Sliding Friction of Kr Films Adsorbed on Single-Crystalline Graphite Substrate

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Abstract. We have performed a quartz crystal microbalance (QCM) experiment for Kr films adsorbed on a single-crystalline graphite substrate at various temperatures. The substrate enables us to study the oscillation direction dependence of the sliding friction. In the present experiment, the direction is parallel to the $a$-axis of graphite. It was found that the resonance frequency at 85 K does not change greatly until the film enters the commensurate phase. At the commensurate phase, the resonance frequency starts to decrease. In addition, at the transition from the commensurate phase to the incommensurate phase, the coverage dependence of frequency changes slightly.

1. Introduction
Sliding friction is one of oldest problems that has been studied over many years and certainly an important one for practical applications [1]. The development of micro or nanoscale devices necessitates understanding of the sliding friction at nanometer scales [2]. With the introduction of newly developed techniques, peculiar experimental observations of nanoscale friction were reported [3], and nanotribology has been growing rapidly. Regarding physisorbed films, Krim and co-workers developed the quartz crystal microbalance (QCM) technique, and measured the sliding friction of various films adsorbed on metal substrates. For Kr monolayer films adsorbed on Au, they reported that the friction of the fluid film is larger than that of the incommensurate-solid one [4]. In addition, Mistura and co-workers revealed the structural pinning of Ne monolayer films adsorbed on Pb: Ne films are nearly locked to the oscillating substrate in the low coverage region, while they slide in the incommensurate phase [5].

Most of QCM experiments made use of metal deposited films for the substrate. Then, it is difficult to control the sliding direction with respect to the crystal orientation of substrates. On the other hand, we may expect that the sliding friction of physisorbed films depends on the sliding direction [6]. It is therefore of great interest to measure the sliding friction with controlling the crystal orientation of substrates. Thus motivated, we have started a QCM experiment of Kr films adsorbed on a single crystalline graphite. In the present experiment, the graphite was exfoliated to increase its effective surface area. We found that it remains the crystal orientation after this exfoliating, and set the oscillation of the crystal was parallel to the $a$-axis of graphite.
2. Experimental
In the QCM technique, the change in the resonance frequency is related to the coupled mass of film with the oscillating substrate. When the film moves in concert with the oscillating substrate, the resonance frequency decreases from that of bare substrate as $\Delta f/f_R = -\sigma/M$, where $f_R$ is the resonance frequency, $\sigma$ and $M$ are the areal mass densities of the film and the crystal. The resonance frequency was 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 an 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.

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 at 900 $^\circ$C for 4 h. The Laue photograph of the exfoliated graphite is shown in Fig. 1 (c), and demonstrates that it remains the crystal orientation in the a-b plane. Next, a thin film of Ag was deposited on the graphite and the Ag-plated graphite was bonded on one side of the Ag electrodes by pressing together and heating in a vacuum at 290 $^\circ$C for 0.5 h. The $Q$ value of the crystal remained about $10^4$. The crystal was set in the sample cell. In order to increase the surface area and to minimize the effect of the desorption of Kr, heat-treated Grafoil disks (exfoliated graphite) were set in the cell, together with the crystal. Then, the cell was heated at 120 $^\circ$C in a vacuum to remove water. After heating, the crystal was not exposed to air.

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 around 90K. The equilibrium pressure was measured simultaneously. It is known that the pressure isotherm bends clearly at the commensurate-incommensurate (C-IC) transition [7]. Form the bend in pressure isotherm, the fractional coverage of Kr film was determined and the gas dosage was calibrated.

3. Results and Discussion
We have carried out a QCM experiment of Kr films adsorbed on a single crystalline graphite at various temperatures. In the present experiment, the oscillation direction of the crystal is parallel to the a-axis of graphite and the oscillation amplitude is about 0.4 nm.

Figure 1 (a) shows the resonance frequency as a function of coverage at 85 K, 90 K, and 95 K. The coverage was calibrated by the bend in pressure isotherm, and the horizontal axis is normalized by the coverage of $\sqrt{3} \times \sqrt{3}$ commensurate phase with respect to graphite, which corresponds to an areal density of 0.36 atoms/nm$^2$. The phase of Kr film is determined on referring to Refs. 7 and 8. In the figure, C, F, and IC indicate the coverage region of the commensurate, the fluid, and the incommensurate phases, respectively. In the present temperature range, the coverage region does not depend strongly on temperature. It was found that the frequency does not change greatly until the film approaches the commensurate phase. This means that the sliding friction below the commensurate phase is significantly small at these temperatures. When the film enters the commensurate phase, the frequency decreases, i.e., the friction increases. The decrease in frequency continues in the incommensurate phase, and becomes small around the coverage of 1.2.

Figure 1 (b) shows an expanded view at 85 K in the neighborhood of the transition. The
frequency decreases continuously at the transition with increasing coverage, and no discontinuous change is observed. It was found, however, that the decreasing ratio of the frequency becomes small at the transition. This demonstrates that the sliding friction changes at the C-IC transition, but shows a different behavior from a naive idea that the commensurate film does not slide easily because of the structural pinning.

We also found that the resonance frequency shows a strong temperature dependence. At higher temperatures of 90 K and 95 K, the onset of the decrease in frequency shifts to a lower coverage, and the magnitude of the decrease becomes large with increasing temperature, which means that the friction increases with increasing temperature. In addition, there still exists a small change in the decreasing ratio at the C-IC transition.

It is interesting to compare the sliding friction between the present experiment and $^4$He films adsorbed on Grafoil [9,10]. For $^4$He films, the resonance frequency does not change greatly until the first layer completion, i.e., the sliding friction does not increase at the commensurate phase. Thus, it can be concluded that the friction of Kr films is affected significantly by the structure. Here, we comment shortly on the observed difference. It is expected that the friction depends...
on the interaction between the adatom and the substrate. The magnitude of the adsorption potential of graphite is 1430 K for Kr atom and 191 K for $^4$He atom, respectively, but the difference in the corrugation potential becomes relatively small because of the adatom size: 76-126 K for Kr atom and 24-43 K for $^4$He atom [11]. The corrugation potential for Kr atom is, however, still larger than that for $^4$He atom, which may result in the difference.

Finally, it should be commented that a small sliding friction for thin films is observed both in Kr films adsorbed on graphite and in $^4$He films adsorbed on Grafoil. For thin Kr films adsorbed on Au [4] and thin Ne films adsorbed on Pb [5], the friction is relative large. The smallness of friction for thin films may be a common feature of graphite substrate, but the origin is an open question.

4. Summary
We have performed QCM measurements of Kr films adsorbed on a single crystalline graphite at various temperatures. The sliding friction is small for thin Kr films. When the film enters the commensurate phase, the resonance frequency starts to decrease largely. At the C-IC transition, the frequency decreases continuously at the transition with increasing coverage, and no discontinuous change is observed. It was found, however, that the decreasing ratio of the frequency becomes small at the transition. The observed behavior is different from that of Kr films adsorbed on Au.

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