Observation of Superlubricity by Scanning Tunneling Microscopy

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Experimental evidence of superlubricity, the state of vanishing friction, is obtained by examining systems of sliding atomically clean surfaces by using ultrahigh vacuum scanning tunneling microscopy. The experimental results agree with theoretical predictions: Friction is not observed in the superlubricity regime in measurements capable of resolving a friction force of 3×10^{-9} N, whereas friction of 8×10^{-8} N, which is comparable to theoretical values, is observed in the friction regime. [S0031-9007(97)02468-X]

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Scientists have long been intrigued by the phenomenon of friction, which occurs when two objects come into contact and rub against each other. They have recently discovered a new regime of friction—superlubricity—where friction completely vanishes [1–3]. We have theoretically shown that this occurs even at strongly interacting interfaces at which realistic interatomic potentials, such as those in metallic bonds, operate [1,2]; other researchers have shown that it occurs only at weakly interacting interfaces [4–6].

The purpose of this study is to find experimental evidence for superlubricity in actual systems of atomically clean surfaces by using ultra-high-vacuum scanning tunneling microscopy (UHV-STM) [7]. To do this, we examined whether or not friction was observed in well-defined systems of clean surfaces when the experimental conditions satisfied those for the appearance of superlubricity or friction. We found that friction was not observed in the superlubricity regime in measurements capable of resolving a friction force of 3×10^{-9} N, whereas friction with a magnitude of 8×10^{-8} N, which is comparable to theoretical values, was observed in the friction regime. Thus, our experimental results agree with theoretical predictions, implying the existence of superlubricity.

We have postulated that friction forces completely vanish when, for example, incommensurately contacting surfaces slide against each other [1,2]. In such contact, the ratio between the lattice units of the surfaces is irrational along the sliding direction, so each individual atom receives different amounts of force from different directions. These forces consequently offset each other, resulting in zero friction. This offsetting of forces is made possible by the continuous motion of atoms, which is the basic principle behind superlubricity [1,2]. High dimensionality of systems is crucial for atoms to move continuously [2].

Two experiments [3,8] have suggested the existence of superlubricity. We observed that the friction forces on cleaved mica surfaces decreased as the contacting surfaces approached being incommensurate [3]. Martin *et al.* [8] found an ultralow friction coefficient (below 10^{-3}) in MoS_2 solid lubricant film and attributed it to the friction-induced lattice orientation change of an intercrystallite slip system, in which the basal planes were aligned in the sliding direction and disordered around the c axis.

In the present work, we directly observed superlubricity using UHV-STM. We used this method because it achieves "sliding in elastic contact" between atomically clean surfaces by utilizing the tunneling between the surface of the tip of a probe wire and the surface of a single crystal. Therefore, plastic deformation does not occur at sliding interfaces, as it does with conventional friction testing when surface asperities interact with each other under the application of a certain amount of load normal to surfaces. We measured the friction between the surfaces rather than the adhesion between them, as was done in previous STM studies [9,10].

In the present system, a clean Si(001) (n-type, 0.01 Ω cm) surface was one-dimensionally scanned against a clean W(011) surface at the tip of a polycrystalline tungsten wire (inset, Fig. 1) using a piezoelectric tube scanner. The tunneling gap between the W(011) surface at the tungsten

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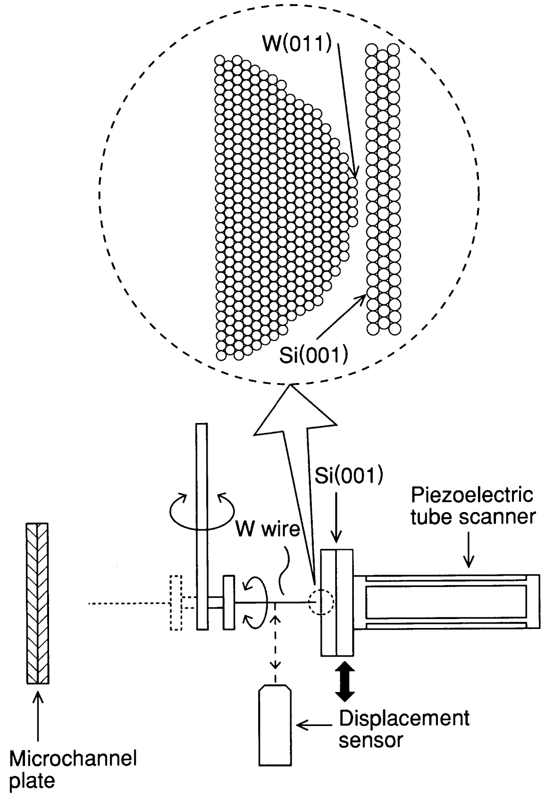

FIG. 1. Schematic illustration of UHV-STM friction measuring system in an ultrahigh vacuum with a base pressure of 10^{-9} Pa. The inset shows an atomic diagram of the tip and surface. We placed the measuring system on a vibration isolation air platform, which had a resonance at 1.2 Hz.

tip and the Si(001) surface was controlled by adjusting the tunneling parameters [11].

