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Experimental observation of phonon generation and propagation at a $MoS_2(0001)$ surface in the friction process

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We report phonon dispersion curves obtained at a $MoS_2(0001)$ surface in the friction process with a load and shear. An atomic force microscope tip used to apply stresses generated lattice strain on an oscillating $MoS_2(0001)$ surface, which dissipated via acoustic phonons. The dissipation energy of the phonons strongly depended on the size of the lattice strain. The motion of the acoustic phonons consisted of a longitudinal mode and a transverse mode, but the occurrence of their phonon modes depended on the crystallographic direction, which reflects the atomic arrangement of the $MoS_2(0001)$ surface. Thus, we can control the energy dissipation and friction by using the phonon dissipation curves in the friction process with a load and shear.

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It is well known that energy dissipates through friction between solids. Many studies [1–7] on friction have discussed energy dissipation in terms of phononic and electronic excitations. Studies on the sliding of molecularly thin adsorbed films on a substrate using various spectroscopic techniques have also been reported [8,9]. However, little is known about how phonons are generated [10] 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 and *in situ* measure the energy dissipation during sliding accompanied by a loading force and shear. Here, we report phonon dispersion curves obtained at a $MoS_2(0001)$ surface in the friction process with a load and shear.

We combined an atomic force microscope (AFM) with a quartz-crystal microbalance (QCM) to study the energy dissipation from a substrate in contact with a tip [11,12]. Figure 1(a) is a schematic diagram of the experimental setup. A $MoS_2(0001)$ flake of 1 $mm^2 \times \mu m$ was pasted with varnish onto a QCM, which consisted of an AT-cut crystal with a fundamental frequency of 5 MHz (SEN-5P-H-10, Tamadevice). The QCM and a cantilever with a spring constant of 20 N/m were set up in an AFM (Dimension 3100, Veeco) in a relative humidity of 30%. Also, the experiment was done within 1 day after cleaving. Thus, the $MoS_2(0001)$ flake has adsorbates such as water because the experiment was done in air with a relative humidity of 30%. In the measurement, the QCM was controlled so that it vibrated at its resonance frequency using excitation signals from a function generator. The crystallographic direction of the $MoS_2(0001)$ substrate was aligned along the oscillation direction of the QCM, using scanning electron microscope–electron backscattering diffraction (SEM-EBSD) with an angular accuracy of 0.01°. The Q factor of the resonator with the $MoS_2(0001)$ substrate was approximately 10 000 in air. The AFM tip of Si_3N_4 with a tip radius of ∼20 nm was placed in contact with the MoS_2 substrate by extending a Z piezoactuator, and then the force normal to the $MoS_2(0001)$ substrate was measured using the optical detector of the AFM system. When the AFM tip came in contact with the MoS_2 substrate, the resonance frequency of the QCM markedly changed. The lock-in amplifier detected the change in the amplitude and the phase shift of the QCM. The computer controlled the frequency of the excitation signal to keep the phase shift constant. The amplitude stability in this phase-locked loop was much better than 10^{-3}, when the locked frequency of QCM upon contact of the AFM tip changed within a few hertz [12]. The oscillation amplitude A was directly measured as a function of the drive voltage V_0 using the AFM [13], which is shown in Fig. 1(b) and also in detail in the Supplemental Material [14]. A movie showing the operation of the AFM with the QCM is given in [15].

MoS_2 belongs to the dichalcogenide family of materials and consists of weakly bonded S-Mo-S single layers, as shown in Fig. 2(a). Each of the layers consists of two hexagonal planes of sulfur atoms and an intercalated hexagonal plane of molybdenum atoms bonded with the sulfur atoms in a trigonal prismatic arrangement [16]. The outermost layer of sulfur atoms and the second layer of molybdenum atoms are shown in Fig. 2(b). The Γ, M, and K points in the first Brillouin zone are illustrated in Fig. 2(c).

The change in the factor $1/Q$ in the tip-QCM system, $\Delta(1/Q)$, at the tip contact is given as follows in terms of the additional dissipation energy ΔE per cycle [11,17]:

$$\Delta(1/Q) = \Delta E/2\pi E, \tag{1}$$

where E is the stored energy in the system.

In contrast, $\Delta(1/Q)$ is obtained from the oscillation amplitude A at the resonance frequency of the QCM as [11,17]

$$\Delta(1/Q) = -\frac{\Delta A}{Q\,A}, \tag{2}$$

where ΔA is the change in the oscillation amplitude A at the tip contact.

