Observation of High-Speed Microscale Superlubricity in Graphite

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A sheared microscopic graphite mesa retracts spontaneously to minimize interfacial energy. Using an optical knife-edge technique, we report first measurements of the speeds of such self-retracting motion (SRM) from the mm/s range at room temperature to 25 mm/s at 235 °C. This remarkably high speed is comparable with the upper theoretical limit found for sliding interfaces exhibiting structural superlubricity. We observe a strong temperature dependence of SRM speed which is consistent with a thermally activated mechanism of translational motion that involves successive pinning and depinning events at interfacial defects. The activation energy for depinning is estimated to be 0.1–1 eV.

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Interfaces capable of wearless relative motion at speeds in the meters-per-second range with very low energy dissipation are of crucial importance for a broad spectrum of applications in magnetic storage devices, such as hard disks, and micro- or nanoelectromechanical systems (MEMS, NEMS), such as motors and oscillators [1–6]. Currently, an air gap or a lubricating film is required to reduce to acceptable levels the friction and wear that would otherwise occur at a solid-solid contact during high-speed device operation [1,7]. However, it is difficult to implement the fluid layer configurations in microsystems [1,2], and air-gap suspension structures, as used in hard-disk read-write heads, reduce the rate of transferring information and degrade the signal-to-noise ratio [8]. Therefore, micro- and nanoscale components that can move at high relative speed in direct solid-solid contact with sufficiently low friction and wear could pave the way for a new generation of MEMS and NEMS devices.

Such practical applications as well as the relevance to basic scientific questions have motivated research in the field of superlubricity, or more precisely structural superlubricity [9]. This phenomenon involves relative motion of two incommensurate crystalline surfaces exhibiting superlow dry friction. Friction force microscopy and microtip manipulation have been used to study nanoscale superlubricity at sliding speeds below 10 μm/s [10–17].

Microscale superlubricity was first observed in the self-retracting motion (SRM) of graphite [18,19], where microscopic flakes of graphite, after being sheared from micron sized mesas fabricated on highly oriented pyrolytic graphite (HOPG), retract back onto the mesas. This effect is driven by a reduction of surface free energy. A similar phenomenon has been observed in telescoping multiwalled carbon nanotubes [20], and has stimulated extensive investigations of potential applications of high-speed SRM in the field of nanomechanical systems, such as gigahertz oscillators [4], nanoswitches [21], linear servomotors [22], and nonvolatile memories [23]. Theoretical studies of gigahertz oscillators indicated that SRM speeds in nanotube systems can exceed 100 m/s [24]. However, no experimental measurement of SRM speed has been reported so far.

In this Letter, we report first measurements of SRM speed over a wide range of temperatures using microscopic graphite mesas and an optical knife-edge technique. Highly reproducible SRM speeds from 10^{-4} m/s to 25 m/s have been measured at different sample temperatures. These speeds cover the range for practical application in micro and nanomechanical devices [1]. The highest speed we measured is close to the upper theoretical limit found for interfaces exhibiting perfect structural superlubricity, and more than 6 orders of magnitude higher than the speeds found in previous experimental studies of superlubricity. The measurements of temperature dependence of friction allow us to elucidate the mechanism of friction, and to achieve a huge increase in the maximum speed attained in the superlubric state. Our results have important implications for understanding the macroscopic properties of graphite and other solid lamellar lubricants.

Fabrication of the self-retracting microscopic graphite mesas by lithographic techniques was described in Refs. [18,19], following a method proposed in Ref. [25]. As sketched in Fig. 1(a), square graphite mesas capped with SiO_2 with linear dimensions (L) of 2 or 3 μm, SiO_2 cap thicknesses (h_c) in the range of 100–200 nm, and the heights of the graphite parts of the mesas (h_g) in the range of 100–200 nm have been fabricated on HOPG

