Dynamic Friction of Nanoscale Sliding on a C₆₀ Deposited Film*

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We measured the frictional behavior acting on C₆₀ films at a small normal load as a function of oscillation amplitude using a MHz-range quartz crystal resonator and an optical AFM cantilever. The frictional behavior for C₆₀ films varies by the amplitude: For the amplitudes smaller than the C-C bond length of the C₆₀ molecule, the dynamic frictional force is directly proportional to the amplitude, while it becomes almost constant for larger amplitudes. Although the observation is in qualitatively the same manner as HOPG, the dynamic frictional force for small amplitudes is significantly larger than that of HOPG. This difference suggests that C₆₀ molecules easily tilt and/or rotate when the tip slides in C₆₀ films, and the dynamic friction arises from the tilting and/or rotating motion. [DOI: 10.1380/ejsnt.2015.135]

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I. INTRODUCTION

Sliding friction is an old problem which has been studied over many years. In macroscopic bodies, the friction is controlled by various ways, i.e., liquid and solid lubrication, etc. In nano- or microscale systems, the friction becomes more important because of their large surface-to-volume ratio, and its control is currently a crucial issue [1, 2].

In 1987, Mate *et al.* opened a new door to the study of nanoscale friction [3]. They first observed atomic-scale features on the frictional force acting on a tungsten wire tip sliding on a graphite surface. After this observation, so many AFM experiments for nanoscale friction were carried out. In 2004, Socoliuc *et al.* measured the nanoscale friction between a Si tip and a NaCl surface [4]. When the normal load is lowered to 3.3 nN, the dissipated energy decreases. For the normal load below a certain threshold, the dissipation disappears within their sensitivity.

On the other hand, in 2003 Miura *et al.* carried out AFM experiments for C₆₀ monolayer films on a graphite surface using a graphite flake tip [5]. They found that the frictional force is significantly small below the normal load of 100 nN. From this observation, they concluded that C₆₀ molecules behave as a molecular-bearing.

Recently, we have developed a new apparatus which combines a MHz-range quartz crystal resonator with a self-detective AFM cantilever. We have reported the dynamic frictional force acting on C₆₀ films and highly oriented pyrolytic graphite (HOPG) in 100 nN range of the normal load as a function of the oscillation amplitude [6]. It was found that the frictional behavior varies by the amplitude: For amplitudes smaller than the period of the substrate, the frictional force is proportional to the amplitude. For larger amplitudes, it does not depend on the amplitude. This behavior can be qualitatively understood

by a simple one-dimensional (1D) Tomlinson model. In the previous experiments, it should be noted that the period of C₆₀ films is about 1 nm, which is much the same as the molecular size.

To measure the dynamic frictional force at a small normal load, we combined a MHz-range quartz crystal resonator with an *optical* AFM cantilever. In this paper, we report the frictional behavior acting on C₆₀ deposited films on an atomically flat Au surface, and compared it with that of HOPG.

II. EXPERIMENT

We prepared monolayer and 5 layer C₆₀ films by thermal deposition on an atomically flat Au surface on a 5 MHz AT-cut quartz crystal resonator. To prepare the Au surface, we used the transferring process from an Au film on mica [7]. First, an Au film with the diameter of 1 mm was sputtered on a thin single-crystalline mica sheet by 150 nm at 300°C. The Au-plated mica sheet was pressed at 1.6×10^6 Pa in vacuum, and was heated for 3 h at 300°C. The Au film was transferred to the electrode of the resonator. The surface roughness of the Au surface, R_a , was smaller than 0.25 nm in arithmetic average roughness in the range of 100 nm × 100 nm. After preparing the Au surface, C₆₀ films were deposited on the resonator at the deposition rate of 0.05 ML/s in an ultra-high vacuum of 10^{-6} Pa. The distance between the resonator and the C₆₀ source was about 6 cm, and the temperature of the C₆₀ source was about 360°C. After deposition, the resonator was heated for 80 min at 150°C to smoothen the C₆₀ film. The Q value of the resonator remained larger than 10^4 .

For comparison, the HOPG substrate was prepared to past a HOPG fake of 1 mm × 1 mm × 5 μm on the resonator by vanish. After heating for 1 h at 130°C, the fake was cleaved to prepare a clean surface.

To measure the frictional behavior by changing the sliding distance at a small normal load, we combined an optical AFM cantilever with the resonator, as shown in Fig. 1. The resonator was mounted on a piezo-scanner

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FIG. 1. Schematic diagram of the present apparatus. An optical AFM cantilever was combined with an AT-cut quartz crystal resonator.

base and was set facing as the AFM cantilever. The normal load acting the tip was measured by a quadrant photodiode. In the present experiments, the AFM cantilever (RC800PSA, Olympus) with a spring constant of 0.1 N/m was used, and the typical radius of the tip was 15 nm.

The energy dissipation of friction and the effective spring constant of contact are connected to the changes in Q factor and resonance frequency as

$$\Delta\left(\frac{1}{Q}\right) = \frac{\Delta E}{2\pi E}, \quad \frac{\Delta f_R}{f_R} = \frac{1}{\omega_R^2 M_C} \cdot \kappa, \quad (1)$$

where ΔE is the energy dissipated per cycle, E is the energy stored in the system, M_C is the mass of the oscillating area and κ is the effective spring constant.

