Mechanical response of Kr films adsorbed on graphite substrate with a quartz tuning fork

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Abstract. We have developed a quartz-crystal microbalance (QCM) using a quartz tuning fork resonator, and have carried out experiments for Kr films adsorbed on a single crystalline graphite at LN₂ temperature. For the monolayer film, the coupled mass to the oscillating substrate is significantly small until the film enters the commensurate (C) phase. It starts to increase at the C phase, and the increase in the coupled mass with respect to the coverage decreases at the coexistence phase between the C and the incommensurate (IC) phases. It is enhanced again when the film enters the IC phase. We compared the observed behavior with that of 5 MHz QCM experiments, and found that the sliding motion does not depend on oscillation frequency.

1. Introduction

Sliding motion of physisorbed films on the lateral oscillating substrate has attracted interest because of a study on the atomic-scale mechanism of sliding friction. Noble gas films adsorbed on graphite take the commensurate (C) and the incommensurate (IC) phases by changing the fractional coverage. By using these films, it is possible to make clear the relation between the sliding friction and the commensurability of film.

We have already reported 5 MHz AT-cut quartz-crystal microbalance (QCM) experiments for Kr films adsorbed on a single-crystalline graphite (Kr/Gr) [1]. It was found that the coupled mass starts to increase at the C phase, and that this increase continues after the commensurate-incommensurate (C-IC) transition. The observed behavior is different from a naive idea that films of the C phase do not slide easily because of their structural pinning [2].

Thus motivated, we planned to measure the mechanical response of Kr/Gr when an inertial force acting on film is small. Since the inertial force is proportional to the product of the oscillation amplitude and the square of the angular frequency in the QCM technique, we developed QCM using a quartz tuning fork resonator, and carried out experiments for Kr/Gr. In this paper, we explain the present results of a 32 kHz quartz tuning fork of Kr/Gr, focusing on two topics: one is the relation between the coupled mass and the coverage of film, and the other is the sliding direction dependence. We also compare them with those of 5 MHz AT-cut QCM experiments.
2. Experimental

A quartz tuning fork oscillates flexurally perpendicular to the arms. In QCM using the tuning fork, the substrate of film is attached at the tips of the arms. When the film adsorbed on the substrate moves in concert with the tuning fork, the resonance frequency decreases from that of no films is expressed as

$$\frac{\Delta f}{f} \sim -2 \frac{m}{M}$$

where $m$ is the coupled mass of film and $M$ is the mass of the arms. In the present experiments, the resonator is a 32 kHz quartz tuning fork.

The experimental procedure is similar to 5 MHz AT-cut QCM experiments [1]; here, we describe it briefly. Single-crystalline 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°C for 15 s. For cleaning, the exfoliated graphite was heat-treated in a vacuum at 900°C for 4 h. The Laue photograph of the exfoliated graphite is shown in Fig. 1 (a), and demonstrates that it remains the crystal orientation in the $a$-$b$ plane.

To prepare a quartz tuning fork with graphite, 200 nm-thick Ag film was deposited on the graphite. Then, the tuning fork and Ag-plated graphite were pressed together and were heated in hydrogen atmosphere at 300°C for 1 h. After bonding, any excess graphite was carefully removed. The tuning fork with graphite is shown in Fig. 1 (b). The effective surface area of graphite on the arms is about 2 cm$^2$, and the $Q$ value of the tuning fork was higher than $2 \times 10^4$ at LN$_2$ temperature.

We prepared two quartz tuning forks with graphite: one of the tuning forks oscillates parallel to the $a$-axis of graphite, while the other in the direction inclined at about 30° with respect to the $a$-axis. The tuning forks were set in a sample cell. In addition to the tuning forks, 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. After setting, the cell was sealed with helicoflex (HN100), and was evacuated at 120 °C for 96 h to remove water, and was cooled down to LN$_2$ temperature. The temperature was measured by a Si diode thermometer, and was stabilized better than 1 mK. Furthermore, the equilibrium pressure was measured simultaneously. It is known that the pressure isotherm bends clearly at the C-IC transition [3]. From this bend, the fractional coverage of Kr film was determined and the gas dosage was calibrated.