$\Delta(1/Q)$ (black line) and the force F (red line) acting between the tip and the MoS_2 are shown in Fig. 2(d) for the

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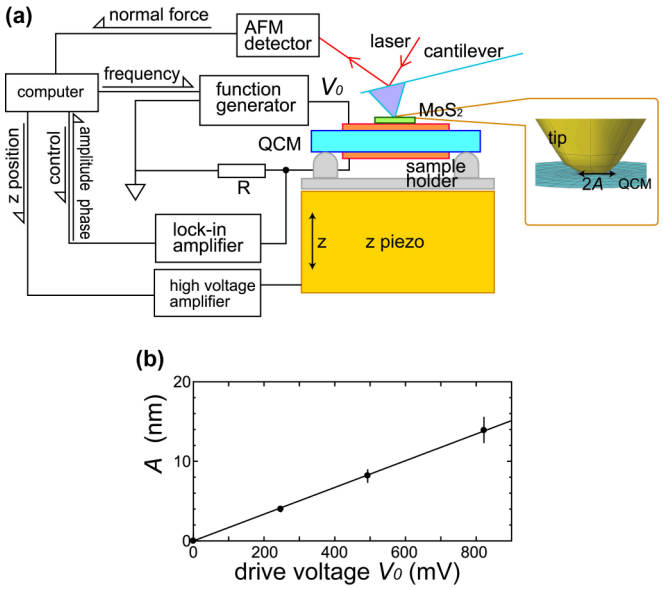

FIG. 1. Experimental setup and method of determining oscillating amplitude. (a) Experimental setup combined atomic force microscope (AFM) with a quartz-crystal microbalance (QCM). (b) Oscillation amplitude A vs drive voltage V_0.

tip displacement z from the $MoS_2(0001)$ surface, which were measured simultaneously. F suddenly changes at the point P, indicating that the tip has come in contact with the $MoS_2(0001)$ surface and that the energy has started to dissipate.

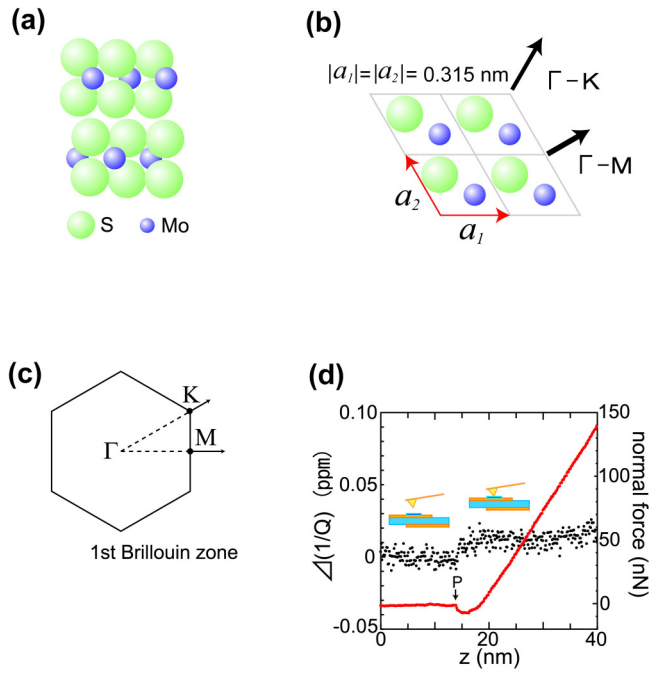

FIG. 2. Atomic structure of MoS_2 and dissipation energy $\Delta(1/Q)$. (a)–(c) Each of the layers of MoS_2 consists of two hexagonal planes of sulfur atoms and an intercalated hexagonal plane of molybdenum atoms bonded with the sulfur atoms in a trigonal prismatic arrangement. a_1 and a_2 are the lattice vectors. The Γ, M, and K points in the first Brillouin zone are illustrated in (c). (d) $\Delta(1/Q)$ (black line) and force F (red line) acting between tip and MoS_2 for tip displacement z from the $MoS_2(0001)$ surface.

