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Surface potential measurements by the dissipative force modulation method

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In this study, we propose a novel surface property measurement technique using noncontact atomic force microscopy (NC-AFM), which is referred to as the “dissipative force modulation (DM) method.” NC-AFM-based surface property measurements have mostly utilized conservative tip-sample interaction forces, which induce a frequency shift of cantilever resonance without dissipating cantilever vibration energy. In the DM method, local surface properties are measured by detecting a modulated dissipative tip-sample interaction force which dissipates cantilever vibration energy and hence induces an amplitude variation in cantilever vibration. Since the force sensitivity to dissipative interactions obtained in a typical NC-AFM setup is much higher than that to conservative ones, the DM method can improve the sensitivities of conventional NC-AFM-based techniques that utilize conservative interactions. Combining this method with Kelvin-probe force microscopy, we present the first quantitative surface potential measurement through dissipative tip-sample interactions. © 2004 American Institute of Physics. [DOI: 10.1063/1.1805291]

I. INTRODUCTION

Noncontact atomic force microscopy (NC-AFM) using the frequency modulation (FM) detection method¹ has attracted much attention due to its capability of imaging atomic-scale structures even on insulating surfaces² as well as on conductive surfaces.^{3,4} In addition to the imaging of surface structures, NC-AFM has also been used for the investigation of local surface properties at a nanometer-scale resolution. In particular, Kelvin-probe force microscopy (KFM) combined with NC-AFM (Ref. 5) has been applied to the measurement of local surface potential distributions at a nearly atomic-scale resolution.

In NC-AFM, a microfabricated cantilever with a sharp tip mounted at its end is brought close to the surface to detect various tip-sample interaction forces. These tip-sample interaction forces detected in NC-AFM are classified into two categories: “conservative” forces and “dissipative” forces.^{6,7} Conservative forces induce a frequency shift of cantilever resonance without dissipating cantilever vibration energy. On the other hand, dissipative forces reduce cantilever vibration amplitude, which means that the mechanical energy of the cantilever is dissipated through some of the tip-sample interactions.

Since tip-sample interaction forces in NC-AFM are mostly conservative, conservative forces, rather than dissipative forces, have been utilized thus far in NC-AFM applications. The frequency shift induced by a conservative tip-

sample interaction force is detected and used for tip-sample distance regulation. In KFM, an ac bias voltage is applied between a tip and a sample, which modulates the magnitude of a conservative electrostatic force. Then the resultant change in cantilever resonance frequency is detected and used for bias feedback regulation.⁵

In contrast to the conservative force measurements, surface property measurements hardly use dissipative forces. This is because energy dissipation in NC-AFM has different origins related to the electrical and mechanical properties of a tip and a sample.^{8,9} Thus, the quantitative evaluation of surface properties is difficult by a simple measurement of the total amount of energy dissipation. However, previously reported energy dissipation values measured by NC-AFM have suggested that the force sensitivity to dissipative interactions obtained with a typical NC-AFM setup is much higher than that to conservative ones.^{10,11} For example, an energy dissipation of less than 1 fW was accurately measured in previous studies,^{10,11} which means that a dissipative electrostatic force of less than 0.01 pN is readily detected in NC-AFM. This indicates that the use of dissipative forces instead of conservative ones should improve such sensitivity in surface property measurements.

In this article, we propose a novel NC-AFM-based technique referred to as the “dissipative force modulation (DM) method.” By introducing and detecting a modulated dissipative force, the method enables the separation of the dissipative interaction of interest. Combining this method with KFM, we have developed a modified type of KFM that enables quantitative surface potential measurement with an ex-

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tremely high sensitivity. To show the clear contrast between the currently used KFM and the newly developed one, we hereafter describe these two methods as conservative force modulation KFM (CM-KFM) and dissipative force modulation KFM (DM-KFM), respectively. In this article, the basic principle and experimental setup of DM-KFM are presented. The extremely high sensitivity of NC-AFM to a dissipative interaction force is experimentally demonstrated. In addition, the preliminary results of surface potential measurements using DM-KFM are presented.