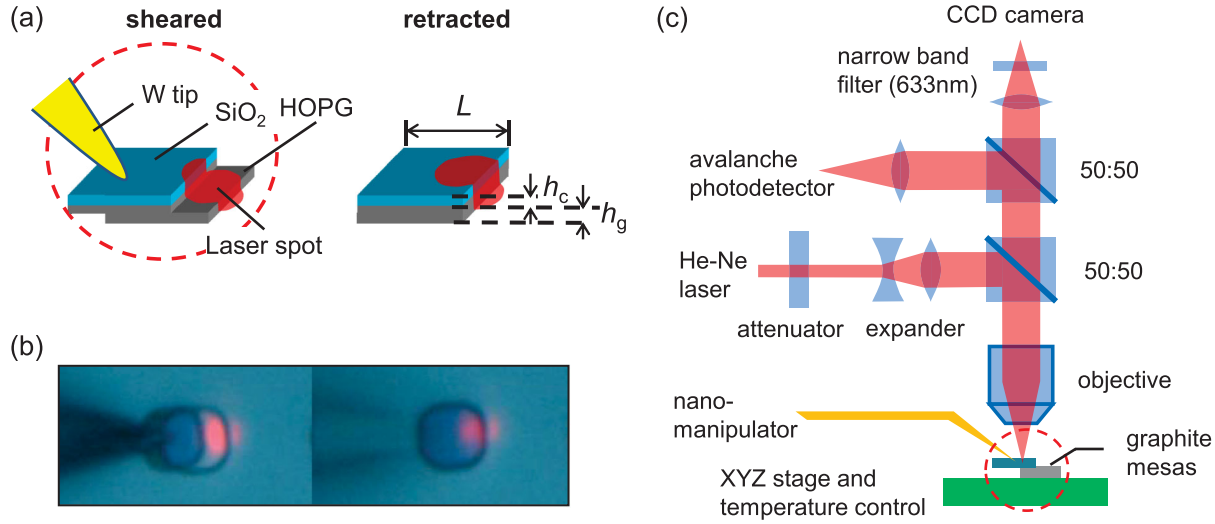

FIG. 1 (color online). (a) Structure of the graphite mesa and the scheme of the manipulation process; (b) shearing and retraction under optical microscope; and (c) experimental setup used for optical knife-edge method.

(Veeco, ZYH grade) substrate. The mesas have been fabricated in six batches, and each batch corresponds to a different piece of HOPG and contains about 400 mesas. The manipulation of mesas was performed under an optical microscope (Olympus, BX51; Hirox, OL-700 lens). We used a tungsten tip with an apex diameter less than 1 μm and controlled by a micromanipulator (Kleindiek, MM3A) to shear the graphite mesa under the SiO_2 cap as shown in Figs. 1(a) and 1(b). Releasing the tip from the cap, the sheared section of the graphite mesa, hereinafter referred to as graphite flake, slid back onto the bottom mesa, and aligned spontaneously with the mesa due to a reduction of the surface energy. According to our previous study [19], the sliding interface between the self-retractable graphite flake and the bottom mesa corresponds to an incommensurate twist boundary in the HOPG that provides structural superlubricity. As noted in the previous study, only a fraction of mesas from a given batch exhibit SRM. However, for those that can self-retract, the effect is highly reproducible. And for those that cannot, the flakes remain locked due to the commensurate alignment of the crystalline lattices. In our experiment, the SRM probability is 10%–30%.

To measure the SRM speed, a He-Ne laser beam (JDSU, 1125P) was focused to a micrometer-sized spot on the edge of the graphite mesa as illustrated in Figs. 1(a) and 1(b). Taking into account the difference between laser reflectivities on the exposed graphite and the SiO_2 cap, we have detected the motion of the retracting graphite flake by measuring the variation of the power of the reflected signal with an avalanche photodetector (Thorlabs, APD110A/M). The optical arrangement is sketched in Fig. 1(c).

Using a simple relation between the power of the reflected light and the displacement of the retracting flake (see Supplemental Material [26]) we have calculated the displacement curves. Two typical displacement curves, measured for the same mesa in ambient environment (relative humidity 38% $\pm$ 7%) at sample temperatures 26 °C and 40 °C are presented in Fig. 2(a). This mesa belongs to a batch, which we denote as batch 1, that has dimensions of $L = 3$ μm, $h_c = 120$ nm, and $h_g = 100$ nm. The plateau sections at the beginning and the end of the displacement curves define the initial sheared position and the final position where the flake is realigned, respectively. Figure 2(a) exhibits two important features of the SRM phenomenon. First, the retracting flake accelerates briefly and then maintains a constant velocity, V_m, for the main part of the retracting motion. Second, the retracting speed strongly depends on the sample temperature. For example, as shown in Fig. 2(a), the retracting speed V_m increases by an order of magnitude, for a temperature increase of just 14 °C.

