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Atomic-scale stick-slip processes on Cu(111)

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Friction force microscopy experiments in ultrahigh vacuum allow the observation of atomic-scale stick-slip processes on Cu(111) surfaces. The lateral stiffness of the contact and the electrical characteristic of the junction are discussed. It is suggested that the tip is covered by copper forming a contact of a few atoms with the Cu(111) surface. The mean friction exhibits a clear dependence on the scan velocity.
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I. INTRODUCTION

In 1987, Mate *et al.*[1] presented atomic-scale stick-slip motion of a tungsten tip sliding on graphite in ambient pressure with normal forces between $10^{-8}-10^{-5}$ N. A rather linear behavior with a friction coefficients as low as $\mu=0.012$ was determined. Subsequent experiments have confirmed the occurance of atomic-scale stick slip on ionic crystals in ultrahigh vacuum.[2] The lateral force images showed the lattice of the equally charged ions. However, individual point defects could not be observed. According to lateral force imaging at step edges and continuum elasticity calculations, the contact diameter was estimated to be of the order of nanometers. It was found that the range of loading, where stick slip is observed, is limited to some nanonewtons. Higher forces would lead to plastic deformation of the crystal.[3] Atomic-scale stick slip could also be observed on the highly reactive surface of Si(111)7×7. In this case, the probing tip had to be covered by polytetrafluoroethylene (PTFE). Other tip materials (Si, Pt, Au, Ag, Cr, Pt/C) were found to be ineffective and led to strong adhesion and destructive processes during imaging between tip and sample, which was related to chemical reactions in the contact region.[4] Molecular-dynamic simulations of metallic surfaces have indicated that phenomena, such as ploughing, cutting, chip formation and neck formation can be observed.[5–8] However, recent work by Sørensen *et al.* has shown that atomic-scale slip might also exist on metals.[9] The present paper is dedicated to the microscopic study of friction on a clean metallic surface, Cu(111).

II. EXPERIMENT

The combined scanning tunneling microscopy atomic force microscopy (STM/AFM) instrument has been described previously.[2] The beam deflection method is used to measure both lateral and normal forces. The polished (111)-face of a copper single crystal was prepared by repeated cycles of sputtering with argon ions (600 eV) and annealing at 850 K. The resulting flat terraces of 50–250 nm width, separated by monatomic steps, are shown in Fig. 1(a). This image was recorded in the STM-mode using a conductive tip and cantilever made from *n*-type silicon. Typical mean tunneling currents are $\overline{I}_t=35$ pA. The impurities, which appear as black dots in Fig. 1(a) are identified by Auger spectroscopy to be sulfur atoms which diffuse to the surface during annealing. By limiting the last annealing step to a few minutes at 700 K, the sulfur content could be reduced below the detection limit of our standard Auger electron spectrometer. It cannot be excluded that single sulfur atoms are involved in the imaging process in contact mode. However, the resulting sulfur coverage of about 5×10^{12} m^{-2} is too small to act as a significant lubricant in friction measurements.

In order to investigate the frictional forces at low-loading forces, a silicon cantilever with low normal and torsional spring constant ($k_N=0.024$ N/m, $k_T=16.5$ N/m) has been selected. The spring constants have been determined from geometrical factors and the resonance frequency.[10] From large scan images in contact mode, shown in Fig. 1(b), we conclude that the surface can be imaged rather stable. However, it is observed that small particles are moved by the action of the tip, typically starting at step edges.

The surface of the cantilever is covered with a thin native oxide layer. This also applies for the tip after scanning in contact with the sample surface. Current vs. bias voltage measurements as the one shown in Fig. 2 were performed after prolonged scanning. They produce I-V-characteristics typical for the tunneling resistance of a metal-oxide-semiconductor system:[11] for negative bias voltage electrons simply tunnel from the metal into the valence band while for positive bias voltages the semiconductor band structure distorts the I-V-characteristic. These curves did not change upon unloading up to −1 nN and, therefore, did not allow to draw conclusions on the elastic behavior of the contact as it

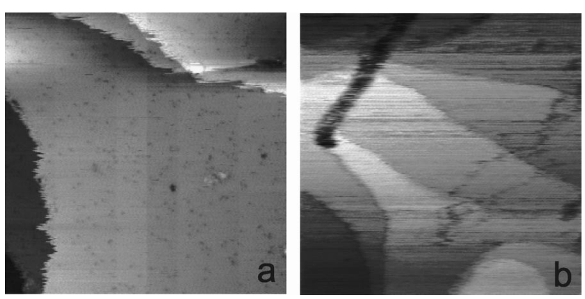

FIG. 1. Overview images of the Cu(111) surface. (a) Image taken in the STM mode (92 nm×92 nm), showing terraces of 50–250 nm width, separated by monatomic steps. The black dots represent single atom sulfur impurities. (b) Contact-mode force microscopy image (114 nm×114 nm) of the same sample.