The resonator was placed in a transmission circuit, in which a 50 Ω cw signal generator and an rf lock-in amplifier were connected in series. The signal transmitted through the resonator was detected by the lock-in amplifier, and the frequency of the signal generator was controlled in order to keep the inphase signal zero. The frequency was then locked to the resonance frequency. The quadrature signal at this frequency was the resonance amplitude, and this decrease was converted to the decrease in Q factor. The sliding distance corresponded to the oscillation amplitude of the resonator, and was controlled by the output signal of the signal generator.

III. RESULTS AND DISCUSSION

We measured the resonance frequency and Q factor for C_{60} films and the HOPG substrate while advancing and retracting the tip under the condition of constant oscillation amplitudes. Figure 2 shows typical data of the variation of the normal load N , the frequency shift $\Delta f_R/f_R$, and the change in Q factor $\Delta(1/Q)$ for the 5 layer C_{60} film as a function of piezo travel. These set of data were taken when the tip was advancing. When the tip was in contact with the C_{60} film, $\Delta f_R/f_R$ and $\Delta(1/Q)$ increased rapidly. It was found that the increase depends on the amplitude. As the amplitude increased, $\Delta f_R/f_R$ decreased monotonously. In contrast, $\Delta(1/Q)$ took the maximum

FIG. 2. Variation of (a) the normal load N , (b) the frequency shift $\Delta f_R/f_R$ and (c) the change in Q factor $\Delta(1/Q)$ for the 5 layer C_{60} film. These set of data were taken when the tip was advancing. Different colors correspond to different oscillation amplitudes of the resonator, and figures in (b) are the amplitude. The data in (b) and (c) are shifted vertically.

value at a certain amplitude. For the monolayer C_{60} film and the HOPG substrate, the similar behavior was observed.

Figures 3 and 4 show $\Delta f_R/f_R$ and $\Delta(1/Q)$ for C_{60} films and the HOPG substrate at the normal load of 5 nN as a function of amplitude. The observed behavior is qualitatively the same in three samples: $\Delta f_R/f_R$ and $\Delta(1/Q)$ remained constant at small amplitudes. As the amplitude increased, $\Delta f_R/f_R$ started to decrease gradually and $\Delta(1/Q)$ took the maximum at a certain amplitude. $\Delta(1/Q)$ is converted by Eq. (1) and the amplitude to the energy dissipation per unit distance, i.e., the average dynamical frictional force. Figure 5 shows this force as a function of amplitude. For small amplitudes, the force of three samples is directly proportional to amplitude, and the transition occurs around 0.2 nm. Then, it becomes almost constant at large amplitudes.

The observed behavior can be understood qualitatively as follows: For small amplitudes, the energy dissipation is decreased because the tip is trapped in the periodic potential of the substrate. In contrast, the tip overcomes the potential for large amplitudes and a rapid sliding motion causes a large energy dissipation. In this case, the energy dissipation is roughly proportional to the sliding distance, i.e., the average dynamical frictional force does not depend on amplitude.

In the previous experiments, which were carried out at a large normal load of 400 nN, the maximum in $\Delta(1/Q)$ for C_{60} films occurs at about 1 nm, while for the HOPG substrate at about 0.2 nm. From this observation, we have concluded that the maximum in $\Delta(1/Q)$ is related to the period of the corrugation potential. In contrast, in the present experiments, the amplitude at the maximum

FIG. 3. Oscillation amplitude dependence of $\Delta f_R/f_R$ and $\Delta(1/Q)$ for C_{60} films at the normal load of 5 nN. The solid lines are calculated numerically from Eq. (2).

value of $\Delta(1/Q)$ for C_{60} films is close to that of the HOPG substrate although the maximum of C_{60} films is gentle. This amplitude is about 0.2 nm, which is close to the C-C bond lengths in C_{60} molecules. Thus, it is concluded that the tip only feels the topmost part of C_{60} molecules and follows the corrugation potential of intramolecular bonds at a small normal load.

In addition, it should be noted that $\Delta(1/Q)$ for C_{60} films is significantly larger at small amplitudes than that of the HOPG substrate, although the maximum value is much the same. This means that C_{60} films have an additional energy dissipation mechanism at small amplitudes, and one of the possibilities is the tilting and/or rotational motions of C_{60} molecules.

Here, we make a comment on rotational C_{60} dynamics. It is well known that the C_{60} molecule executes continuous rotation in solid C_{60} above the phase transition of around 260 K [8, 9]. In addition, Wang and Cheng calculated the rotational barriers on Au and Ag surfaces, and found that they are small enough that the C_{60} molecule can rotate freely at room temperature [10]. As mentioned above, it was found that the tip follows the corrugation potential of intramolecular bonds. This means that the tip freezes a quasi-free rotation of C_{60} molecules even at a small normal load of 5 nN.