The reproducibility of the SRM speed for a given mesa at a fixed temperature is very high, as illustrated in Fig. 2(b), where we show several displacement curves measured for a mesa from another batch, batch 2. This mesa exhibits the highest retraction speeds that we were able to detect. As we will discuss below, there is some variability in the SRM speeds measured for different mesas from the same batch, as well as large and systematic differences for mesas from different batches [see Fig. 3(a)].

The blue triangles in Fig. 3(a) show the temperature dependence of the SRM speed measured for batch 1. Each point corresponds to the average of several measurements with a spread indicated by the error bar. The blue filled triangles in Fig. 3(a) show the SRM speed, V_m, as a function of sample temperature, T, measured for a single mesa from batch 1. V_m increases approximately exponentially from 1 mm/s to 1 m/s as T increases from 26 °C to 160 °C. A similar exponential dependence has been observed for 20 other mesas from batch 1 [blue open triangles in Fig. 3(a)]. The red squares in Fig. 3(a) show

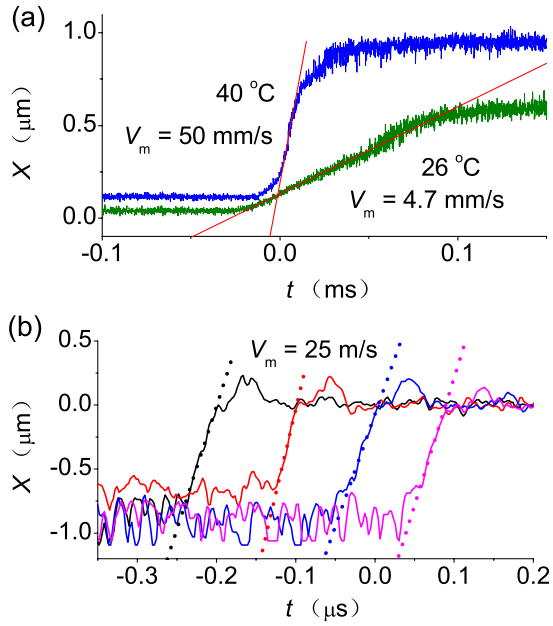

FIG. 2 (color online). (a) Two typical displacement vs time curves showing SRM of a graphite mesa at 26 °C and 40 °C, respectively. The curves are shifted slightly for comparison. (b) The displacement vs time curves for a mesa showing a maximum SRM speed of 25 m/s. Several SRMs for this mesa are shown, to demonstrate the reproducibility of the process. The speeds obtained from fitting the linearly rising section of the curve are 21 m/s, 25 m/s, 17 m/s, and 20 m/s from left to right.