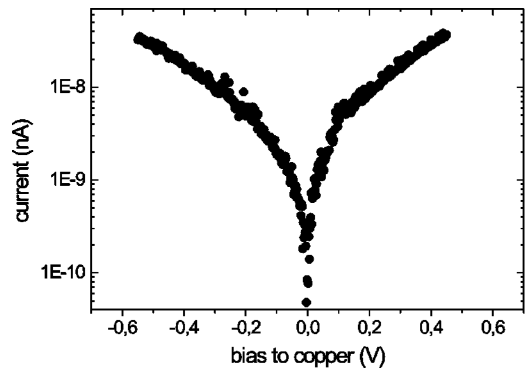

FIG. 2. I-V-characteristic of the tip in contact with the sample. The absolute value of the current is given in a logarithmic scale.

has been reported for other conductive systems.[12]

High-resolution images (Fig. 3) reveal clear atomic-scale stick slip with the hexagonal symmetry of the Cu(111) surface and a lattice constant of 2.5 Å. Stick-slip friction has been achieved not only for soft cantilevers but also for stiffer cantilevers with a normal spring constant of $k_N=26$ N/m and a torsional spring constant of $k_T=4475$ N/m [Fig. 3(b)]. For the measurements an external load of 0.6 and 10 nN, respectively, was applied. The height regulation feedback loop was adjusted very slow in order to compensate for long-term drift but not to follow any signals correlated with the stick-slip process. Typical adhesive forces were around 15 nN estimated from the force needed to retract the tip from the surface after scanning. Usually it was necessary to scan a larger range of about 40 nm first and then to zoom to 3-5 nm in order to obtain atomic stick-slip behavior.

Scanlines of the lateral force along a (110)-direction are presented in Fig. 4. The calibration of the lateral force has been described by Meyer *et al.*[13] The mean friction force $\overline{F_L}$ is given by the area inside the friction loop divided by the scanned distance. It is determined to be $\overline{F_L}=0.48$ nN for the softer and $\overline{F_L}=1.28$ nN for the stiffer cantilever. This is an excellent agreement taking into account the total load, which is the sum of the higher external load in the latter experiment and the adhesive force. The torsional spring constants of the two cantilevers differ by a factor of 270 and, therefore, this result demonstrates a validating reproducibility of the experiment. From the slope of the sticking part of these friction loops the lateral stiffness of the contact can be estimated.[14]

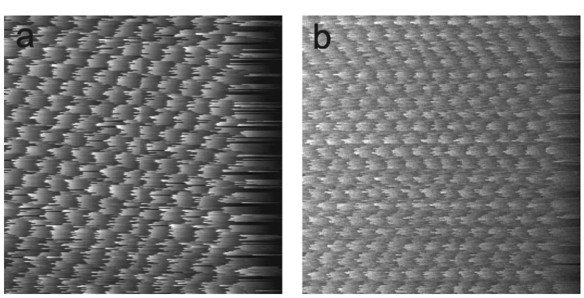

FIG. 3. Atomic stick-slip behavior of the lateral force measured on a Cu(111) surface. Dark correponds to low forces, bright to high forces. Two different spring constants were used: (a) Image size 3 nm×3 nm, $k_n=0.01$ N/m. (b) Image size 3.5 nm×3.5 nm, $k_n=24$ N/m.

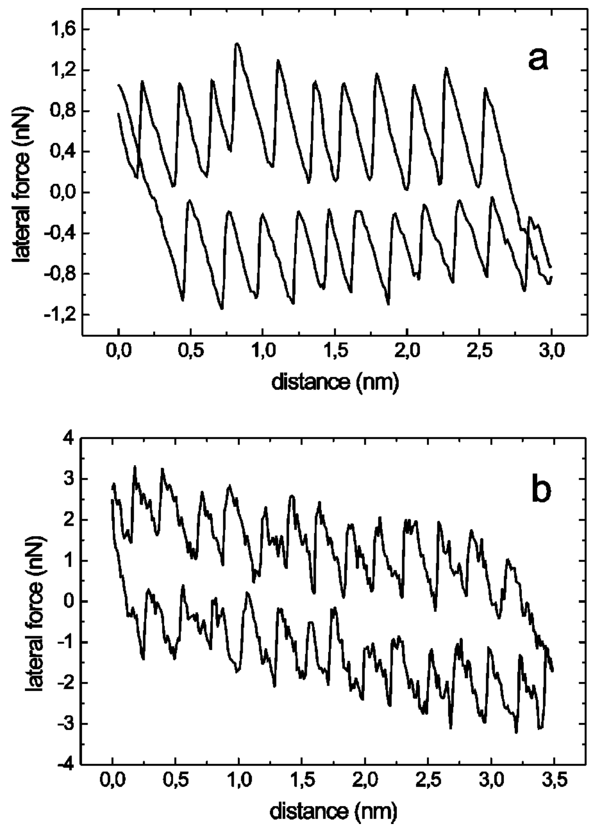

FIG. 4. Lateral force along a (110) direction. Two different spring constants were used: (a) $k_n=0.01$ N/m. (b) $k_n=24$ N/m.

