Invited Paper

Present status and future prospects of electric force microscopy

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Abstract: Electric force microscopy (EFM) and Kelvin probe force microscopy (KFM) have been widely used for studying electrical properties of nanometer-scale structures. Since they were invented at the early stage of atomic force microscopy (AFM) history, both techniques have been drastically developed with dynamic-mode AFM, where the cantilever is used as a mechanical oscillator. They are capable of mapping local work function and electronic states of a wide variety of material surfaces on an atomic/molecular scale. Here in this article we review the present status of EFM and KFM mainly based on frequency modulation AFM and discuss the future prospects.

Key Words: electric force microscopy, Kelvin probe force microscopy, frequency modulation AFM

1. Introduction

Electric force microscopy (EFM) is a scanning probe method visualizing nanometer-scale surface electric properties including local charge and contact potential difference by detecting the electrostatic force between a probe tip and a sample surface. The method has been widely applied to the investigations of local electronic states and trapped charges at surfaces and/or interfaces as a nondestructive, high-resolution measurement tool. The sharp resonance of the cantilever vibration with a high quality factor (Q -factor) [1–3] is utilized for the highly sensitive detection of interaction forces acting on the probe tip. Furthermore, Kelvin probe force microscopy (KFM), which is basically a similar technique to EFM, allows quantitative potential measurements by applying an external voltage to cancel the sample potential to be investigated.

In this article the present status of EFM and KFM, which have been rapidly developed over the past two decades, are reviewed and the future prospects for these methods are discussed.

2. Dynamic mode atomic force microscopy (AFM)

The working principle of EFM/KFM is based on the dynamic mode AFM, where the motion of the probe tip is simplified as a forced harmonic oscillator with an external complex nonlinear interaction force. In fact the motion of the tip with a effective mass m^* at a position z is described by the following equation.

Fig. 1. Schematic diagrams for typical implementation of the AM detection method and the FM detection method. (a) In the AM method, a lock-in amplifier is commonly used for detecting a change in amplitude. (b) In the FM method, a phase-locked loop circuit is often used for detecting the frequency shift.

$$m^* \ddot{z} + m^* \frac{\omega_0}{Q} \dot{z} + k(z - z_0) = F \cos \omega_d t + F_{ts}(z), \quad (1)$$

where ω_0 , k , and Q are the angular resonance frequency, the spring constant, and the mechanical Q -factor of the cantilever resonance, respectively. z_0 is the equilibrium position of the tip. $F \cos \omega_d t$ is the external oscillatory force given by the actuator. $F_{ts}(z)$ is the tip-sample interaction force as a function of z . The resonance frequency of the cantilever ($f_0 = \omega_0/2\pi$) is written as

$$f_0 = \frac{1}{2\pi} \sqrt{\frac{k}{m^*}}. \quad (2)$$

There are two basic working modes for the tip-sample distance regulation in dynamic mode AFM. One is amplitude modulation AFM (AM-AFM, often referred to as tapping mode AFM) using amplitude modulation (AM) detection, which usually works in the intermittent contact regime. The other is frequency modulation AFM (FM-AFM) using frequency modulation (FM) detection, which are mainly used in the noncontact regime. Both modes utilize a large change of the resonance frequency of the cantilever when the tip is brought in close proximity to the sample surface. In addition the average interaction/contact forces in typical imaging conditions of each mode are extremely small compared to the case of contact mode AFM and hence sample damages can be avoided.

In the AM detection the cantilever is vibrated at a fixed frequency near the resonance by an external piezoelectric actuator. The oscillation amplitude of the cantilever end is monitored with a displacement sensor such as an optical beam deflection sensor. The amplitude signal is obtained with a root-mean-square to direct current (RMS-to-DC) converter or a lock-in amplifier. Figure 1(a) shows an experimental setup for the AM detection method.

In the FM detection the cantilever is kept oscillated at its resonance frequency by a self-oscillation circuit and an FM detector (demodulator) are required. Figure 1(b) shows an experimental setup for the FM detection method. The self-oscillation circuit has two key components, a phase shifter and a variable gain amplifier (VGA). The phase shifter adjusts the signal phase such that the total phase inside the self-oscillation loop is kept at 2π . The VGA regulates the oscillation amplitude of the cantilever. In fact there are two amplitude regulation modes in the FM detection, constant excitation (CE) mode and constant amplitude (CA) mode. In CE mode, the excitation signal for the cantilever vibration is constant so that the actual oscillation amplitude of the cantilever may be changed depending on the dissipative interaction forces. On the other hand, in CA mode, the excitation signal is dynamically controlled to keep the cantilever oscillation amplitude constant. The control signal compensates the energy loss due to the dissipative forces so that the signal amplitude corresponds to the magnitude of the dissipation.

Table I. Electric force detection based on FM-AFM.

mode combination	tip-sample distance control	cantilever frequency	Electric force detection	modulation frequency	signal frequency spectrum
(1) FM-FM	FM	f_0	FM	$f_0 \pm f_m$
(2) FM-AM	FM	f_0	AM	$\sim f_{2nd}$ ($f_{2nd} = 6.3 \times f_0$)

3. Detection of local electric forces

Although the major task in EFM/KFM is the detection of electric forces, the regulation of the tip-sample distance is still required to avoid the topographic effects. Either AM detection or FM detection can be used for the electric force detection and for the tip-sample distance regulation. However, since EFM/KFM is often used in vacuum, the use of the FM detection (FM-AFM) is much more appropriate for the distance regulation than that of the AM detection (AM-AFM). The response time of the cantilever oscillation in AM-AFM is far too long (proportional to Q -factor). Thus, FM-AFM is used for the topographic measurement. Even in this case we can still use AM or FM for the electric force detection (See Table I: (1) FM-FM method, (2) FM-AM method).

