Dynamic Friction of Nano-Sliding between Graphite*

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We measured the dynamic friction of nano-sliding between graphite surfaces using a new apparatus. This apparatus enables us to obtain the frictional force of nano-sliding down to a sub-atomic distance. For large sliding distances above 0.68 nm, it was found that the frictional force, *i.e.*, the energy dissipation per distance, is constant. In contrast, for small sliding distances below 0.68 nm, this force was proportional to distance. From these observations, we can conclude that the mechanism of dynamic friction undergoes a drastic change when the sliding distance becomes smaller than the lattice constant. [DOI: 10.1380/ejssnt.2012.100]

Keywords: Quartz crystal microbalance; Atomic force microscopy; Friction; Graphite

I. INTRODUCTION

Physical property of small contacting asperities is a subject of study attracting the interest of many researchers because of the importance to macroscopic and microscopic applications.

In 1987, Mate *et al.* first observed atomic-scale features on the frictional force acting on a tungsten wire tip sliding on a graphite surface [1]. Its friction loops shows an atomic-scale stick-slip behavior during sliding. It was found that the frictional force is proportional to normal load with a small friction coefficient $\mu = 0.012$. And they also obtained an atomic friction map of graphite. The applied normal load is in the range of tens of μN , and the observed pattern is not honeycomb but rhombic. In 1997, Schwarz *et al.* studied the load dependence of the frictional behavior of carbon compounds (graphite, diamond, amorphous carbon, and C_{60}) using the atomic force microscope (AFM) [2]. For diamond, amorphous carbon, and C_{60} , the frictional force are proportional to two-third power of normal load. Assuming a Hertzian-type tip/sample contact, it was concluded that this force is proportional to contact area. On the other hand, for graphite, this force does not depend strongly on normal load. Furthermore, Zwöner *et al.* measured the velocity dependence over a wide range of sliding velocities from nm/s to $\mu\text{m/s}$ and reported the dependence for these compounds is very small [3].

Miura *et al.* measured an atomic friction map of a silicon nitride (Si_3N_4) tip and a graphite flake tip sliding on a graphite surface [4]. For the Si_3N_4 tip, the map shows a honeycomb-like pattern whose repetition period is about 0.2 nm. However, as the normal load increases up to 0.012 nN, this pattern vanishes and only the straight pattern parallel to the scan direction appears. For the graphite flake tip, the rhombic pattern are observed and its repetition has a period of about 0.5 nm. It was concluded that the graphite flake undergoes the zigzag mo-

tion and rotates around the pivot point.

The AFM is a powerful tool to investigate the frictional behavior at small contacting asperities. It is also recognized that a probe tip-quartz crystal microbalance (QCM) has large potential as a sensitive probe of the physical properties for the asperities [5].

In 1999, Laschitsch and Johnmann studied by approaching a small sphere to a quartz surface for friction measurements and reported a positive frequency shift and a decrease in the Q factor [6]. They explained these observations by the emanation of a spherical sound wave from the point of contact into the sphere. In addition, they also reported an additional decrease in the Q factor for high-friction interfaces of a metal-metal contact which may be attributed to frictional processes in the contact area. In succession, Borovsky and Krim measured nanomechanical properties using a depth-sensing nanoindenter probe and a QCM [7].

Recently, we have developed an AFM combined with an AT-cut quartz resonator. In this proceedings, we report the dynamic friction of nano-sliding at an small contacting asperity of graphite surfaces.

II. EXPERIMENTAL

We used a Si_3N_4 self-detective micro cantilever (NPX1CTP003, SII) of a spring constant of 2.2 N/m, as a force sensor. The typical radius of the probe-tip is 20 nm. The sensor connects with the DC bridge circuit applied 1.0 V as bias voltage. Then we can easily measured the normal load less than 0.2 nN. We prepared the graphite flake tip by attaching a highly oriented pyrolytic graphite (HOPG) flake of $0.25\text{ mm}^2 \times 5\text{ }\mu\text{m}$ onto the cantilever with epoxy resin. An AT-cut quartz crystal with a fundamental resonance frequency of 3.26 MHz (SMD-49, Daishinku Corporation) was used as the resonator. To prepare a graphite substrate on the resonator, HOPG substrate of $1\text{ mm}^2 \times 5\text{ }\mu\text{m}$ was pasted with varnish. After heating at 130°C for 1 h, the substrate was cleaved to prepare a clean surface. The Q factor of the resonator with the HOPG substrate remained higher than 2×10^4 in air. The accuracy is better than 0.05 Hz for the resonance frequency and 0.05% for the resonance amplitude, respectively.

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FIG. 1: Schematic diagram of an AFM-QCM combined apparatus.

The decrease in Q factor due to the contact is connected to the energy dissipation, while the change in resonance frequency to the *effective* spring constant, as follows,

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

where ΔE is the energy dissipated per cycle, E is the energy stored in the system, $\Delta f_R/f_R$ is the changing ratio of the resonance frequency, $\omega_R = 2\pi f_R$ is the angular frequency, M_C is the mass of the quartz crystal resonator, and κ is the *effective* spring constant [7]. The resonator was placed in a transmission circuit, in which a 50 Ω cw signal generator and a RF lock-in amplifier were connected in series. The transmitted signal through the resonator was detected by the lock-in amplifier, and the frequency of the signal generator was controlled in order to keep the in-phase 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. On the other hand, the sliding distance corresponded to the oscillation amplitude of the resonator, and was controlled by the output signal of the signal generator.

