolved as indicated by the black arrows, indicating that true-molecular resolution FM-AFM imaging was performed even in a moderate vacuum environment. The hexagonal arrangement of the molecules is more clearly seen in Fig. 2(b), which was taken with a smaller scanning area. The image also shows small height variations with a lateral period of about 1 nm, which agrees well with the lattice constant of the $c(4\times2)$ superlattice structure.[12]

The Q factor obtained in the moderate vacuum environment was about 19 000, which was as high as those obtained in UHV environments. Even with such a high Q factor and B_{FM} of 1 kHz, δf in this experiment was determined by δf_{th} and the contribution of δf_{ds} was negligible owing to the low noise of our deflection sensor (Fig. 1). Thus, we achieved true-molecular resolution with a relatively fast scanning speed (v_{tip}):168 nm/s for Fig. 2(a) and 224 nm/s for Fig. 2(b). From a practical point of view, this ability significantly facilitates to suppress image distortions caused by the thermal and/or mechanical drifts. Compared with UHV-AFMs, multienvironment AFMs have a relatively primitive sample scanning stage having a large scanning range with less mechanical/thermal stability. Thus, high-resolution imaging with a slow scanning speed generally results in severe image distortions for such a simple AFM setup.[15] However, we obtained molecular-scale images with sufficient quality by imaging with a relatively fast scanning speed.

Figure 3 shows FM-AFM images of C_{12} SAM on Au(111) surface obtained in air. Figure 3(a) shows molecular stripes with a spacing of 0.43 nm. A molecular-scale defect was also imaged as indicated by the black arrow in Fig. 3(a), revealing that true-molecular resolution FM-AFM imaging is possible even in air. The individual molecules are more clearly seen in the image shown in Fig. 3(b). Figure 3(c) shows a cross-sectional plot measured along a black line A–B in Fig. 3(b). The plot shows that the measured molecular corrugation has 0.5 nm period and 20–40 pm height variation.

Since Q factor measured in air (Q=390) was much smaller than those obtained in vacuum, the frequency noise was not as small as that obtained in vacuum as expected
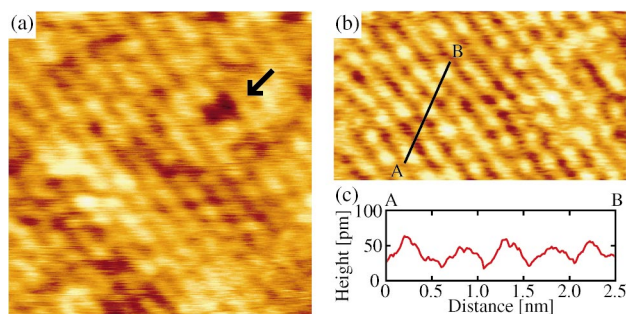
FIG. 3. (Color) FM-AFM images of C_{12} SAM on Au(111) surface obtained in air. A tilt compensation and a low pass filtering were applied to the images. The Q factor measured in air was 390. (a) 5.5 nm × 5.5 nm, $\Delta f = -105$ Hz, $A = 7.5$ nm, $v_{tip} = 224$ nm/s. (b) 7 nm × 4 nm, $\Delta f = -135$ Hz, $A = 6$ nm, $v_{tip} = 224$ nm/s. (c) Cross-sectional plot measured along a black line A–B in (b).

from Fig. 1. However, it was still small enough for us to obtain molecular resolution with a relatively fast scanning speed ($v_{tip} = 224$ nm/s for images in Fig. 3). We reproducibly obtained true-molecular resolution images with several different cantilevers whose Q factors ranged from 300 to 500. Thus, we conclude that the minimum Q factor for molecular-resolution FM-AFM imaging can be less than a few hundred. The cantilever excitation signal required for maintaining the oscillation amplitude during the imaging was almost the same as that for a freely oscillating cantilever. Possible influence of water and/or other contaminations in air was not evident in our experiment. This is probably because the surface of an alkanethiol SAM is terminated with an array of hydrophobic methyl end groups.

In summary, a relatively compact and easy-to-use FM-AFM with a low noise deflection sensor ($n = 0.02$ pm/$\sqrt{\text{Hz}}$) has been developed. With this AFM, we have presented true-molecular resolution FM-AFM images of alkanethiol SAMs obtained in moderate vacuum and ambient conditions. Lat-

eral and vertical resolutions of 0.5 nm and 20–40 pm were obtained in air with a relatively fast tip scanning speed of 224 nm/s. The results demonstrate that the Q factor to achieve true-molecular resolution can be less than a few hundred. Further experiments in air and liquid environments are required to elucidate the minimum Q factor.

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