For the two different cantilevers effective lateral spring constants of $k_{eff}^x=5.3\pm0.4$ N/m and $k_{eff}^x=8.8\pm1.0$ N/m, respectively can be determined. Taking into account the torsional spring constant of the cantilevers k_T and the elastic compliance of the probing tip $k_{tip}^x=84$ N/m, estimated from finite element analysis,[15] the lateral contact stiffness k_{con}^x can be determined

$$\frac{1}{k_{con}^x}=\frac{1}{k_{eff}^x}-\frac{1}{k_{tip}^x}-\frac{1}{k_T}. \quad (1)$$

The resulting values of $k_{con}^x=8.6\pm1.1$ N/m and $k_{con}^x=9.8\pm1.3$ N/m are in good agreement indicating that a quite similar type of contact area determined the frictional behavior in both experiments. No significant dependence of the mean frictional force on the load was found for external loads between -0.4 and 0.6 nN once atomic stick-slip behavior could be observed with the softer cantilever.

The dependence of the frictional force on the scan velocity as measured with the stiffer cantilever is presented in Fig. 5. Each point represents an average over an image of 3.5 nm×3.5 nm. We observe a clear increase of the frictional force with scan velocity and have chosen a logarithmic scale for the latter in order to point at the almost linear dependence on the logarithm of velocity. The extension of such experiments to higher scanning velocities is currently limited by the speed of data acquisition. For very slow measurements, images are subject to a distortion due to the drift of the piezo actuators. Furthermore, on the time scale of 30 min

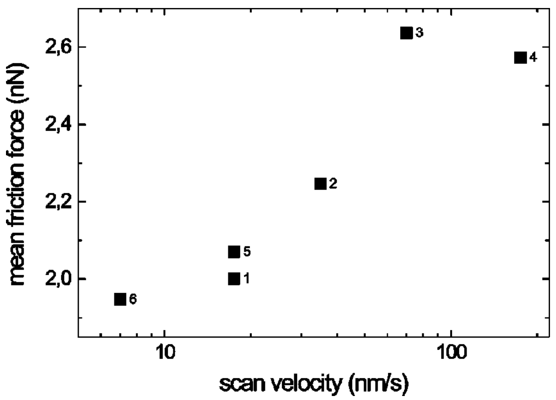

FIG. 5. Velocity dependence of atomic-scale friction on Cu(111). The labels indicate the temporal order of measurement.

we often observe substantial changes of the contact, which foreclose comparison with images taken before.

III. DISCUSSION

Having found atomic-scale stick-slip behavior on the soft metal copper, the size and shape of the contact area between tip and surface are key features for an understanding of the underlying process. In the framework of continuum mechanics the radius a of the contact can be estimated from the lateral contact stiffness to be $a=k_{con}^{x}/8G^{*}$, G^{*} being the effective shear modulus of the contact.[14] With $G_{Si/Cu}^{*}=16.5$ GPa we end up with a contact radius of only 0.07 nm. A contact area smaller than one atom indicates that this kind of analysis is not appropriate for the current experiment and that an explanation for the softness of the contact has to be looked for in its physical nature. Likewise the I-V-measurements do not allow a conclusion on the contact area since the absolute current depends exponentially on the unknown thickness of the oxide layer.

Recently, two simulations of metallic tips scanning over a metal surface have been reported. Both studies predict a stick-slip motion on atomic-scale including wear phenomena which would prevent stable scanning with a friction force microscopy (FFM).[9,8] As an exception, Sørensen *et al.* predicted a stick-slip motion with atomic periodicity for a Cu-tip sliding on a Cu(111) surface. The authors simulated a pyramidal copper tip of eight dynamic layers and a Cu(111) surface of five dynamic layers with a commensurate contact area of 5×5 Cu atoms.[9] The lateral contact stiffness of $k_{contact}^{x}=41.7$ N/m found for this model tip would in the above analysis correspond to an contact area of 0.4 nm^2 for $G_{Cu/Cu}^{*}=14.5$ GPa, smaller but still in some agreement with the contact area of 1.4 nm^2 put into the simulation. In this analysis, we have used the total lateral stiffness of the model tip as lateral contact stiffness.