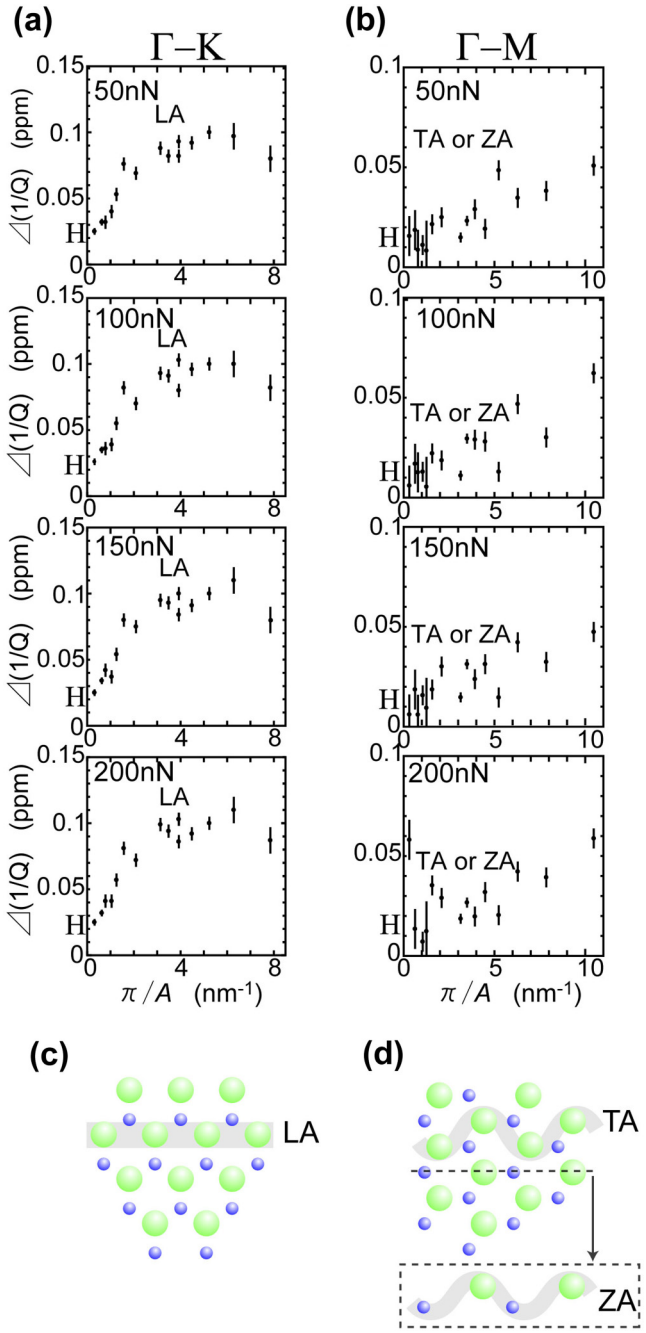

FIG. 3. $\Delta(1/Q)$ vs π/A along the Γ to K and Γ to M directions. $\Delta(1/Q)$ along the (a) Γ to K and (b) Γ to M directions as a function of loading force. (c) and (d) One-dimensional lattice strain (gray band) is easily induced along the Γ to K direction and readily exhibits the LA mode, although two-dimensional lattice strain (gray bands) is generated along the Γ to M direction and induces the TA (or ZA) mode. The broken lines in (d) illustrate a cross section normal to the surface.

Figures 3(a) and 3(b) show $\Delta(1/Q)$ values along the Γ to K and Γ to M directions as a function of the loading force, respectively. Since $\Delta(1/Q)$ decreases as A increases, $\Delta(1/Q)$ increases with π/A. It was found that the $\Delta(1/Q)$ values along the Γ to K direction are considerably different from those along the Γ to M direction. Thus, $\Delta(1/Q)$ strongly depends

on the crystallographic direction. However, it was found that the $\Delta(1/Q)$ values along the Γ to K and Γ to M directions hardly change with increasing loading force up to 200 nN. This suggests that $\Delta(1/Q)$ is quite sensitive to the shear stress generated by the tip but an increase of loading force only contributes to a small change of the shear stress, as discussed later.

According to a report on the phonon dispersion curve $\omega(k)$ [18], bulk and/or surface phonon dispersions have three acoustic modes; those that vibrate in the in-plane longitudinal acoustic (LA) and transverse acoustic (TA) modes have a linear dispersion and higher energy than those vibrating in the out-of-plane acoustic (ZA) mode. Interestingly, it was found that the shape of the $\Delta(1/Q)$ along the Γ to K direction in Fig. 3(a) is in excellent agreement with that of the LA mode along the Γ to K direction in the phonon dispersion curve $\omega(k)$ [18] with a scaling efficiency of 3.9×10^{-10} cm. Moreover, the shape of the $\Delta(1/Q)$ along the Γ to M direction in Fig. 3(b) is also in excellent agreement with that of the TA (or ZA) mode along the Γ to M direction in the phonon dispersion curve $\omega(k)$ [18] with the same scaling efficiency as the Γ to K direction. We reported in a previous paper [19] that, as illustrated in Figs. 3(c) and 3(d), a tip easily induces one-dimensional strain along the Γ to K direction, although it easily induces two-dimensional strain along the Γ to M direction, which reflects the atomic arrangement of the $MoS_2(0001)$ surface. Namely, static one-dimensional lattice strain is easily induced along the Γ to K direction and readily exhibits only the LA mode, although two-dimensional lateral lattice strain (or vertical lattice strain) is easily generated along the Γ to M direction and induces the TA (or ZA) mode. The dissipation energy at a large lattice strain is concentrated around the point. Also, the LA, TA, and ZA modes degenerate into point H at the Γ point, which indicates that the lattice strain induced by tip contact generates bulk phonons that originate deep beneath the outermost layer.

