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Molecular-scale Investigations of Organic Molecular Films by Dynamic Force Microscopy

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The application of non-contact atomic force microscopy (NC-AFM) to the molecular-scale investigations of organic molecular films is presented. Molecular arrangements of fullerene thin films on the Si(111)-7x7 reconstucted surface and self-assembled monolayers of alkanethiol molecules on Au(111) were successfully imaged. In addition, surface potential measurements of the fullerene films by NC-AFM revealed the local charge transfer from the Si danging bond to the adsorbed molecular layer.

Keywords: dynamic force microscopy, non-contact force microscopy, fullerene, alkanethiol, single molecular electronics

INTRODUCTION

The degree of miniaturization in microelectronics has been steadily increased these years. The feature size of the present device is already on a submicron-scale and the simple extrapolation gives the size of 50 nm in the year of 2011. Therefore, there have been growing interests in *single molecular electronics,* where each individual molecule can be an electronic/optical device as an independent functional unit. One of the remarkable features in organic molecules is that each molecule shows characteristic electrical and/or optical properties which are greatly sensitive to its molecular structure and conformation. This allows us to design a wide variety of functional devices.

However, direct access to a single molecule and measuring its properties are essential for establishing the molecular electronics. Developments of *scanning probe microscopy* (SPM) including *atomic force microscopy* (AFM) has brought a great advance in the molecular technology since even atoms or molecules can be imaged, manipulated and/or controlled by SPM[1-4]. In addition, local surface properties on an atomic or molecular scale can be investigated.

There were several studies demonstrating the possibility of imaging of organic materials on a molecular scale by atomic force microscopy (AFM) in contact mode, especially in liquid environment[5, 6]. However, one can often experience that the scanning process in contact mode modifies or damages organic samples most of which are formed by weak van der Waals interaction. It is essential to reduce the forces between a tip and a sample for molecular scale imaging of organic films. Recent progress in *dynamic force microscopy* (DFM) including *non-contact atomic force microscopy* (NC-AFM) has shown the possibility of its overcoming the difficulties[7]. It has already demonstrated a large number of successful results including atomically resolved images on semiconductor surfaces[8, 9]. However, only few results for the molecular resolution imaging of organic thin films have been reported so far[10, 11]. The applications of NC-AFM for a wide range of the samples are greatly important for the comprehensive understanding for the contrast mechanisms of NC-AFM.

In this paper the principle and some basics of DFM are first reviewed and then the applications of NC-AFM to organic molecular films are described. The samples investigated are fullerene (C_{60}) thin films on the Si(111)-7x7 reconstucted surface and self-assembled monolayers (SAMs) of alkanethiol molecules deposited on Au(111). Since both samples have been intensively studied by STM and well understood, they are suitable for NC-AFM applications as model samples. In addition, local surface potential measurements which can give novel information realted to molecular electric dipoles or charge transfer are described.

DYNAMIC FORCE MICROSCOPY

There have been a great progress in dynamic force microscopy where the cantilever is vibrated at its resonance frequency to detect the tip-surface interaction. In 1994 Giessible succeeded in imaging a Si(111) 7x7 reconstructed surface with true atomic resolution by DFM[7]. The result has generated a series of the following developments of dynamic mode. The principle of the method was actually proposed in the first memorial paper of AFM by Binnig et al.[2] and then Williams et al. reported the first

experimental data taken by dynamic mode in 1986[12]. However, it was impossible to image a sample with an atomic resolution by this method because the tip was vibrated in the range where the tip-to-sample distance was relatively far above the sample surface. It was mainly used for detction of long range interaction such as electrostatic or magnetic forces. Depending on the operating range of the tip, the present dynamic mode is classified into the following three categories.

(1) Dynamic contact mode
(2) Intermittent contact mode
(3) Non-contact mode (i) with repulsive force detection
(ii) with only attractive force detection

Each mode was separatedly developed depending on a different purpose. Dynamic contact is often known as the force modulation method which is used for measuring the surface viscoelastic properties. Intermittent contact mode often referred to as tapping mode was developed for reducing the damage to a sample. Our concern in this paper is the non-contact mode with repulsive force detection, which can give atomic or molecular resolution.

When the cantilever is brought in close proximity to a surface, the center frequency and the amplitude of the cantilever resonance are changed due to the tip-surface interaction. In the non-contact mode both quantities of the resonance are monitored by FM (frequency modulation) detection method[13], which is very suitable for the precise control of the tip. This is because the tip-surface interaction affects the resonance spectrum of the cantilever and consequently changes both quantities. In contrast, only amplitude is monitored in the intremittent contact mode.