Comparing the simulations of Sørensen *et al.* with our experimental results we propose that the Si/SiO_2-tip is covered with some layers of copper, which forms a contact with the Cu(111) surface. This contact is commensurate in the sense that all Cu atoms at the tip which are in contact with the Cu(111) surface contribute with the same phase to the stick-slip process. Similar to the model tip of Sørensen *et al.*, this configuration exhibits a reduced lateral stiffness compared to the contact considered in continuum mechanics. For example, the mean lateral force of $\overline{F_L}=0.48$ nN measured for the softer cantilever would correspond to a contact area constituted by six atoms according to the simulations.[9] The hypothesis of a small copper tip at the silicon tip is supported by several experimental findings: First, the current through the contact is independent of the external load while retracting the tip. During formation of the copper tip a certain area of the tip is covered by copper. This area determines the tunneling current through the oxide layer, while the resistance of the copper neck is orders of magnitude smaller than the tunneling resistance. Therefore, changes of the contact resistance upon unloading do not show up in the I-V curves. Second, a contact in the form of a small copper tip may also explain that no dependence of the mean friction force during stick-slip motion on the external load could be observed. In the simulations Sørensen found a friction coefficent of only 0.03 for atomic-scale stick slip. In the small experimentally accessible range of total load no significant dependence of the frictional force can be detected. In a recent study of metallic necks, it is found that for neck diameters smaller than a few nanometers, as in our case, homogenous slip becomes dominant compared to dislocation-mediated slip for larger contacts.[16] Such homogenous slips might be helpful to obtain stick slip motion with atomic periodicity experimentally. Third, we recall the finding that scanning over larger ranges has to preceed measurements of atomic-scale stick slip. We suspect that the scan over a larger range helps to form the copper contact between the silicon tip and the Cu(111) surface, which then exhibits stick-slip friction with the observed low-lateral contact stiffness. The formation of the contact as well as healing of the Cu(111) surface would be supported by the mobility of copper atoms at room temperature, which can even be enhanced by the interaction with the tip. This mobility also leads to the frizziness of the monatomic steps observed in Fig. 1(a).

Sørensen *et al.* have also emphasized that a stiff instrument is needed to observe all details of the mechanical behavior of small necks under stress, while for a softer cantilever the movement of the contact is not necessarily proportional to the externally applied movement and, therefore, some smaller changes in the configuration will not be registered.[16] In Fig. 4, the curves, which were measured with the stiffer cantilever exhibit not only the stick-slip motion with the periodocity of the Cu(111) surface but also some smaller force instabilities in between. These instabilities could be due to rearrangements of the contact during the stick phase, which are not enforced during measurements with a soft cantilever. However, it is difficult to extract quantitative information from the smaller instabilities since the signal-to-noise ratio in friction measurements is very low for such stiff cantilevers.

There have been very few studies of the velocity dependence of FFM measurements. One reason is the limited range of velocities that are experimentally accessible as pointed out above. Several mechanisms resulting in a velocity dependence of stick-slip behavior are conceivable: If the slip process can be thermally activated, an increased velocity could decrease the mean frictional force by increasing the local temperature of the contact. This process has been found in the simulations of Sørensen *et al.* for rather high-scanning velocities and low temperatures.[9] On the other hand, the frictional force could rise with scan velocity when the characteristic time for a thermally activated slip process becomes longer than the typical duration of the sticking to one position. We suggest that the latter situation is given in our experiments, where a temperature rise due to scanning is most probably negligible. The smaller frictional forces at lower velocities reflect the relaxation of the stressed system by thermally activated slip processes. A detailed description of this thermodynamic approach together with experimental results obtained on NaCl surfaces are subject of a forthcoming paper.[17] The logarithmic dependence of frictional forces in this velocity regime has also been experimentally found and thermodynamically discussed in a study of polymer films.[18] The delay of the tip with respect to the support[9] and inertial effects[19] have been proposed to contribute to the velocity dependence of stick-slip motion. However, we believe that these contributions take effect only for much higher scanning velocities than the ones used in this study.

IV. CONCLUSION

Atomic-scale stick-slip behavior has been found in friction-force microscopy experiments on Cu(111) surfaces. A small lateral contact stiffness, a very small load dependence, and the I-V characteristic of a metal-insulator-semiconductor junction lead us to the conclusion that a small copper tip is formed at the scanning silicon tip. The experimental results are in good agreement with simulations for such kind of tips.[9] We found an increase of the mean frictional force with increasing scanning velocity during stick-slip motion, and interprete this effect as a result of a competition between thermally activated and externally enforced slip processes.

ACKNOWLEDGMENTS

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