II. BASIC PRINCIPLE

A. Conservative and dissipative forces

In NC-AFM, the phase difference between cantilever oscillation and its excitation signal (v_{exc}) is continuously kept constant at 90° with a self-excitation circuit. Thus, v_{exc} and tip position (z_t) can be described as

$$v_{\text{exc}} = V_{\text{exc}} \cos(\omega t), \quad (1)$$

$$z_t = z_{t0} + A \sin(\omega t). \quad (2)$$

V_{exc} and ω are the amplitude and frequency of the cantilever excitation signal, respectively. z_{t0} and A denote the mean tip position and the amplitude of the cantilever vibration, respectively.

Due to the high Q -factor of the cantilever, cantilever motion, particularly in vacuum, is predominantly affected by the ω -components of tip-sample interaction forces. Accordingly, the tip-sample interaction force (F_{ts}) can be approximately described by two trigonometric functions whose phases differ by 90° ,

$$F_{ts} = F_{ts,c} \sin(\omega t) + F_{ts,d} \cos(\omega t). \quad (3)$$

The first component ($F_{ts,c} \sin(\omega t)$) changes with the same phase as that of the cantilever vibration, which induces a frequency shift (Δf) of cantilever resonance without dissipating vibration energy. On the other hand, the second component ($F_{ts,d} \cos(\omega t)$) changes with the same phase as that of the cantilever excitation signal, which dissipates some energy of the cantilever vibration. The energy dissipation results in an amplitude variation (ΔA) of the cantilever oscillation. In this article, we refer to the former component as conservative force and to the latter as dissipative force.

From the equation of motion, Δf and ΔA are given by

$$\Delta f = -\frac{f_0}{2kA} F_{ts,c}, \quad (4)$$

$$\Delta A = \frac{Q}{k} F_{ts,d}, \quad (5)$$

where f_0 , k , and Q are the resonance frequency, the spring constant and the Q -factor of the cantilever, respectively. Thus, the minimum detectable force for conservative interactions ($\delta F_{ts,c}$) and that for dissipative interactions ($\delta F_{ts,d}$) are given by

$$\delta F_{ts,c} = \frac{2kA}{f_0} \delta f, \quad (6)$$

TABLE I. Typical values of parameters of cantilever under vacuum and experimental conditions in NC-AFM experiments.

Parameter	Value	Unit
f_0	300	kHz
k	40	N/m
Q	30 000	
T	300	K
f_m	1	kHz
B	200	Hz
n_{ds}	0.1–1	pm/ $\sqrt{\text{Hz}}$
A	5	nm
z_{t0}	6	nm
R	5	nm

$$\delta F_{ts,d} = \frac{k}{Q} \delta A, \quad (7)$$

where δf and δA are the minimum detectable frequency and amplitude, respectively.

There are two major noise sources that limit the sensitivities to frequency and amplitude in NC-AFM, which are the thermal vibration of the cantilever and noise from the deflection sensor. In both CM- and DM-KFM, a conservative force or a dissipative electrostatic force is modulated at a frequency of f_m by applying an ac bias voltage ($f_m \ll f_0$). Thus, the spectral noise density of a cantilever deflection signal at a frequency of $f_0 + f_m$ has to be taken into account for the evaluation of the force sensitivities. For the noise arising from the cantilever thermal vibration, the root-mean-square (RMS) value of spectral noise density (n_{th}) at a frequency of $f_0 + f_m$ is approximately expressed by¹

$$n_{\text{th}} = \sqrt{\frac{k_B T f_0}{2\pi k Q f_m^2}}. \quad (8)$$

Table I shows an example of typical cantilever parameters under vacuum and experimental conditions. Under these conditions, n_{th} is 13 fm/ $\sqrt{\text{Hz}}$. On the other hand, the typical RMS value of the spectral noise density arising from a deflection sensor (n_{ds}) falls in the range of 0.1–1 pm/ $\sqrt{\text{Hz}}$, which is much larger than n_{th} . Thus, n_{ds} predominantly determines δf and δA for typical NC-AFM setups operating in vacuum.