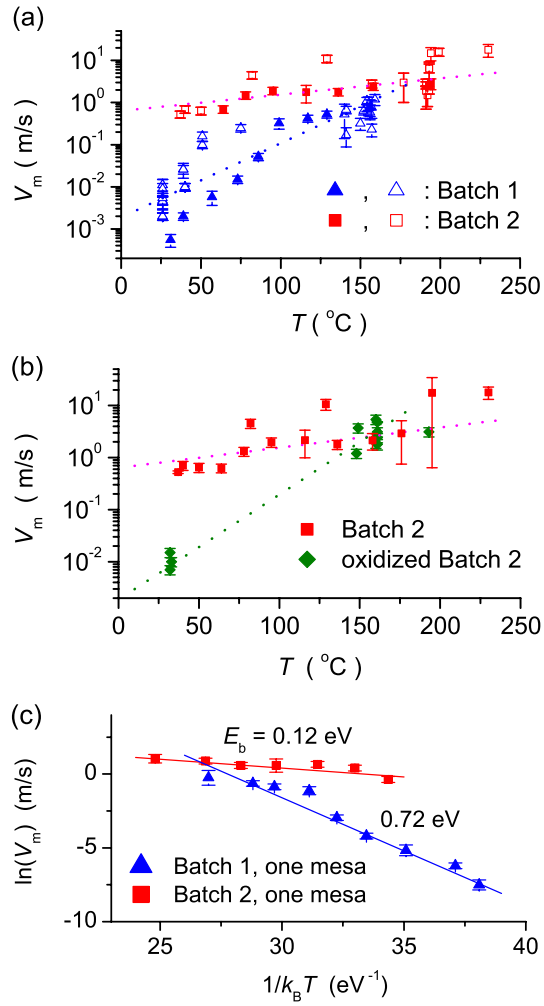

FIG. 3 (color online). (a) Temperature dependence of SRM speed, V_m, for mesas from two batches. The filled triangles and squares present measurements performed for one mesa from batch 1 and 2, correspondingly. The open triangles show the speeds obtained for 20 other mesas from batch 1. Similarly, the open squares display the speeds for 12 mesas from batch 2. (b) Results obtained for 8 mesas from batch 2 after oxidation at high temperature are indicated by green diamonds. Data for batch 2 before oxidation are shown for comparison. (c) Linear fits of $\ln(V_m)$ (m/s) to $1/k_BT$ for the data corresponding to the filled triangles and squares in (a).

the SRM speeds measured for batch 2, where all mesas have the same dimensions of $L = 3$ μm, $h_c = 100$ nm, and $h_g = 100$ nm. Here red filled squares represent results obtained for one self-retractable mesa, while red open squares correspond to another 12 mesas from batch 2. The SRM speeds of all mesas from batch 2 are much less dependent on temperature and consistently higher than the corresponding speeds for the mesas from batch 1.

In order to understand the origin of the strong temperature dependence of SRM, we compared SRM speeds measured in ambient air (relative humidity 32%) and in dry nitrogen (N_2) environments for 5 mesas from another batch, batch 3, with dimensions of $L = 2$ μm, $h_c = 200$ nm, and $h_g = 200$ nm. At room temperature (30 °C) the SRM speed increases by less than 1 order of magnitude when switching from air to a N_2 environment. At high temperatures, above 150 °C, the SRM speeds are the same, within error bars, in both environments. Thus, we conclude that, although the adsorption of water significantly affects SRM, it cannot fully explain the changes in SRM speed with temperature.

We have investigated the impact of quality of the edges of the mesas which we can alter by deliberately oxidizing them. This has been done for batch 2, by leaving it in ambient air at 650 °C for 1 min. Since the SiO_2 cap protects the graphite mesa surface, the oxidation only occurs at the edges of the mesas [27]. Comparison of the retracting speeds before and after oxidation is shown in Fig. 3(b), where the results after oxidation are presented by green diamonds. For temperatures close to room temperature, the SRM speed drops significantly after oxidation by nearly 2 orders of magnitude, while at high temperatures (above 150 °C), the speed after oxidation remains similar to that for the unoxidized mesas. This suggests that the distinction between the batches may be related to differences in the edge structures, as discussed in more detail in the Supplemental Material [26]. However, we cannot rule out other possible explanations for the dissimilarity between the batches. For example, differences in the

quality of the incommensurate twist boundaries that enable superlubricity could play a role.

To analyze the dynamics of the SRM, we use the equation of motion

$$mL^2\ddot{X} + F_f(\dot{X}, T) = F_{\rm ret}, \quad (1)$$

where $X(t)$ is the displacement of the retracting graphite flake as a function of time, $F_{\rm ret} = 2\gamma_g L$ is the retracting force [19], γ_g denotes the surface energy of the graphite basal plane recently measured to be about 0.095 $\mathrm{J/m^2}$ [28], m is the mass density per unit area of the sheared flake, and F_f is a friction force. Taking into account that the flake rapidly reaches a constant velocity regime, while $F_{\rm ret}$ remains constant during the whole interval of retracting motion, we can conclude that F_f increases with sliding velocity until it counterbalances $F_{\rm ret}$.

The upper bound for the SRM speed corresponding to frictionless motion, $F_f(\dot{X}, T) = 0$, can be deduced from Eq. (1), as $V_{\rm upper} = 2(\xi\gamma_g/m)^{1/2}$, where ξ denotes the ratio of the initial sheared distance to the mesa side length, L, and in our experiment ξ varies from 1/6 to 1/2. For the self-retractable mesas from batch 2, which have the SiO_2 of mass density 2.3 $\mathrm{g/cm^3}$ [29] and thickness $h_c = 100$ nm, we obtain an upper bound of $V_{\rm upper} = 29$ m/s. The maximum SRM speed we have observed is about 25 m/s in Fig. 2(b) at temperature of 235 °C. This is within 20% of the upper bound for frictionless retraction.