The resonance frequency of the quartz tuning fork was measured using a transmission circuit. In the circuit, the tuning fork was placed in series with a coaxial line connecting to a 50 Ω cw signal generator and a lock-in amplifier. The frequency of the signal generator was controlled in order to keep the in-phase signal zero, and was locked to the resonance frequency. The quadrature signal at this frequency was the resonance amplitude.

3. Results and discussion

3.1. Coverage dependence

Tuning fork experiments were carried out at 79.8 K with increasing the coverage of Kr film monotonously. Figure 1 (a) shows the variation of the resonance frequency as a function of fractional coverage, together with that of 5 MHz QCM experiments at 85.8 K. The oscillation amplitude is about 1.4 nm in both experiments, and the oscillation direction is inclined at about 30° with respect to the $a$-axis of graphite. The vertical axis is normalized by the mass loading at the commensurate phase.

In the present experiments, the resonance frequency does not change greatly in the fluid (F) phase and the C+F phase. When the film enters the C phase, it starts to decrease. This decrease continues at the IC phase, and the ratio of decrease with respect to coverage at the IC phase is
larger than that of the C phase. The first layer completion occurs around a coverage of 1.1 and
the film becomes bilayer in the higher coverage. Above a coverage of 1.4, the frequency becomes
almost constant.

It is interesting to compare this behavior with that of 5 MHz QCM experiments. Since the
inertial force is proportional to the square of the frequency, the force acting on film of the present
experiments is about four orders of magnitude smaller than that of 5 MHz QCM experiments.
It was found that the observed behavior for the present experiments is similar to that of 5 MHz
QCM experiments, although the frequency for 5 MHz QCM experiments decreases slightly at
the C+F phase [4]. It should be noted that the decrease of the frequency at the C phase for both
experiments is significantly smaller than the mass loading. This means that the film of the C
phase undergoes decoupling from the oscillating substrate under both experimental conditions.

Figure 1 (b) shows the variation of the resonance frequency in the vicinity of the C-IC
transition. For the present experiments, the frequency decreases with increasing the coverage at
the C phase. In the coexistence region between the C and IC phases, the decrease in frequency
becomes small. Then, it is enhanced again at the IC phase. The coverage dependence of the
coupled mass changes at the C-IC transition. The observed behavior is, however, different from a
naive idea that the film of the C phase does not slide easily because of the structural pinning [2].
We also compare the present results with that of 5 MHz QCM experiments. It was found that
the observed behavior for the present experiments is similar to that of 5 MHz QCM experiments.
The bend at the coexistence region seems to be somewhat clear compared with 5 MHz QCM
experiments of 1.4 nm.

3.2. Sliding direction dependence
In the present experiments, we set two quartz tuning forks in the sample cell and measured
them simultaneously. One of the tuning forks oscillates in the direction parallel to the a-axis of
graphite, while the other in the direction inclined at about 30°. Figure 2 shows the variation of
the resonance frequency for the two tuning forks. As seen in the figure, two sets of data almost
coincide with each other. At present, we have no clear explanation that the direction dependence
is very weak. There is, however, a possibility that the adatoms of film on the substrate slide
not along the oscillation direction but along the inclined direction which is the direction to the
saddle point of the corrugation potential.