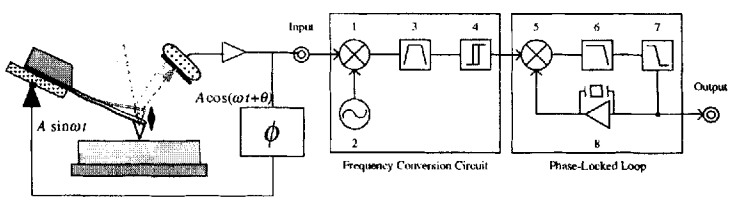


FIGURE 1 A schematic diagram of an FM detection setup.

Figure 1 shows a schematic diagram of an FM detection setup[14]. The cantilever is mechanically equivalent to a harmonic oscillator which is used as a resonator like a quartz crystal in the oscillation circuit so that the oscillation frequency of the circuit is determined by some external forces changing the mechanical characteristics of the cantilever resonator. The change in the oscillation frequency is detected by the following frequency detector which is a phase-locked loop circuit. The amplitude of the oscillation can be also monitored in this case, which gives the information of energy dissipation of the vibration.

When the cantilever with a spring constant of k is vibrated with an amplitude of A, the frequency shift (Δf) caused by a weak external perturbation potential V can be calculated using the Krilov-Bogoliubov-Mitropolsky method[15] or the Hamilton-Jacobi formalism[16], both of which give the same result as follows.

$$\Delta f = \frac{f_0}{2\pi k A^2}\int_0^{2\pi}\frac{\partial V(d + A\cos\psi)}{\partial z}\cos\psi d\psi$$

where f_0, z and d are the resonance frequency of the free cantilever, the instantaneous and the average height of the tip, respectively. The typical frequency shift from the free resonance is 10 - 100 Hz when the tip is close enough to interact with the surface. Frequency resolution is directly connected to the minimum detectable force in the experiment. In order to improve the frequency resolution especially for imaging the organic molecular films on a account of the reason discussed in the following chapter, we developed our own frequency detector where the minimum detectable frequency change is better tahn 10 mHz with a bandwidth of 1 kHz[14]. The detector is a PLL circuit including voltage controlled crystal oscillator (VCXO) of which frequency stability is extremely high.

AFM IMAGING OF ORGANIC MOLECULES

Organic molecular films often have large topographic structures of which scale is larger than the molecular size while atomically flat surfaces can be prepared for semicondutig materials such as Si. In fact, since the molecules with long alkyl chains are arranged with their axes perpendicular to the substrate surface due to van der Waals interaction

between the alkyl chains, the films of these molecules consist of some islands with the step height of a few molecular layers which can reach more than 10 nm. On the other hand the range of the repulsive force interaction between the tip and the surface is the order of 0.1 nm. In addition, the typical oscillation amplitude of the AFM tip is ranged between 1 nm and 10 nm. This variation of the scales perturbs the tip from tracking the surface strucures precisely.

For the application of NC-AFM to organic molecules we first used fullerene (C_{60}) thin films on the Si(111)-7x7 reconstucted surface and self-assembled monolayers (SAMs) of alkanethiol molecules deposited on Au(111)[17-19]. Fullerene molecules, which has the unique optical and electrical properties due to the characteristic electronic structures originating from the highly symmetrical molecular structures, have recently attracted much interest as an organic semiconductor material or non-linear optical material. On the other hand, alkanethiols, which are spontaneouly formed into well-ordered single molecular films on a Au(111) surface, have also gained much attention due to their self-organized structures. In addition, since the strong interaction between the gold atom and the thiol is related to not only anchoring of the molecule to the substrate but making good electronic junction, this sample can be a model system for the molecular electronics.

NC-AFM imaging was performed with a commercially available instrument (JEOL) using degenerately doped n-type Si cantilever of which spring constant and resonant frequency were typically 30 N/m and 280 kHz, respectively. A measured Q-factor of the resonance in vacuum environment was about 30,000. The cantilever was not specially cleaned but baked around 150 deg. for 12 hours before use. The amplitude of the cantilever oscillated by constant excitation mode was about 10 nmp-p. The typical frequency shift used was 10 - 30 Hz.