In the case of frictionless motion, the flake should overshoot the mesa by as much as it was initially retracted, and oscillate back and forth [4,18]. However, as we noted above, our system exhibits a frictional dissipation since the flake rapidly reaches a constant velocity during retraction. From the difference between the theoretical upper bound, $V_{\rm upper}$, and the measured V_m, the fraction of energy dissipated during retraction can be estimated as $1 - V_m^2/V_{\rm upper}^2$. Using this expression, we estimate that for $V_m < 1$ m/s, more than 99.8% of the available initial potential energy is dissipated during the retraction, and no detectable overshoot is expected. Even for the largest values of V_m, which we have observed, only a small overshoot of 0.2–1 μm is expected. An overshoot in the range 0.1–0.3 μm has been observed for the fastest mesas, as shown in Fig. 2(b).

To compare our results quantitatively with previous measurements of superlubricity, we need to estimate the kinetic friction force per unit area of the flakes. In the constant velocity regime, Eq. (1) gives

$$F_f(V_m, T) = 2\gamma_g L. \quad (2)$$

Estimating the contact area during retraction to be between $(1 - \xi)L^2$ and L^2 gives values of friction force per unit area of 0.06 MPa to 0.13 MPa ($\xi < 0.5$). This range is similar to measurements in other systems exhibiting superlubricity, including: 1.1 MPa for MoO_3 on MoS_2 [30], 0.1 MPa for C_{60} on NaCl [31], 0–1.0 MPa for Sb particles on graphite [14], 0–0.8 MPa for the MoS_2 interlayer [32], 0–0.3 MPa for incommensurate shells of multiwalled carbon nanotubes [10,12], and 0.02–0.04 MPa for the incommensurate interlayer of graphite mesa [19].

It is remarkable that we obtain such low values of kinetic friction at speeds over 6 orders of magnitude higher than in previous studies. However, the kinetic friction estimated here is still much higher than the theoretical value predicted, with phonon dissipation alone, for defect-free sliding of incommensurate surfaces. For graphite, the friction has been calculated to be approximately proportional to speed and about 10^{-5} Pa at 1 cm/s [33]. Theoretical studies also indicated that pinning at adsorbed molecules [34], atomistic defects, and edge structures [35] could suppress superlubricity between two incommensurate surfaces. Thus, reducing imperfections at the sliding surfaces and edges of the mesas could yet lead to a significant reduction of the observed kinetic friction.

The temperature dependence of the SRM speed, V_m, in Figs. 3(a) and 3(b) can be well approximated by a simple Arrhenius relation, indicating that the frictional sliding is assisted by thermal fluctuations. We propose that the observed thermally activated motion of the flake results from successive pinning and depinning events at atomistic defects or at edge structures of the sliding surfaces. Considering the constant retracting force and Eq. (2), an average energy barrier for depinning, E_b, can be estimated from the following expression [36]:

$$\ln V_m = \ln(V_0) - \frac{E_b}{k_B T}, \quad (3)$$

where T is the absolute temperature of the sample, k_B is the Boltzmann constant, and V_0 is a constant. A linear plot of $\ln V_m$ versus $1/k_B T$ presented in Fig. 3(c) yields an E_b of 0.12 and 0.72 eV for mesas from batch 2 and batch 1, respectively. The lower value of activation barrier for batch 2 is consistent with the higher velocities measured for mesas from this batch. The activation barrier is comparable with typical atomistic bonding energies [37]. In the Supplemental Material [26], molecular dynamics simulations show that a periodic array of potential barriers can originate from interactions of dangling functional groups at the edge of the mesa.

To summarize, self-retracting motion of sheared microscale graphite mesas exhibit remarkably high speeds, up to 25 m/s have been measured, which are close for frictionless retracting motion. A strong temperature dependence of the SRM speed is interpreted in terms of thermally activated translational motion. The optical technique developed here provides a new tool for quantitative measurements of superlubric systems with applications in MEMS and NEMS.

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