Assuming that the modulated frequency and amplitude are detected with a lock-in amplifier with a bandwidth of B , δf , and δA at a modulation frequency of f_m are, respectively, given by¹²

$$\delta f = \frac{\sqrt{12}}{\pi A} f_m n_{\text{ds}} \sqrt{B}, \quad (9)$$

$$\delta A = n_{\text{ds}} \sqrt{B}. \quad (10)$$

Note that the condition $f_m^2 \gg B^2$ is assumed in obtaining δf . With the typical conditions given in Table I, δf is approximately 0.3–3 Hz while δA is approximately 1.4–14 pm.

From Eqs. (6), (7), (9), and (10), $\delta F_{ts,c}$ and $\delta F_{ts,d}$ are, respectively, obtained as

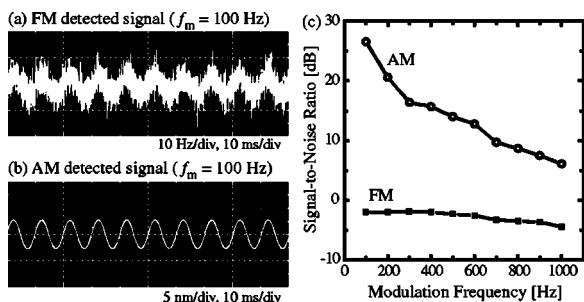


FIG. 3. (a), (b) Waveforms of FM- and AM-detected signals at modulation frequency of 100 Hz. (c) SNRs of FM- and AM-detected signals plotted as functions of modulation frequency ($V_{ac}=0.1$ V, $V_{bias}=1.0$ V, $A=5$ nm, $\Delta f=-20$ Hz).

measured with an FFT analyzer (softDSP: SDS-200). The cantilever was a Pt-coated Si cantilever (Nanosensors: NCHPt) with a nominal spring constant of 40 N/m and a resonance frequency of approximately 300 kHz. The Q -factor measured under UHV conditions was approximately 30 000. The sample was a Pt thin film deposited on a SiO_2/Si substrate. The measurements were performed at a tip position where $\Delta f=-20$ Hz. V_{bias} and V_{ac} were set at 1.0 V and 0.1 V, respectively.

Figures 3(a) and 3(b) show the waveforms of FM- and AM-detected signals obtained at a modulation frequency of 100 Hz, respectively. These waveforms reveal that the AM-detected signal has a much higher SNR than the FM-detected signal. This result experimentally demonstrates that the force sensitivity of NC-AFM to dissipative interactions is much higher than that to conservative ones. Figure 3(c) shows the frequency dependences of the SNRs of AM- and FM-detected signals. The result indicates that the SNR of the AM-detected signal decreases with increasing modulation frequency while the SNR of the FM-detected signal remains almost constant. However, the result also shows that the AM-detected signal still exhibits a higher SNR than the FM-detected signal even at a modulation frequency of 1 kHz.

The amplitude variation induced by a dissipative force settles on a time scale of $\tau_{AM} \approx 2Q/f_0$ while the response time for the frequency variation induced by a conservative force is given by $\tau_{FM} \approx 1/f_0$.¹² Namely, AM detection has a slower time response by a factor of Q than that of FM detection, which decreases force sensitivity to dissipative forces at higher modulation frequencies. Thus, the DM method is most effective for applications that require an extremely high force sensitivity but not a very high scanning speed. The use of a high-resonance-frequency cantilever is the most effective way of enhancing force sensitivity and improving the time response of AM detection.

