Sliding friction of Kr films adsorbed on graphite substrate

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Abstract. We have carried out a quartz crystal microbalance experiment of Kr films adsorbed on exfoliated single crystalline graphite. The graphite enables us to study the direction dependence of the sliding friction because it remains the crystal orientation after exfoliating. In the present experiment, the oscillation of the crystal is inclined at about 30° to the a-axis of graphite. It was found that the resonance frequency does not decrease until the commensurate phase and decreases rapidly at this phase.

1. Introduction

Sliding friction of physisorbed films is an interesting topic of nanotribology. Krim and co-workers developed the quartz crystal microbalance (QCM) technique, and measured the sliding friction of various films adsorbed on metal substrates.[1][2] For Kr monolayer films adsorbed on Au (Kr/Au), they reported that the friction of the fluid film is larger than that of the incommensurate one.[3] On the other hand, Mistura and co-workers revealed the structural pinning of Ne monolayer films adsorbed on Pb: Ne film was nearly locked to the oscillating substrate in the low coverage region, while it slides in the incommensurate phase.[4]

Regarding the sliding friction between single crystals on a nanoscale, the direction dependence is a subject of study attracting the interest. Hirano et al. measured the frictional force of muscovite mica as a function of lattice misfit angle between contacting lattices. They found that the frictional force increases when the contacting surfaces approach being commensurate.[5]

These results indicate that the sliding friction is strongly affected by the commensurability between the contacting lattices. It is therefore of great importance to reveal whether the sliding friction of physisorbed films depends on the sliding direction in various phases. Thus motivated, we have started a QCM experiment of Kr films adsorbed on single crystalline graphite. The graphite enables us to study the direction dependence of the sliding friction because it remains the crystal orientation after exfoliating. In the present experiment, the graphite was bonded thermally using a new technique developed by Hosomi et al.,[6] and the oscillation of the crystal is inclined at about 30° to the a-axis of graphite.
2. Experimental

The sliding friction of Kr monolayer films was measured by the QCM technique, and obtained from the changes in the frequency and Q value of the quartz crystal. When the friction is proportional to the sliding velocity $v$, as $F = -(\sigma/\tau) \cdot v$, where $\sigma$ is the areal mass density of the film, these changes are related to the slip time $\tau$ as

$$\frac{\Delta f}{f_R} = -\frac{\sigma}{M} \frac{1}{1 + (\omega \tau)^2} \quad (1)$$

$$\Delta(\frac{1}{Q}) = \frac{2\sigma}{M} \frac{\omega \tau}{1 + (\omega \tau)^2} \quad (2)$$

where $M$ is the areal mass density of the crystal and $\omega$ is the angular frequency of oscillation. As the friction decreases, i.e., $\omega \tau$ increases, the film undergoes decoupling from the oscillating substrate and the resonance frequency increases.

The resonance frequency and $Q$ value were measured using a transmission circuit. In the circuit, the quartz crystal was placed in series with a coaxial line connecting to a 50 $\Omega$ cw signal generator and a RF lock-in-amplifier. The frequency of the signal generator was controlled in order to keep the in-phase output zero and was locked to the resonance frequency. The quadrature output at this frequency is the resonance amplitude, and the change in $Q$ value is calculated from this amplitude.

In the present experiment, the quartz crystal was a 5 MHz AT-cut one, which was commercially available. On one side of the Ag electrodes, exfoliated single crystalline graphite was thermally bonded. The graphite was first obtained from a kind of mineral called Franklin Marble, by dissolving it out with hydrochloric acid. To exfoliate, a piece of graphite was immersed in the reaction mixture of concentrated sulfuric acid and nitric acid under stirring for 16 h. After the neutralization and dehydration, the interlayer space was expanded by heating in furnace at 1050 $^\circ$C for 15 s. For cleaning, the exfoliated graphite was heat-treated in a vacuum of 10$^{-5}$ Pa at 100 $^\circ$C for 2 h. After bonding, the Q value of the crystal remained about $10^4$. The crystal was heated in 10$^{-5}$ Pa at 100$^\circ$C for 2 h, and was mounted in the sample cell. In addition to the crystal, Grafoil disks (exfoliated graphite) were set in the cell, in order to increase the surface area, and to minimize the effect of the desorption of Kr.

The sample cell was set in a N$_2$ cryostat, and was surrounded by a thermal shield. It was weakly connected to a temperature-regulated plate cooled by liquid N$_2$. The temperature of the cell was measured by a Si diode thermometer, and was stabilized better than 1 mK at 85 K. The frictional coverage of Kr film was evaluated from the equilibrium pressure. From the commensurate-incommensurate (C-IC) transition point observed in the Kr pressure isotherm, Kr gas dosage was calibrated.

3. Results and Discussion

We have carried out the QCM experiment of Kr films adsorbed on exfoliated single crystalline graphite at 85 K. In the present experiment, the oscillation of the crystal is inclined at about 30$^\circ$ to the $a$-axis of graphite, and the oscillation amplitude is about 0.1 nm.

Figure 1 shows the resonance frequency as a function of the fractional coverage of Kr film. As the coverage increases, the frequency does not change greatly until the commensurate phase,
which means that the sliding friction below the commensurate phase is small. When the film enters the commensurate phase, the frequency starts to decrease, i.e., the sliding friction increases. Then, when the film enters the incommensurate phase, the slope of the decrease becomes large.

![Figure 1](image)

**Figure 1.** (a) Laue photograph of the exfoliated single crystalline graphite. (b) Resonance frequency as a function of fractional coverage. The coverage is divided by that of the commensurate film (6.35 atoms/nm$^2$). (c) Expanded view around the commensurate phase. C, F, and IC indicate the commensurate, the fluid, and the incommensurate phases, respectively.[8]

It is interesting to compare the coverage dependence of sliding friction between the present experiment for Kr film and $^4$He film adsorbed on Grafoil (assembly of exfoliated microcrystalline graphite).[6] In the case of $^4$He film, the sliding friction is also small in the coexistence of commensurate-solid and fluid (C+F). In contrast to Kr film, the sliding friction of $^4$He films remains small in the commensurate phase. As the coverage increases further, the friction increases rapidly at around the coverage of the first layer completion. In comparison between Kr and $^4$He monolayer films, the sliding friction of Kr films is affected significantly by the film structure. The sliding friction is thought to be dependent on the interaction between the adatoms and the substrate. The interaction for Kr atom is larger than that for $^4$He, which results in the difference of the sliding friction.
Next, we compare the sliding friction of Kr films adsorbed on graphite with that of Kr films adsorbed on other substrates. According to the QCM experiment of Kr/Au [2], the resonance frequency decreases with increasing coverage in the fluid film, while no decrease was observed in the present experiment. This indicates that the sliding friction of the fluid film on graphite is smaller than that of Au. There are some possibilities as an origin of the difference: (1) For semimetal substrate (graphite), the electronic friction is expected to be small compared with that for metal substrate (Au). (2) The pinning effect caused by impurities is small in the present experiment.[7]

4. Summary
We have performed the QCM measurement of Kr film adsorbed on exfoliated single crystalline graphite. It was found that the sliding friction of Kr film is small until the commensurate phase. As the coverage increases, the resonance frequency starts to decrease at the commensurate phase and the slope of the decrease in frequency becomes large at the incommensurate phase. The observed behavior is different from that of Kr films adsorbed on Au.

5. References
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