The area of the W(011) surface, i.e., the interaction area of contact, was estimated to be a few nanometers square, based on our observations of the tip with a scanning electron microscope (SEM), the same method as used by Kuroda *et al.* to observe a W(011) surface and other various crystal planes located near the tip [12]. The tungsten wire was also used as a flexible cantilever beam to probe the friction force between the W(011) and Si(001) surfaces. This force was determined by measuring the deflection of the beam using a focusing-error-detection optical displacement sensor [13] with a resolution of 2 nm. The friction forces to be measured were on the order of 10^{-7} N in the friction regime, based on calculated values [1]. Prior to scanning, we determined the commensurability, which is determined by the lattice misfit between the W(011) and Si(001) surfaces, by rotating the tungsten wire around its longitudinal axis (Fig. 1). Theoretical predictions indicated that superlubricity (friction) appears when surfaces come into contact incommensurately (commensurately). We then examined how the measured friction forces changed with the lattice misfit between the W(011) and Si(001) surfaces. The lattice orientation and cleanliness of the surfaces were determined by field electron microscopy (FEM) for the W(011) of the tip, and by low-energy electron diffraction (LEED) and Auger electron spectroscopy (AES) for the Si(001) [14].

The flat W(011) surface was made at the tungsten tip by heating (flashing) the tip to over 2300 K in a UHV environment by electron bombardment. The tungsten tip was fabricated by electrochemically etching a polycrystalline tungsten wire with a diameter of 0.25 mm [15]. Prior to etching, the wire was straightened by stretching it in a hot atmosphere. The straight wire could be set perpendicularly within 1° to the Si(001) surface by careful mechanical alignment. The FEM image shown in Fig. 2(a) is a typical image of a clean tungsten tip, as previously observed by Müller [16]. The image reflects differences in the work function of the crystal planes located at the tip, and this determines the lattice orientation of the W(011), shown in Fig. 2(b). The dark area at the center of the FEM image represents the W(011) because it has a high work function; its area was roughly estimated to be a few nanometers square from simple geometrical calculations.

We obtained clean Si(001) surface as follows: A carbon-free SiO_2 film was formed on a silicon wafer by immersing the wafer into several solutions [17]; the film was then removed by heating the wafer at 1173 K for 1 h in UHV by electron bombardment. Clear (2×1) LEED patterns, as shown in Fig. 2(c), were routinely obtained. The AES measurements showed the typical spectra for clean silicon and no carbon spectra on the Si(001) surface.

Fortunately, commensurate contact between W(011) and Si(001) is obtained by appropriately aligning the lattice orientations of their surfaces [Figs. 2(b) and 2(d)] in such a way that the $[11\bar{1}]$ direction of the W(011)

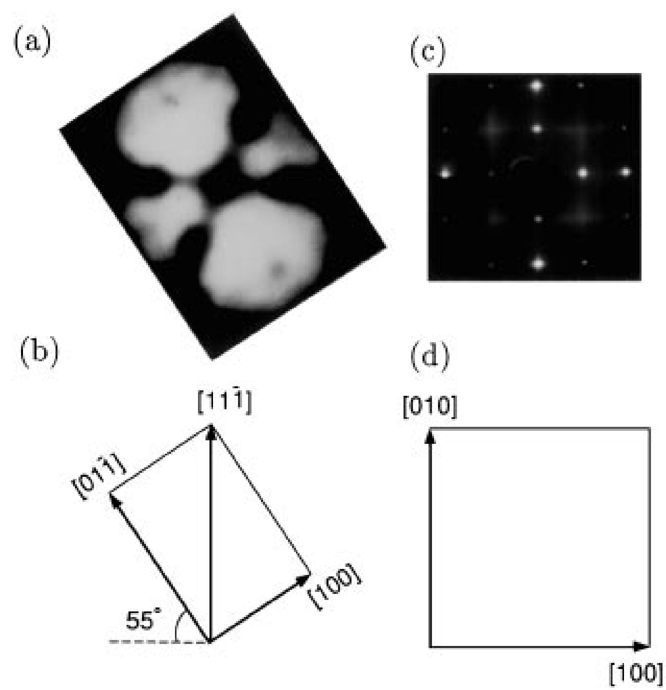

FIG. 2. (a) FEM image of clean tungsten tip, (b) lattice orientation of W(011), (c) LEED pattern of clean Si(001), and (d) lattice orientation of Si(001).

