Superlubricity of MoS₂ at Submicron Scale

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When the mean free paths of acoustic phonons are larger than half the MoS₂ island size, the generated acoustic phonons remain at nonequilibrium and are confined within the island or form standing waves. In contrast, when the island size decreases to less than 1 μm , surface softening increases, reducing the barrier of the tip–surface interaction potential. Unexpectedly, the friction force from an island with a size of 0.2 μm abruptly decreases to below 10 pN. The superlubricity described here is a novel type involving phonon confinement and surface softening that is easily achievable and very simple because it uses only nanostructures smaller than 1 μm .

Keywords Superlubricity; Submicron island; Phonon confinement; Surface softening; Energy dissipation

I. INTRODUCTION

It is well known that energy dissipates through friction between solids. Many studies [1] on friction have discussed energy dissipation in terms of phononic and electronic excitations. Studies on the sliding of adsorbed films with single-molecule thickness on a substrate using various spectroscopic techniques have also been reported [2, 3]. However, little is known about how phonons form [4] and propagate in the friction process with a load and shear, although phonons ultimately change into heat. This is because it would be difficult to directly measure the energy dissipation in situ during sliding accompanied by a loading force and shear. Thus, we have established tribo-phonon spectroscopy (TPS), which can measure the dissipation energy of a phonon [5].

On the other hand, nanomaterials have very different physical and chemical properties from their bulk counterparts. For example, nanoparticles often have lower melting points, transition pressures, and stiffness. Such differences also apply to the tribological behavior of lubricants [6]. The coefficient of friction of nanoparticles is much smaller than that of the corresponding bulk materials. Nanoparticle can be added to solids and oil to greatly reduce their friction [7]. Moreover, acoustic or sonic lubrication occurs when sound-induced vibration introduces a gap between sliding faces. Although a number of mechanisms that explain the beneficial effect of these particles on lubrication have been proposed (introducing the protection of sliding surfaces

from close contact, the delamination and release of molecular lubricants, and the ball-bearing effect), a full elucidation has not yet been given because the various shapes and sizes of nanoparticles make it difficult to clarify their behavior in solids and in oil.

II. EXPERIMENTAL

MoS₂ is a dichalcogenide and comprises weakly bonded S–Mo–S single layers, where the outermost and second layers consist of sulfur and molybdenum atoms, respectively. The Γ , M, and K points of MoS₂ in the first Brillouin zone are illustrated in Figure 1(a) [8]. A MoS₂ substrate was prepared by cleaving a natural MoS₂ block. Here, small islands with a height of 100 nm surrounded by four square holes with a depth of 100 nm were fabricated on a MoS₂(0001) flake of 1 mm² $\times$ 5 μm using a focused ion beam (FIB). A scanning electron microscopy (SEM) image of small square islands with a size of 0.2 μm to 5 μm and a height of 100 nm taken in the Γ –M direction is shown in Figure 1(a). Frictional force loops (FFLs) were measured at a relative humidity of less than 50% at room temperature using a commercially available device (Seiko Instruments Inc., SPI-3700). The friction force was directly calibrated by the simultaneous use of two cantilevers [9]. An atomic force microscopy, (AFM) system for use with a quartz crystal microbalance (QCM) was also developed to study the frictional dissipation energy rate from a substrate in contact with a

Figure 1: Scanning electron microscopy (SEM) image of small islands constructed at MoS₂(0001) surface and frictional dissipation energy rate $\Delta 1/Q$. (a) SEM image of square islands of size 0.2 μ m to 3 μ m and 100 nm height on a MoS₂(0001) surface, around which four square holes of 100 nm depth are fabricated with a focused ion beam (FIB). Each of these single layers consists of two hexagonal planes of sulfurs (green) and an intercalated hexagonal plane of molybdenum atoms (blue) bonded with the sulfur atoms in a trigonal prismatic arrangement. a_1 and a_2 are the lattice vectors. The Γ , M, and K points in the first Brillouin zone are illustrated. (b) $\Delta 1/Q$ in Γ -K and Γ -M directions on an infinite MoS₂(0001) surface. The red and blue lines represent the calculated LA in the Γ -K direction and the calculated TA in the Γ -M direction, respectively. Adapted from Ref. 13.

tip, as reported previously [5, 10]. Figure 2(a) is a schematic diagram of the experimental setup. The QCM comprises an AT-cut crystal having a fundamental frequency of 5 MHz (SEN-5P-H-10, Tamadevice) and a vibrational mode corresponding to shear deformation in the thickness direction. The QCM was set up with a cantilever having a spring constant of 20 N m⁻¹ in the AFM system (Dimension 3100, Veeco). In the measurement to obtain the frictional dissipation energy rate $\Delta 1/Q$, the QCM was controlled using excitation signals from a function generator so that it vibrated at its resonance frequency. The crystallographic direction of the MoS₂(0001) substrate was aligned with the oscillation direction of the QCM using SEM-electron backscattering diffraction (SEM-EBSD). The resonator with the MoS₂(0001) substrate had a Q factor of about 10,000 in air. The AFM tip was moved so that it came in contact with the MoS₂ substrate through the extension of a Z piezoactuator,