However, note that $\Delta(1/Q)$ in Fig. 3(a) is plotted against π/A, whereas the phonon dispersion curve $\omega(k)$ [18] is plotted against the wave number. Since the values of $\Delta(1/Q)$ closely coincide with those of LA in the Γ-K interval and TA (ZA) in the Γ-M interval of the phonon dispersion curve $\omega(k)$ [18], respectively, the magnitude of π/A corresponds to that of the wave number $2\pi/\lambda$ (λ: wavelength). Thus, it means that twice the oscillation amplitude almost equals to the wavelength: $2A \cong \lambda$.

Here, to consider the physical meaning of $2A \cong \lambda$, we assume a lattice strain on a one-dimensional chain on the substrate surface owing to tip contact, which corresponds to a sinusoidal type (shear type) of longitudinal wave [see Fig. 4(a) and Ref. [20]]. When the lattice strain d decreases, the dissipation energy $\varepsilon(d)$ released through the relaxation of the lattice strain increases, where $2d = \lambda$ (λ: wavelength of a wavelet) and lattice constant a is 0.15 nm. Thus, $\varepsilon(d)$ increases with π/λ, as plotted in Fig. 4(a) and Supplemental Material [14]. In contrast, Fig. 4(b) shows $\Delta(1/Q)$ vs π/A obtained in the experiment, where the direction of the oscillation amplitude A is not along the Γ to K and Γ to M directions in this case. Interestingly, it was found that $\varepsilon(d)$ in Fig. 4(a) is in reasonable agreement with the experimentally obtained characteristic of $\Delta(1/Q)$ in Fig. 4(b). In this Rapid Communication, it remains unclear why information of the phonon frequencies is detected

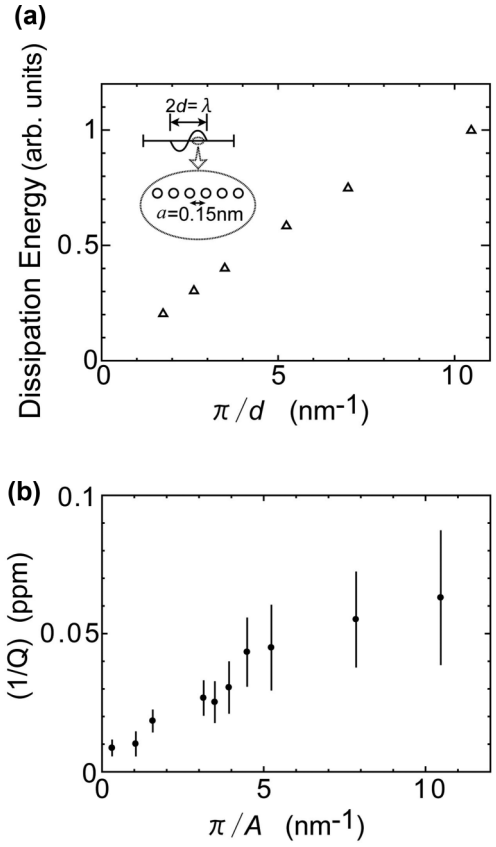

FIG. 4. Dissipation energy vs π/d and $\Delta(1/Q)$ vs π/A. (a) Dissipation energy vs π/d, where the longitudinal wave is depicted as a transverse wave. (b) $\Delta(1/Q)$ vs π/A obtained in the experiment.

in spite of the large difference between the tip oscillation frequency and the phonon frequency. This paradox comes from the complexity of the tip-surface contact mechanics, including various time scales ranging from picosecond to microsecond. Furthermore, the elastic contact diameter of the tip-surface interface is more than 10 nm under the condition of the loading force of 50–200 nN [21]. The finite dimension of the elastic contact diameter produces localized phonons which develop in the tip-induced strain field. Energy dissipation instantaneously occurs through the phonon which is along the direction of the tip-induced strain field. Then the QCM oscillates and moves in the reverse direction toward the opposite side; the lattice strain of a localized wave relaxes and propagates to both sides [22].