3.3. Comparison with $^4$He films adsorbed on graphite
It is interesting to compare Kr/Gr with that of other noble gas films adsorbed on graphite. Here,
we make a comment on $^4$He films adsorbed on graphite ($^4$He/Gr). Tuning fork experiments for
$^4$He/Gr were carried out at 1.0 K, and the oscillation amplitude is 10 nm [6]. Figure 4 shows
Figure 2. (a) Comparison of the coverage dependence between the present experiments at 79.8 K and 5 MHz AT-cut QCM experiments at 85.8 K [1]. The horizontal axis is the fractional coverage divided by the value of the commensurate phase (6.36 atoms/nm$^2$). The vertical axis is normalized by the mass loading at the commensurate phase. The estimated mass loading is represented by the solid line. C, F, and IC indicate the coverage region of the commensurate, the fluid, and the incommensurate phases, respectively. These phases of Kr film are determined on referring to Refs. [3] and [5]. (b) Expanded view in the vicinity of the commensurate-incommensurate (C-IC) transition.

Figure 3. Comparison of the coverage dependence between two quartz tuning forks; One of the tuning forks oscillates in the direction parallel to the $a$-axis of graphite, while the other in the direction inclined at about 30$^\circ$.

The comparison of the coverage dependence between Kr/Gr and $^4$He/Gr. The horizontal axis is the coverage divided by the value of the first layer completion $\sigma_{1st}$, and the vertical axis is normalized by the mass loading at $\sigma_{1st}$. For $^4$He/Gr, the resonance frequency starts to decrease before the C phase, and continues to decrease with increasing coverage. At $\sigma_{1st}$, the decrease is close to the mass loading. It was found that in the monolayer region, $^4$He/Gr does not slide easily compared with Kr/Gr.

We consider the inertial force acting on the films and the corrugation potential for Kr/Gr and $^4$He/Gr. It is expected that the film undergoes slipping from the oscillating substrate when the inertial force $F$ is large and the corrugation potential $V$ is small, and the ratio of two values $F/V$ may be a measure for decoupling. When the film moves in concert with the oscillating
substrate, the amplitude of inertial force per adatom is expressed by \( F = mA\omega^2 \), where \( m \) is the mass of atom, \( A \) is the oscillation amplitude and \( \omega \) is the angular frequency. Then, these values are shown in Table 1. As seen in the table, \( F/V \) for Kr/Gr is approximately equal in magnitude to that of \(^4\)He/Gr, and we expect that they show a similar behavior. Contrary to this expectation, the coverage dependence for \(^4\)He/Gr is clearly different from Kr/Gr: \(^4\)He/Gr in the monolayer region does not slide easily compared with Kr/Gr. At present, the origin is an open question.

Table 1. Comparison between Kr/Gr and \(^4\)He/Gr

|                | Atomic weight of adatom \( m \) (u) | Oscillation amplitude \( A \) (nm) | Corrugarion potential\(^a\) \( V \) (K) | \( F/V \) (1/m)       |
|----------------|------------------------------------|-----------------------------------|-----------------------------------------|-----------------------|
| Kr/Gr          | 83.80                              | 1.4                               | 76-126                                  | 4.5-7.5 \times 10^{-3} |
| \(^4\)He/Gr    | 4.00                               | 10                                | 24-43                                   | 4.5-8.1 \times 10^{-3} |

\(^a\) From Ref. [8].

\(^b\) The resonance angular frequency \( \omega \) is \( 2\pi \times 32 \) kHz.

4. Summary

We have developed QCM using a 32 kHz quartz tuning fork resonator, and have carried out experiments for Kr films adsorbed on a single-crystalline graphite at LN\(_2\) temperature. It was found that the coupled mass to the oscillating substrate does not depend on the oscillation direction with respect to the crystal axis of graphite. In addition, the coupled mass is significantly small until the film enters the C phase. Then, it starts to increase slightly at the C phase, and it is enhanced when the film enters the IC phase. The coverage dependence is different from a naive idea that films of the C phase do not slide easily, and is similar to the previous experiments of 5 MHz AT-cut QCM. From the comparison between Kr/Gr and \(^4\)He/Gr, we concluded Kr/Gr slides more easily than \(^4\)He/Gr.
References

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