Figure 2: Experimental setup and method of determining oscillating amplitude. (a) Experimental setup combined atomic force microscope (AFM) with a quartz-crystal microbalance (QCM). (b) Oscillation amplitude A vs. drive voltage V_0 . Adapted from Ref. 5.

then the optical detector of the AFM system was used to measure the force normal to the MoS₂(0001) substrate. When contact was made between the AFM tip and the MoS₂ substrate, the resonance frequency of the QCM markedly changed. A lock-in amplifier was used to detect the change in the amplitude and the phase shift of the QCM. A computer controlled the frequency of the excitation signal so that a constant phase shift was maintained. $\Delta 1/Q$ was obtained from the oscillation amplitude A at the resonance frequency of the QCM using [5, 10]

$$\Delta 1/Q = -\frac{1}{Q} \frac{\Delta A}{A} = \frac{\Delta E}{2\pi E}.$$

Here, ΔA is the change in the oscillation amplitude A , ΔE is the dissipation energy, and E is the energy stored in the system, where A was directly measured as a function of the drive voltage V_0 by AFM [11] and is shown in Figure 2(b).

III. RESULTS

By choosing an appropriate value of A for the QCM, acoustic waves with different wavelengths, ranging from the atomic scale (corresponding to lattice vibration) to the microscale (corresponding to a continuum elastic wave) can be generated, where the wavelength depends on the magnitude of the strain [5]. The lateral elastic strain (deformation) generated by tip shearing with nonzero A becomes an acoustic longitudinal mode (LA) in the Γ -K direction and an acoustic transverse mode (TA) in the Γ -M direction owing to the atomic arrangement of the MoS₂(0001) surface. Using the

relation between the oscillation amplitude of the tip and the phonon wavenumber $k = \pi/A$ and scaling $\Delta 1/Q$ with an appropriate constant ($E = 5.6 \times 10^{-15}$ J), $\Delta 1/Q$ for an infinite $\text{MoS}_2(0001)$ surface was empirically found to be in agreement with the value obtained from the phonon dispersion relations, as shown in Figure 1(b), in which the red and blue lines respectively indicate the calculated LA in the Γ -K direction and the calculated TA in the Γ -M direction. Interestingly, this also suggests a method of generating phonons with different wavelengths, i.e., this method can be used to provide a source of phonons. The mean wavelength of the wave packet $2A$ was used to obtain the phonon wavenumber $k = \pi/A$. This also satisfies the de Broglie equation, and the uncertainty of the wave packet is related to that of the wavenumber via the uncertainty principle [12], i.e., the error bars of $\Delta 1/Q$ for a small k are small, whereas those of $\Delta 1/Q$ for a large k are large, as shown in Figure 1(b). On the other

hand, $\Delta 1/Q$ for an infinite $\text{MoS}_2(0001)$ surface can be approximated using the phonon dispersion relations.

The main finding in this work [13] is that $\Delta 1/Q$ markedly changes with the island size in both the Γ -K and Γ -M directions. As shown in Figure 3, $\Delta 1/Q$ significantly decreases with decreasing island size. The difference $\Delta 1/Q_\infty - \Delta 1/Q$, where $\Delta 1/Q_\infty$ denotes the dissipation energy in MoS_2 with infinite size (∞), indicates the effect of confinement on the dissipation energy due to the finite size of the island. Since the dissipation energy changes with $k = \pi/A$, the difference is further normalized by defining

$$C = \frac{\Delta 1/Q_\infty - \Delta 1/Q}{\Delta 1/Q_\infty}$$

to quantify the mode dependence of the degree of confinement. The values of C in the Γ -K and Γ -M directions for an island size of $10 \mu\text{m}$ markedly decrease when π/A exceeds 7

Figure 3: $\Delta 1/Q$ in Γ -K and Γ -M directions vs. island size. The difference $\Delta 1/Q_\infty - \Delta 1/Q$ indicates the effect of confinement on dissipation energy due to the finite size of the island, where $\Delta 1/Q_\infty$ represents the dissipation energy of the infinite surface. $(\Delta 1/Q_\infty - \Delta 1/Q)/(\Delta 1/Q_\infty)$ is the degree of phonon confinement. Adapted from Ref. 13.