When the modulation frequency of the electric force in FM-FM method is sufficiently low compared to the cantilever resonance frequency (fundamental working frequency in FM-AFM), meaning that modulation frequency f_m is located inside the FM detection bandwidth, electric force signal is detected as a modulated frequency shift of the resonance [4]. In other words we can expect a gain factor in the force detection sensitivity of f_0/B (B : measurement bandwidth) while the gain factor is unity in a simple modulation method. For example, the factor goes up to about 370 in a typical case with $f_0 = 300$ kHz, $B = 1$ kHz.

The difference in the spatial resolution in the electric force detection between FM and AM methods should be noted. The signal in FM-AFM (frequency shift) reflects the interaction force when the tip is positioned at the closest point to the sample surface. In contrast that in AM-AFM (change in amplitude) corresponds to the force when the tip is positioned at the middle point of the oscillation. Thus better spatial resolution can be obtained in FM-AFM.

4. Recent EFM topics and future prospects

One of characteristic features in EFM (also in KFM) is its high spatial resolution that can achieve the atomic/molecular scale. Since sub-molecular resolution imaging with a CO tip at a low temperature by FM-AFM was successfully demonstrated [5], molecular chemical “bonds” can be directly visualized. Furthermore, EFM/KFM based on this method was successfully applied to the visualization of the potential and the charge distribution inside a single molecule, Naphthalocyanine [6]. While high-spatial resolution imaging by FM-AFM is the present trend, EFM/KFM have also attracted much attention in practical applications including high-speed electric force measurement and potential/charge measurement in liquids.

4.1 High-speed electric force measurement

Since the probe tip is mechanically scanned over the sample surface in scanning probe methods, high-speed imaging/measurement has been always a big issue. There were several pioneering studies to detect high-speed physical and/or chemical phenomena even at the early stage of the EFM/KFM development. For example, high-frequency response in the GHz range was converted into the detectable frequency range using the heterodyne sampling by mixing 2 different frequencies [7, 8]. However, the technique of the tip-sample distance regulation at that time was not sufficiently developed and the

obtained resolution was relatively low.

Several studies have been recently made on time-resolved EFM/KFM. D.S. Ginger and co-workers developed time-resolved EFM based on a transient response analysis [9]. The time response to an impulse input was recorded at each point of the sample surface. The recorded response was mathematically analyzed as a complex analytical function in the post process and the fast response was finally reconstructed. L.M. Eng and co-workers applied the pump-probe method to the detection of time-resolved response (pump probe KFM), which utilizes a modified heterodyne sampling [10, 11]. In these methods the time response measurement at a single position is repeated at other different positions over the surface to be investigated so that the time-resolved response imaging having a high-spatial resolution is practically realized. Since the 3-dimensional force mapping method on an atomic scale has been well established, these novel techniques based on the point-by-point detection method are highly promising.

4.2 Potential/charge measurement in liquids

High-resolution in EFM/KFM imaging is essentially based on the detection of local electric field having a strong dependence on the tip-sample distance. In electrolyte solution electric double layers (EDL) are made on the entire surfaces of a probe tip and a cantilever. The electrical situation is extremely different from air and vacuum environments where a capacitance coupling is basically made only between the tip and the surface. The voltage modulation of the sample can induce charging and discharging of the EDL on the cantilever even when it is located far from the sample, resulting in the modulation of the mechanical stress on the cantilever. Thus large tip-sample distance dependence of electric field cannot be expected at all.

When the modulation frequency exceeds a characteristic frequency f_D corresponding to the reciprocal of a time constant determined by an EDL capacitance and a bulk solution resistance, EDL effect is decreased. When the frequency is further increased and exceeds another characteristic frequency f_c , tip-sample distance dependence of electric field is recovered, allowing us to detect the local electric field. However, f_c is usually an extremely high frequency in an electrolyte solution having a realistic ion concentration [12, 13].

Derivation of electric surface information by multifrequency measurement: As mentioned above, when the modulation frequency is not sufficiently high, the detection of local electric force is practically difficult. There are several novel approaches, the detection of the transient response (not stationary response) to the external modulation [14] and the detection of the harmonic response rather than a single frequency response [15]. In addition response signals having a wide bandwidth are recorded and analyzed (G-mode) [16].

EDL force detection: When a tip approaches a sample surface within a Debye screening length, two EDLs on both tip and sample surfaces are overlapped with each other causing an interaction force (EDL force). The EDL force is produced only in the region where the two EDLs are overlapped so that local interaction force can be detected [17]. Since the EDL force depends on several experimental parameters including a tip shape, a sample surface structure, and surface charges, measurement results do not simply correspond to the electric information. Nevertheless the method is most promising because it is relatively direct compared to the multifrequency measurements.

5. Summary

Fundamental concept of EFM/KFM was described based on the dynamic force microscopy in this article. The technique is actually categorized by the combination of the AM and FM detection modes, used for the tip-sample distance regulation and the electric force detection. The present trend and the future development of EFM/KEM were explained.

Although the scanning probe method is basically time-consuming, the recent, rapid progress in high-speed visualization of electric forces utilizing the point-by-point measurement is literally beyond all expectations. On the other hand, since EFM/KFM was originally thought to be naturally applied to the liquid environments, the present difficulty in the measurement seems much more serious.

Nevertheless, both new technical development and novel analysis idea are surely expected to be breaking the barrier.

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