B. Surface potential imaging

Using DM- and CM-KFM, we have measured the surface potential distribution of a dimethylquinquethiophene (M5T) monolayer formed on a Pt surface. M5T molecules [Fig. 4(a)] deposited on a Pt surface form monolayer islands with their molecular axes perpendicular to the surface, as shown in Fig. 4(b). It has been reported that these monolayer

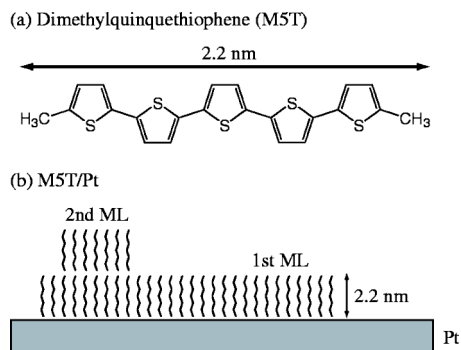


FIG. 4. (Color online) (a) Molecular structure of the M5T molecule. (b) Schematic model of the M5T monolayer formed on a Pt surface.

islands have 100–200 mV higher surface potential than Pt surfaces.¹⁶

Figure 5 shows the topographic and potential images taken by CM- and DM-KFM. The film/substrate potential difference measured from these two potential images [(Figs. 5(b) and 5(d))] agreed well and the value was approximately 100 mV. Owing to the excellent SNR of AM detection, the potential image obtained by DM-KFM shows a much clearer contrast than the CM-KFM image. Namely, the result demonstrates that DM-KFM has a higher potential resolution than CM-KFM.

In CM-KFM, it was difficult to obtain a clear surface potential image with V_{ac} values of less than approximately 1 V while clear potential contrast was obtained in DM-KFM even with V_{ac} of 0.1 V as shown in Fig. 5(d). The result shows that DM-KFM enables us to achieve a sufficiently high potential sensitivity even with a small V_{ac} , markedly suppressing the possible formation of topographic artifacts and the influence of the bias application on the sample properties. DM-KFM is also suitable for NC-AFM operation with a small cantilever vibration amplitude, which has been recently proven to be beneficial for enhancing spatial resolution in topographic imaging.¹⁷ δV_{CPD} for CM-KFM increases

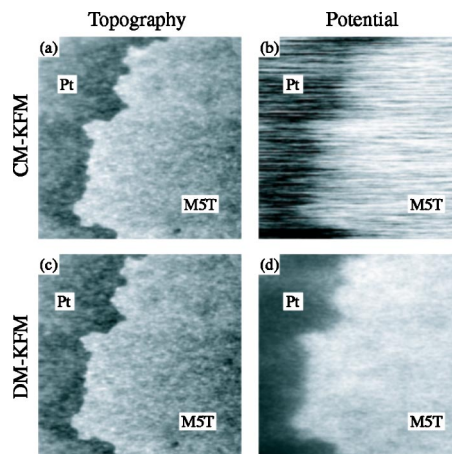


FIG. 5. (Color online) NC-AFM images of the M5T monolayer on a Pt surface. (a) Topographic and (b) potential images obtained by CM-KFM. (c) Topographic and (d) potential images obtained by DM-KFM. The experimental parameters used in both CM- and DM-KFM: $\Delta f=-20$ Hz, $A=1$ nm, $V_{ac}=0.1$ V, $f_m=1$ kHz. The scanned area and imaging speed were $1 \mu\text{m} \times 1 \mu\text{m}$ and 15 min/frame, respectively.

with decreasing cantilever vibration amplitude while that of DM-KFM remains almost constant as expected from Eqs. (19) and (24).

In terms of the spatial resolution of a potential image, CM-KFM has an advantage over DM-KFM. Comparing Eqs. (18) and (23), we can find that Δf_m is proportional to $1/z_{r0}^2$ while ΔA changes in proportion to $1/z_{r0}$. Thus, DM-KFM is more sensitive to long-range interaction force than CM-KFM. If we use an ac bias voltage of $V_{ac} \cos(\omega_m t) \cot(\omega t)$ instead of $V_{ac} \cos(\omega_m t) \cos(\omega t)$, we would be able to make ΔA proportional to $1/z_{r0}^2$. In that case, however, a high-voltage pulse will be intermittently applied between a tip and a sample, which may influence the sample properties to be measured by KFM.

In this study, we applied the DM method to surface potential measurements by KFM. However, the DM method can be applied to not only KFM but also other surface property measurements such as magnetic force microscopy and photo induced force microscopy.¹⁸

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