We measured the resonance frequency and Q factor during proceeding and retracting the tip under the condition when the resonator oscillates in a constant oscillating amplitude. In the experiments, the oscillating amplitude was controlled in the range of 0.02–2 nm, which corresponds to the maximum substrate velocity of 0.4–40 mm/s. The experiments were conducted in at atmospheric pressure with less than 40% relative humidity.

III. RESULTS AND DISCUSSION

Figures 2 (a)–(c) shows the variation of the normal load, N , the frequency shift, $\Delta f_R/f_R$, and the energy dissipation, $\Delta(1/Q)$ under the condition of various oscillation amplitudes. These sets of data were taken when the tip was proceeding at 6 nm/s. When the tip proceeded, a clear jump-in was observed at the contact and N increased almost linearly. At the jump-in, both $\Delta f_R/f_R$ and $\Delta(1/Q)$ increased rapidly. As N increased, both $\Delta f_R/f_R$ and $\Delta(1/Q)$ increased gradually. In the present measurements, the crystal orientation of HOPG substrate at the contact area was not determined. We observed, however, qualitatively the same behavior as different positions and substrates.

FIG. 2: Variation of (a) the normal load, N , (b) the frequency shift, $\Delta f_R/f_R$, and (c) the energy dissipation, $\Delta(1/Q)$ for a graphite flake tip on a graphite surface. These sets of data were taken when the tip was proceeding, and the horizontal axis is the z -position of the stage. Different colors correspond to different oscillation amplitudes. (d) $\Delta f_R/f_R$ and $\Delta(1/Q)$ of an oscillation amplitude of 0.11 nm as a function of normal load. The solid lines proportional to the contact area of the JKR model is well fitted above 200 nN.

In Fig. 2 (d), $\Delta f_R/f_R$ and $\Delta(1/Q)$ for an oscillation amplitude of 0.11 nm are plotted as a function of N during proceeding the tip. According to the Johnson-Kendall-Roberts (JKR) model, the contact area for a sphere-on-plane situation is expressed as

$$S = \pi \left\{ \frac{3R}{4E^*} \left(N + 3\pi\gamma R + \sqrt{6\pi\gamma RN + (3\pi\gamma R)^2} \right) \right\}^{2/3}, \quad (2)$$

where R is the radius of sphere, E^* is the effective Young's modulus [9], and γ is the surface tension of sphere and plane. Two calculated curves in the figure are proportional to S . It was found that both $\Delta f_R/f_R$ and $\Delta(1/Q)$

FIG. 3: Oscillation amplitude dependence of (a) $\Delta f_R/f_R$, (b) $\Delta(1/Q)$, and (c) the frictional force at normal loads of 200 nN (diamonds) and 1000 nN (circles).

are well fitted by the two curves above about 200 nN. This strongly suggests that the energy dissipation and the *effective* spring constant due to the contact of a graphite flake tip on a graphite surface are proportional to the contact area. Here, when we adopt $\gamma = 70 \text{ mJ/m}^2$ [8], $R = 430 \text{ nm}$ and $S = 3.5 \times 10^{-15} \text{ m}^2$ for 1000 nN.

Figures 3 (a) and (b) show $\Delta f_R/f_R$ and $\Delta(1/Q)$ for the graphite flake tip as a function of oscillation amplitude for normal loads of 200 and 1000 nN. For both normal loads, $\Delta f_R/f_R$ and $\Delta(1/Q)$ show a similar oscillation amplitude dependence, although their magnitude is different slightly. In the normal load of 200 nN, $\Delta f_R/f_R$ remained constant at 0.21 ppm up to 0.11 nm, and then it decreased gradually with increasing amplitude. On the other hand, $\Delta(1/Q)$ remained constant at 0.23 ppm up to 0.33 nm, and decreased with increasing amplitude. The decrease in Q factor is connected to the energy dissipated per cycle as Eq. (1). Figure 3 (c) shows the oscillation amplitude dependence of the energy dissipation per unit distance, *i.e.*, the dynamical frictional force [10]. It was found that the dynamical frictional force between interfaces is proportional to the lateral oscillation when its amplitude is adequate smaller than the lattice constant (viscous friction). In contrast, when its amplitude is larger than the lattice constant, the force does not depend on it (Coulomb friction). This feature can be explained as follows: For a small amplitude, the deformation of contact interfaces is in proportion to amplitude, and it is expected the energy dissipation per unit time is proportion to deformation. On the other hand, it is reasonable that the *average* dynamical frictional force is constant for a large amplitude even if an instantaneous lateral force has the periodicity of lattice. Thus, it is concluded that an atomic slip-to-stick transition is observed when the lateral oscillation exceeds the lattice constant.

IV. CONCLUSION

In conclusion, we have measured the dynamical frictional force of a nanoscale contact as a function of sliding distance by using the quartz crystal microbalance technique. A graphite flake tip was slid on an oscillating graphite substrate. It was observed that an atomic slip-to-stick transition occurs when the amplitude exceeds the lattice constant.

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- [9] The effective Young's modulus is expressed as

$$\frac{1}{E^*} = \frac{1 - \nu_1^2}{E_1} + \frac{1 - \nu_2^2}{E_2},$$

where E_1 and E_2 are the Young's moduli, and ν_1 and ν_2 are the Poisson's number of sphere and plane, respectively.

- [10] The *average* dynamical frictional force is calculated from the energy dissipation per cycle divided by the sliding distance as

$$F = \frac{\pi E}{2A_u} \Delta \left(\frac{1}{Q} \right),$$

where A_u is the oscillation amplitude.