A Si(111) 7x7 reconstructed surface was prepared by heating up the substrate at 1200 deg. and imaged by NC-AFM before the deposition of C_{60} molecules. After a small amount of C_{60} molecules were deposited, single C_{60} molecules with the background of the Si 7x7 structure were imaged. However, it was much more difficult to obtain stable images compared to the case of STM. The instability might come from a large

difference in the tip-surface interaction between the molecule and the Si substrate, which makes the feedback operation unstable. In contrast, when the entire substrate was covered with the molecules, individual molecules were stably imaged. This is probably because the interaction was basically uniform over the scanning area in this case.

When the amount of molecules corresponding to three molecular layers covering the Si substrate were deposited, a large number of the small crystalline islands were formed. The island surface was composed of flat terraces so that the AFM imaging was stably performed. The crystalline structure consisting of hexagonally packed molecules were stably obtained as shown in fig. 2 (a) and (b). The observed lattice constant was about 1 nm, which corresponds to the van der Waals radius of the molecule.

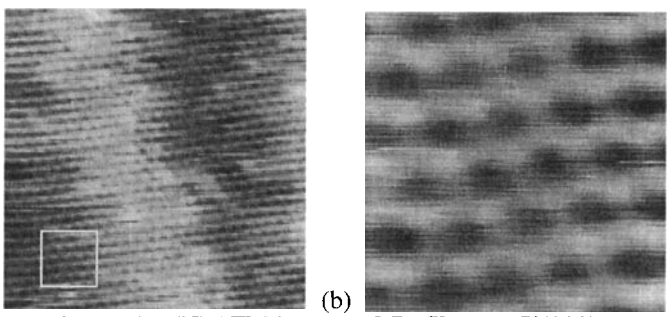
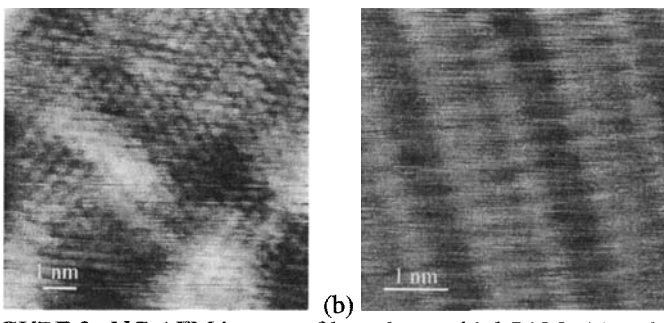


FIGURE 2 NC-AFM images of C_{60} films on Si(111)
Scan area: 30 nm x 30 nm (a), 6 nm x 6 nm (b), Δf =200 Hz

Alkanethiol molecules are spontaneously arranged on a Au substrate and formed into SAMs. The highly ordered structures have attracted a wide variety of interests and have been investigated using various method including STM. We imaged SAMs by non-contact AFM in ultrahigh vacuum environment. SAMs were deposited onto a Au(111) substrate by dipping it in ethanol solution of alkanethiol. Then the smple was baked for 1 hour at 70 deg. in vacuum. Figure 3(a) shows NC-AFM images of hexadecanethiol ($CH_3(CH_3)_{15}SH$) SAMs. We can see hexagonally packed structures with the periodicity of about 0.5 nm, which is consistent with the lattice constant of the $\sqrt{3}$ x$\sqrt{3}$ surface strucure on Au(111). Actually STM imaging of this film is very difficult

because the tunneling current is heavily reduced owing to the non-conductive film thickness of about 1.6 nm.

Another example is shown in fig. 3 (b). The sample is octanethiol ($CH_3(CH_3)_7SH$) SAMs which were annealed for several hours. We can see the stripe structures with the spacing of about 2 nm. Furthermore, each stripe itself consists of the periodic structures with the spacing of 0.5 nm, which agrees well with the width of the molecule. Thus the molecules are arranged with their axes parallel to the substrate in this case due to the long thermal annealing which accidentally made the film in the low-density phase.



(a) (b)

FIGURE 3 NC-AFM images of hexadecanethiol SAMs (a) and octanethiol SAMs (b) on Au(111), Δf =70 Hz

SURFACE POTENTIAL MEASUREMENTS

Since surface potential of organic molecular films is caused by either porlarization of the film originating from the dipole moment of the molecules or the charge transfer as shown in fig 4, the local potential variation is directly related to the electronic structures in the films.