Next, we compare the observed behavior with the calculation of a simple 1D Tomlinson model [11]. Here, the substrate is replaced with a sinusoidal potential, and the tip with a point mass with a spring. The equation motion

FIG. 4. Oscillation amplitude dependence of $\Delta f_R/f_R$ and $\Delta(1/Q)$ for the HOPG substrate at the normal load of 5 nN. The solid lines are calculated numerically from Eq. (2).

TABLE I. The fitted parameters of the 1D Tomlinson model.

	monolayer C_{60}	5 layer C_{60}	HOPG
m/kg	1.9×10^{-14}	2.5×10^{-14}	3.1×10^{-14}
U_0/J	4.4×10^{-19}	1.1×10^{-18}	4.1×10^{-17}
a/m	2.5×10^{-10}	2.5×10^{-10}	2.5×10^{-10}
k/Nm^{-1}	7.6×10^2	1.2×10^3	1.2×10^3
η/Nsm^{-1}	9.1×10^{-7}	1.5×10^{-6}	1.4×10^{-6}
$H = \frac{2\pi^2 U_0}{K a^2}$	0.18	0.30	1.1

is expressed as

$$m \frac{d^2 x}{dt^2} = -kx - \eta \left(\frac{dx}{dt} - \frac{dX(t)}{dt} \right) - \frac{2\pi}{a} U_0 \sin \left\{ \frac{2\pi}{a} (x - X(t)) \right\}, \quad (2)$$

where the first term on the right-hand side is the restoring force, the second one is the viscous force, and the third one is the force from the effective corrugation potential. In calculation, the periodicity of the sinusoidal potential is chosen to be $a = 0.25$ nm of the lattice constant of graphite.

The calculated curves are shown in Figs. 3-5, and the fitted parameters are tabulated in Table I. It was found that $\Delta(1/Q)$ in the calculation takes the maximum value at a certain amplitude, and decreases gradually above this amplitude. On the other hand, $\Delta f_R/f_R$ decreases above this amplitude. In addition, it oscillates vigorously at a large amplitude. The oscillation is caused by enhancement of high-harmonic generation because of the point mass model. On the whole, however, the calculated curves

FIG. 5. Oscillation amplitude dependence of the *average* frictional force for C₆₀ films and the HOPG substrate at the normal load of 5 nN. For the HOPG substrate, the set of data is shifted by multiplying by 30. The solid lines are calculated numerically from Eq. (2).

well explain the amplitude dependence.

Here, we note the stick-slip condition in steady motion, $H = 2\pi^2 U_0 / (Ka^2) > 1$. In Table I, H calculated from

the fitted parameters tabulated. It was found that H for C₆₀ films is obviously smaller than unity, while H for HOPG satisfies the stick-slip condition. This may be interpreted as the decrease in U_0 caused by the tilting and/or rotational motions of C₆₀ molecule. The interpretation is consistent with the existence of an additional energy dissipation mechanism at small amplitudes.

IV. CONCLUSION

We measured the dynamic frictional force acting on C₆₀ films on an atomically flat Au substrate as a function of amplitude using a MHz-range quartz crystal resonator and an optical AFM cantilever, and compared it with HOPG. Although the frictional behavior for C₆₀ films depends on the amplitude in the same manner as that of HOPG, the dynamic frictional force at small amplitudes is significantly larger than that of HOPG. In addition, from the fitted parameters of the 1D Tomlinson model, the stick-slip condition in steady motion does not satisfy. These suggest that the C₆₀ molecule easily starts the tilting and/or rotational motions caused by sliding of the tip.

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- [1] B. N. J. Persson, *Sliding Friction* (Springer, Berlin, 1998).
 - [2] M. Mate, *Tribology on the Small Scale* (Oxford, New York, 2008).
 - [3] C. M. Mate, G. M. McClell, R. Erlandsson, and S. Chiang, Phys. Rev. Lett. **59**, 9 (1987).
 - [4] A. Socoliuc, R. Bennewitz, E. Gnecco, and E. Meyer, Phys. Rev. Lett. **92**, 134301 (2004).
 - [5] K. Miura, S. Kamiya, and N. Sasaki, Phys. Rev. Lett. **90**, 0555091 (2003).
 - [6] D. Inoue, S. Machida, J. Taniguchi, M. Suzuki, M. Ishikawa, and K. Miura, Phys. Rev. B **86**, 115411 (2012).
 - [7] S. Yoshida, T. Ono, and M. Esashi, e-J. Surf. Sci. Nanotech. **6**, 202 (2008).
 - [8] R. Tycko, G. Dabbagh, M. Fleming, R. C. Haddon, A. V. Makhija, and S. M. Zahurak, Phys. Rev. Lett. **67**, 1886 (1991).
 - [9] R. D. Johnson, C. S. Yannoni, H. C. Dorn, J. R. Salem, and D. S. Bethune, Science **255**, 1235 (1992).
 - [10] L. Wang and H. Cheng, Phys. Rev. B **69**, 165417 (2004).
 - [11] G. A. Tomlinson, Philos. Mag. **7**, 905 (1929).