corresponds to the [010] direction of the Si(001). The ratio between the lattice unit along the $[11\bar{1}]$ direction of the W(011) and that along the [010] direction of the (2×1) superstructure of Si(001) becomes rational in this alignment. Incommensurate contact, on the other hand, is easily obtained at arbitrary lattice misfits.

We measured the friction that occurred between W(011) and Si(001) surfaces when they came into contact commensurately and incommensurately. Figure 3(a) shows the data obtained during scanning when the lattice orientations of the contacting surfaces were aligned commensurately along the sliding direction. The scanning amplitude was 100 nm and the scanning frequency was 0.5 Hz. The average tunneling current was maintained at the set value of 1 nA at a bias voltage of -100 mV applied to Si(001). The wire deflection signal oscillated with a period corresponding to that of the scanning, i.e., the wire was actually bent by the friction between the surfaces. The clear FEM image of the tip [Fig. 2(a)] obtained after scanning shows that the tip was not damaged by the scanning and that sliding in elastic contact was achieved. The friction force was determined to be 8×10^{-8} N by multiplying the measured wire-bending deflection of 50 nm by the lateral spring constant of 1.5 N/m. The measured friction force is comparable to that calculated when sliding surfaces interact via short-range interfacial interactions [1].

Figure 3(b) shows the data obtained during scanning when the lattice orientations were aligned incommensurately along the sliding direction in such a way that, for example, the $[01\bar{1}]$ direction of the W(011) corresponded to the [010] direction of the Si(001). The tunneling parameters, scanning amplitude, and scanning frequency were the same as those in the commensurate case. The wire deflection signal was very different from that in the commensurate case. No oscillation of the wire deflection signal was observed in this measurement, which can resolve a wire deflection displacement of 2 nm. The corresponding friction measurement resolution was estimated to be 3×10^{-9} N. As in the commensurate case, the tip was not damaged by scanning. Thus, no friction was observed at this friction-measurement resolution. We also did not observe any wire deflection oscillation in any of the other incommensurate contacts we examined.

The friction forces between W(011) and Si(001) surfaces were very sensitive to the tunneling gap. Figure 4 shows the wire deflection signals at two bias voltages (-100 and -900 mV) and at a tunneling current of 1 nA. At -100 mV, under the commensurate contact condition, using the same tip and Si(001) surface, the wire deflection signal oscillated, showing that friction occurred. Both dynamic and static friction occurred; the latter occurred when the tip stuck to the Si(001) surface.

The question is, what would happen when the bias voltage was decreased to -900 mV to cause the tip and Si(001) to separate. We found that the oscillation disappeared even though the contact was commensurate. The