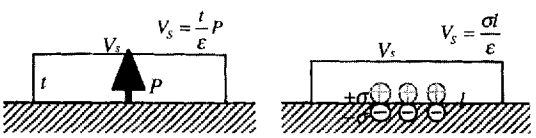


FIGURE 4 Surface potential caused by molecular dipoles (a) and charge transfer at the interface (b).

Surface potential is measured by Kelvin probe force microscopy (KFM) where the electrostatic force between the tip and the sample is detected while a DC bias is added with a modulating AC bias to the sample. The potential of the sample is the sum of the sample surface potential (Vs) and two externally applied potentials, V_{DC} and modulating V_{AC} modualated at a frequency ω. When the tip-to-sample distance and the capacitance between the tip and the sample is z and C, respectively, the elrctrostatic force (F_{el}) is expressed as follows.

$$F_{el} = \frac{1}{2}\frac{\partial C}{\partial z}\left(V_S + V_{DC} + V_{AC}\cos\omega t\right)^2$$
$$= \frac{1}{2}\frac{\partial C}{\partial z}\left[\left(V_S + V_{DC}\right)^2 + 2\left(V_S + V_{DC}\right)V_{AC}\cos\omega t + V_{AC}^2\cos^2\omega t\right]$$

Since the electrostatic force is proportional to the square of the potential, the response includes three frequency terms of DC, ω and 2ω. Surface potetial can be measured when V_{DC} is adjusted such that the ω term can be cancelled out. In non-contact mode, forces are detected as the frequency shift of the resonance by FM detection. Thus, the modulation of the electrostatic force causes the frequency modulation in this case.

Fullerene molecules are fixed on the reconstructed Si(111) surface due to the strong interaction between the molecule and the dangling bond of Si. Since the interaction causes the charge transfer at the interface, the electronic state of the adsorbed molecule is greatly affected. Electric double layer at the interface which probably caused by the charge transfer was invesitigated by KFM. The modulation voltage and frequency were 2Vp-p and 2 kHz, respectively.

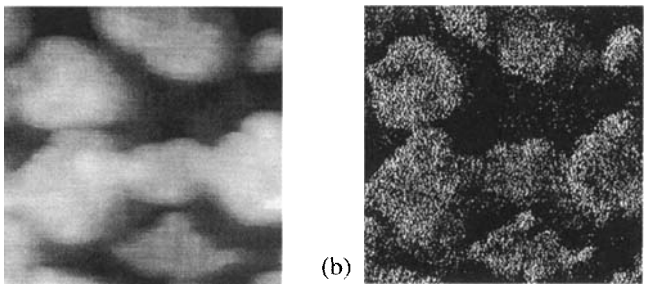


FIGURE 5 NC-AFM image (a) and surface potential image (b) of C_{60} crystalline islands taken simultaneously. Scan area: 200 nm x 200 nm.

Figure 5 shows an AFM image of the C_{60} crystalline islands while the surface potential image taken simultaneously was shown in Fig. 5 (b). The image consists of two regions between which the potential difference was about 20 mV. The difference can be expalined by some charge transfer from the Si dangling bonds to the C_{60} molecular films. A schematic of an energy diagramof the adsorbed C_{60} molecule on Si is ahown in fig. 6. When the charge was transferred from a Si dangling bond to a C_{60} molecule, the LUMO level of the molecule in the first layer above the Si substrate is shifted to the Fermi level the Si(111) surface. On the other hand, since the molecules in the second or higher layers are not likely to have the charge transfer, the surface potentials of these islands are different from the first layer.

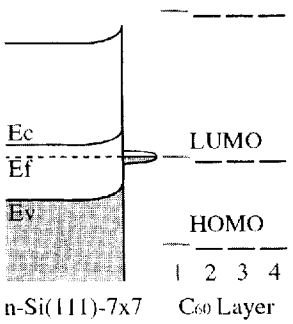


FIGURE 6 Schematic of a band diagram of adsorbed C_{60} molecular layers on the Si(111) 7 x7 surface.

CONCLUSIONS

We described the molecular-scale investigations of organic molecular films by NC-AFM. The model samples investigated were C_{60} thin films on the Si(111)-7x7 reconstucted surface and self-assembled monolayers (SAMs) of alkanethiol molecules deposited on Au(111). The results shows that NC-AFM is a powerful tool for investigating organic molecular films on a molecular scale in terms of not only structural analysis but also measurements of local surface properties. In fact we measured the local surface potentials of the fullerene films on Si. The result indicated the local charge transfer from the Si danging bond to the

first molecular layer.

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