Figure 4: Calculated mean free paths (MFPs) of phonons in Γ -K and Γ -M directions. Adapted from Ref. 13.

nm^{-1} and 9 nm^{-1} , respectively. For an island size of $8 \mu\text{m}$, C markedly decreases in the Γ -K and Γ -M directions when π/A exceeds 10 nm^{-1} and 11 nm^{-1} , respectively. Thus, as the island size decreases, the critical point below which C markedly decreases is shifted to a larger π/A , indicating that acoustic phonons with a shorter wavelength are gradually confined with decreasing island size. Eventually, the critical point finally disappears regardless of π/A . This can be more clearly understood by comparing the mean free paths (MFPs) of phonons with half the island size because of the vibration of the tip at the center of the island. The MFPs of acoustic phonons obtained from first principles strongly depend on the wavenumber and vary from the submillimeter scale to the submicron scale, as shown in Figure 4. When the MFPs of phonons are larger than half the island size, because phonons are ballistically transported and reflected at the edges of the island, the generated acoustic phonons remain at nonequilibrium and are confined within the island or form standing waves. However, the lifetime of the acoustic phonons is only of sub-nanosecond order. Since the MFPs of acoustic phonons with a long wavelength exceed $10 \mu\text{m}$ for both the LA and the TA, these acoustic phonons can be ballistically confined even in a $10 \mu\text{m}$ island for a small π/A . When the island size decreases to below $1 \mu\text{m}$, since the MFPs of acoustic phonons with a wide range of wavevectors are of submicron size, i.e., larger than or similar to half the island size (Figure 4), ballistic phonon confinement occurs regardless of π/A . Therefore, the transition from partial confinement (only for a small π/A) to full confinement (for all π/A) can be explained by the relative sizes of the MFP and island.

On the other hand, when the island size decreases to less $1 \mu\text{m}$, surface softening increases. An increase in surface softening (a decrease in bond strength) induces a decrease in $\Delta 1/Q$ in the dispersion area (or a shift to a lower-frequency area), which appears in both the LA and the TA. Recently, surface softening has been studied in other research fields [14]. Research on surface effects dates back to 1909 [15, 16] and the surface effect has also been reported in the study of ultrafine particles in Japan [17].

Figure 5 shows the FFLs at small square islands with a size of $0.2 \mu\text{m}$ to $5 \mu\text{m}$ and a height of 100 nm and at an

infinite surface (∞) in the Γ -K and Γ -M directions. The FFLs at the infinite surface (∞) exhibit one- and two-dimensional stick-slips of the tip in the Γ -K and Γ -M directions, respectively, as reported previously [18], because the tip moves along the line corresponding to the minimum of the tip-surface interaction potential. With decreasing island size, the FFLs change from clear stick-slips to continuous motion and markedly decrease in magnitude to become frictionless loops in both directions. Unexpectedly, the friction force from the island with a size of $0.2 \mu\text{m}$ abruptly falls to below 10 pN for much of the trace in both directions, which is close to the pN-order detection limit owing to thermal fluctuations.

Interestingly, a recent study revealed that superlubricity occurs even at a cylindrical silicon pillar of 100 nm height (to be surface layers of silicon oxide) [19]. This indicates that superlubricity due to surface softening may occur in materials other than MoS_2 .

IV. CONCLUSIONS

When the MFPs of phonons are larger than half the island size, because phonons are ballistically transported and reflected at the edges of the island, the generated acoustic phonons remain at nonequilibrium and are confined within the island or form standing waves. In contrast, when the island size decreases to below $1 \mu\text{m}$, surface softening increases, reducing the barrier of the tip-surface interaction potential. Unexpectedly, the friction force from an island with a size of $0.2 \mu\text{m}$ abruptly decreases to below 10 pN .

There have been many studies on superlubricity over the last 30 years [20–25]. However, the superlubricity described here is a novel type different from that previously studied and is easily achievable and very simple because it involves only islands (including surface textures) of submicron size. Interestingly, conventional technology has been empirically used to add particles of submicron size to solids and oil to decrease friction in the technical field, despite a lack of understanding of the underlying mechanism. Interestingly, macroscopic superlubricity may be realized when a very large number of submicron pillars are constructed on a macroscopic surface.

Figure 5: (a) Frictional force loops (FFLs) at square islands of size 0.2 μm to 5 μm and 100 nm height and infinite surface in Γ -K direction, where X denotes the sample position, and the black and red lines indicate scans in opposite directions. Frictional force F vs. island size is given on the bottom. (b) FFLs at square islands of size 0.2 μm to 5 μm and 100 nm height and infinite surface in Γ -M direction. The same loading force of 1 nN is used for all island sizes and infinite surface. Frictional force F vs. island size is given on the bottom. Adapted from Ref. 13.

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