By choosing an appropriate oscillation amplitude of the QCM, we can generate acoustic waves with different wavelengths ranging from the atomic scale to the microscale depending on the strain size. Interestingly, this is also a method for generating phonons with different wavelengths, i.e., this method functions as a source of phonons. The resonance frequency used in this experiment was four orders smaller than the phonon frequency, but, as the resonance frequency approaches the phonon frequency, it may be necessary to consider anharmonic phonon-phonon interactions [4] because the occurrence of phonons affects the subsequently generated phonons.

We reported that the energy dissipation in the friction process occurs via acoustic phonons. We clarified how phonons

are generated and propagate with a frequency of approximately 5 MHz through the relaxation of lattice strain, in the friction process accompanied by a loading force and shear. This also leads to a method for generating phonons with different wavelengths. Acoustic phonons traveling in different directions can generate anisotropic friction with different amounts of energy dissipation in different directions [23]. By using the phonon dissipation curves in the friction process, in the future we could control energy dissipation and friction much more easily. Moreover, it may be possible to change energy dissipation channels through a transformation of acoustic phonons in the friction process into optical phonons using other interactions such as with laser beams.

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[1] J. Krim, Adv. Phys. **61**, 155 (2012).
[2] L. W. Bruch, A. P. Graham, and J. P. Toennies, J. Chem. Phys. **112**, 3314 (2000).
[3] M. Cieplak, E. D. Smith, and M. O. Robbins, Science **265**, 1209 (1994).
[4] B. N. J. Persson and A. I. Volokitin, J. Chem. Phys. **103**, 8679 (1995).
[5] J. B. Sokoloff, Phys. Rev. B **52**, 5318 (1995).
[6] E. Meyer, R. M. Overney, K. Dransfeld, and T. Gyalog, *Nanoscience: Friction and Rheology on the Nanometer Scale* (World Scientific, Singapore, 1998).
[7] M. Kisiel, E. Gnecco, U. Gysin, L. Marot, S. Rast, and E. Meyer, Nat. Mater. **10**, 119 (2011).
[8] L. W. Bruch, R. D. Diehl, and J. A. Venables, Rev. Mod. Phys. **79**, 1381 (2007).
[9] A. P. Graham and J. P. Toennies, Surf. Sci. **427-428**, 1 (1999).
[10] R. J. Cannara, M. J. Brukman, K. Cimatu, A. V. Sumant, S. Baldelli, and R. W. Carpick, Science **318**, 780 (2007).
[11] B. Borovsky, J. Krim, S. A. Syed Asif, and K. J. Wahl, J. Appl. Phys. **90**, 6391 (2001).
[12] D. Inoue, S. Machida, J. Taniguchi, M. Suzuki, M. Ishikawa, and K. Miura, Phys. Rev. B **86**, 115411 (2012).
[13] B. Borovsky, B. L. Mason, and J. Krim, J. Appl. Phys. **88**, 4017 (2000).
[14] See Supplemental Material at http://link.aps.org/supplemental/10.1103/PhysRevB.93.201401 for oscillation amplitude vs drive voltage.
[15] A movie appears in http://tf.nist.gov/sim/2010_Seminar/vig3.ppt of National Institute of Standards and Technology.
[16] R. W. G. Wyckoff, *Crystal Structures*, 2nd ed. (Wiley, New York, 1963), Vol. 1, pp. 280–282.
[17] A. Laschitsch and D. Johannsmann, J. Appl. Phys. **85**, 3759 (1999).
[18] A. Molina-Sanchez and L. Wirtz, Phys. Rev. B **84**, 155413 (2011).
[19] K. Miura and S. Kamiya, Europhys. Lett. **58**, 610 (2002).
[20] The spectrum density, energy density, and dissipation energy upon relaxation from a cosine strain (pull type) are also given in the Supplemental Material of Ref. [14].
[21] K. Miura, N. Sasaki, and S. Kamiya, Phys. Rev. B **69**, 075420 (2004).
[22] It is difficult to evaluate the energy dissipation into the tip in this experiment, although the recent experiments on the MoS_2 dot of less than 1 μm detected the optical phonons which are reflected from the dot edge and enter into the tip, which is quite different from the behaviors of the energy dissipation in this experiment.
[23] J. Y. Park, D. F. Ogletree, M. Salmeron, R. A. Ribeiro, P. C. Canfield, C. J. Jenks, and P. A. Thiel, Phys. Rev. B **74**, 024203 (2006).