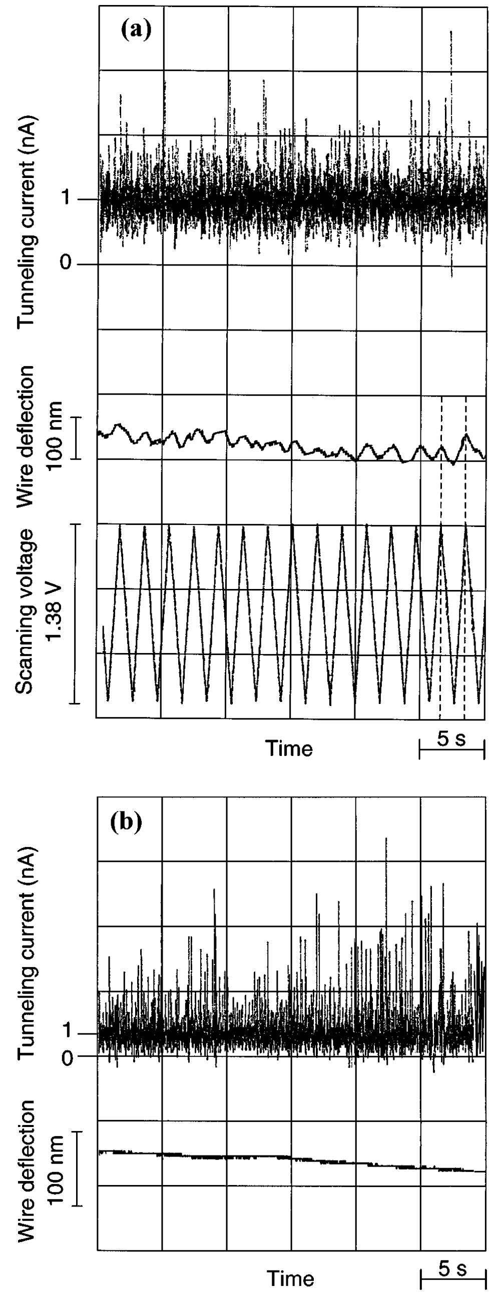

FIG. 3. Scanning in (a) commensurate and (b) incommensurate contact conditions. (a) The tunneling current between the tungsten tip and the Si(001) surface, the deflection of the tip, and the scanning voltage applied to the piezoelectric tube scanner as a function of time. (b) The tunneling current between the tungsten wire and the Si(001) surface and the deflection of the wire as a function of time [the scanning voltage was the same as in (a)].

gap increased by about 10 Å, as measured from the change in z voltage applied to the tube scanner to control the gap. The tunneling gap was thus comparable to the interatomic distance at the tunneling parameters at which the upper curve was measured, and the interacting forces between W(011) and Si(001) were short range.

The change in the gap caused by varying the bias voltage at a certain tunneling current was the same for both

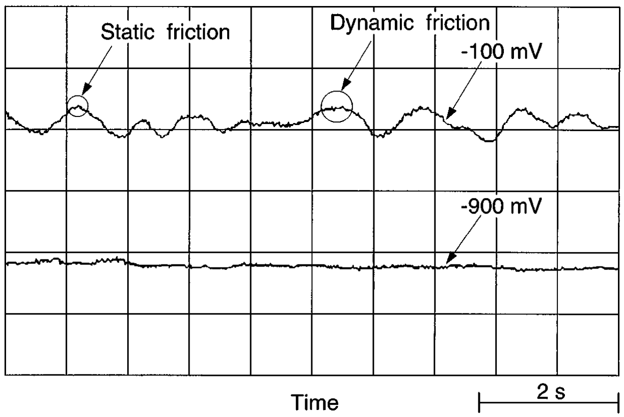

FIG. 4. Dependence of wire deflection signal on bias voltage applied to Si(001) surface.

commensurate and incommensurate contact based on our measurement of z-voltage change at various bias voltages. For example, the gap decreased by about 2 Å when the bias voltage was increased from -100 to -50 mV, and it increased by about 3.5 Å when the bias voltage was decreased from -100 to -200 mV at a tunneling current of 1 nA in both cases. Accordingly, the apparent tunneling barrier is the same for both the commensurate and incommensurate cases, showing that the distance between the W(011) and Si(001) surfaces can be set to the same value for both commensurate and incommensurate contact.

Theoretical studies showed that friction appearing between atomically flat crystal surfaces is irrelevant to a load applied normal to sliding surfaces because the energy barrier resisting a surface sliding a unit distance is unlikely to change when the normal load is changed by changing the interfacial distance. Our calculations actually showed that there exists a case in which friction completely vanishes even when strong adhesion operates under the application of force normal to sliding surfaces.

With our method, we will be able to determine if the adhesive interaction is repulsive or attractive by simultaneously measuring the friction and adhesion by using a flexible wire that can bend horizontally and vertically.

In summary, we measured friction as a function of the commensurability of the contacting surfaces by using UHV-STM and found that our experimental results agreed with theoretical predictions. Friction was not observed in the superlubricity regime when the surfaces contacted each other incommensurately with a friction measurement resolution of 3×10^{-9} N. Friction of 8×10^{-8} N, which is comparable to theoretical values, was observed in the friction regime when the surfaces contacted each other commensurately. It has been observed that the friction forces in some single crystals change with the crystallographic direction of sliding, and these changes were interpreted in terms of the preferred slip system in which lattice slip is likely to occur on a primary slip plane [18,19]. However, the changes in friction force observed here due to commensurability were much larger, by a factor of 15, than those observed in such single crystals. We thus conclude that the observed dependence of friction force on the commensurability of the contacting surfaces implies the existence of superlubricity.

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