Abrasive Wear on the Atomic Scale

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A scanning force microscope in ultrahigh vacuum has been used to realize and detect atomic-scale abrasion on KBr(001). The continuous time evolution of the lateral force under scratching reveals that the wear mechanism is due to the removal and the rearrangement of single ion pairs. The debris is reorganized in regular terraces with the same periodicity and orientation as the unscratched surface, as in local epitaxial growth. The applied load has a strong influence on the abrasive process, whereas the scan velocity is less relevant.

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With the introduction of the scanning force microscope (SFM) it became possible to study dissipation processes in small sliding contact areas down to the atomic scale [1–3]. When the instrument is operated in contact mode, several regimes from frictionless sliding to permanent wear are observed, depending on the applied load. In this way, SFM has been successfully used to characterize microwear processes on materials of technological interest, as silicon for magnetic head sliders [4], polymers for electronic packaging and liquid crystals displays [5], or solid lubricants such as transition metal dichalcogenides [6]. Only a few studies have been reported on atomic-scale wear, mainly due to the fact that the debris removed from the surface adheres strongly to the tip, reducing the resolution of the instrument and making investigations irreproducible. The environment, e.g., humidity, plays an important role in tribological measurements on small scales [7]. Thus, if possible, a controlled atmosphere or, better, ultrahigh vacuum (UHV) conditions are desirable.

In the wear experiments reported thus far, ionic crystals represent an interesting class of materials. Lüthi *et al.* observed that KBr can be scratched by UHV-SFM at very low loads without a significant reduction in the resolution [8]. Carpick *et al.* reported the formation of increased areas of friction induced by a strong tip-sample contact on KF, KCl, and KBr in UHV, and they suggested a possible relation to the formation of defects caused by the SFM tip [9].

In this Letter, we show how the debris extracted from the KBr(001) surface by a silicon tip is reorganized on the atomic scale. The same tip was used for both scratching and observing the surface, without noticeable change in the resolution after thousands of scratches. Thus, the analysis was not limited to a qualitative description of the nanowear process, but quantitative information on the dissipative forces involved in atomic-scale abrasion could also be extracted and compared under different scan conditions.

The experiment was realized with a homebuilt SFM of beam-deflection type [10] operated at room temperature at a pressure $p < 10^{-10}$ mbar. The forces between tip and surface were evaluated with the procedure described by Lüthi *et al.* [11]. A soft cantilever with normal and torsional spring constant $c_n = 0.087$ N/m and $c_t = 48.9$ N/m was used with tip apex radius nominally below 15 nm. The KBr sample was cleaved *in situ* and annealed at 150 °C for 2 h to remove charges. Before scratching, the surface consisted of atomically flat terraces, a few tens of nanometers wide.

Figure 1(a) shows a lateral force image acquired across a region, which was previously scratched with a normal force $F_N = 27.9$ nN and a scan velocity $v = 100$ nm/s.

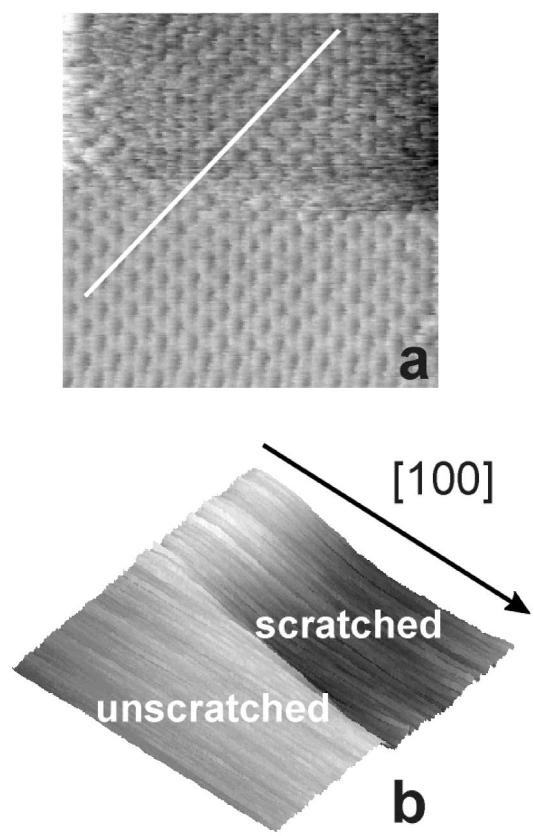

FIG. 1. (a) Lateral force and (b) topography image of KBr(001) after a single scratch along the [100] direction with $F_N = 27.9$ nN and $v = 100$ nm/s. Frame size: 6.5 nm. The white line reveals the phase shift between the atomic periodicity of adjacent atomic layers.

The lower part of the frame represents the undisturbed surface, whereas the upper part was modified by the tip. The atomic lattice is resolved in both parts; as usual only one kind of ions is detected. The topography acquired at the same time [Fig. 1(b)] reveals that the lower part of the frame is flat, whereas the upper part appears smoothly undulated, with a total height difference of 0.25 nm. The left part of the scratch has the same height of the undamaged region and the right part is one monolayer lower. This can be deduced from the straight line in Fig. 1(a), which reveals the shift between ions with the same charge belonging to two adjacent (001) layers. Figure 2 shows a series of lateral force images acquired at the end of a long groove, where an amphitheatric mound was piled up. The groove was created by scratching 256 times with $F_N = 20.9$ nN and $v = 300$ nm/s. Both on the mound and inside the groove, the ions are arranged in terraces exhibiting the same periodicity and orientation as the unscratched regions.

To investigate the dependence of wear vs time, we scratched across a single line for a long time at fixed load and velocity (5120 scans at $F_N = 11.2$ nN and $v = 2.5$ μm/s). The mean lateral force $\langle F_L \rangle$ increased continuously from F_0 to F_∞ as a function of the number of scratches N, according to the law,

$$\langle F_L \rangle = F_0 e^{-N/N_0} + F_\infty(1 - e^{-N/N_0}), \qquad (1)$$

where $F_0 = 1.0$ nN, $F_\infty = 14.6$ nN, and $N_0 = 5.45 \times 10^3$ (Fig. 3). Equation (1) is easily derived assuming that the friction force is proportional to the contact area, and that the mean contact area $\langle A \rangle$ increases with the number of scratches as

$$\frac{d\langle A \rangle}{dN} = \frac{A_\infty - \langle A \rangle}{N_0}, \qquad (2)$$

where A_∞ is the limiting area by which the applied load is balanced without wear to occur.

In addition, we studied the surface damage caused by scratching with different loads and velocities. Figure 4(a) shows five pits obtained after 256 scans on small areas 5×5 nm^2 large with different normal forces F_N (from 5.7 to 22.8 nN) at fixed velocity $v = 25$ nm/s. A detailed image of one of the pits is shown in Fig. 4(b). When the load is increased the pits become wider and deeper and the number of removed terraces varies from 1 to 6. In contrast, Fig. 4(c) shows three pits produced with fixed load $F_N = 14.0$ nN and different velocities v (from 25 to 100 nm/s); the number of removed terraces is now approximately the same (4 or 5). In all cases, the pits are accompanied by lateral mounds, one or two monolayers high. Figure 5 shows friction loops recorded in forward and backward scans when the pits were realized. The stick-slip appears more irregular compared to

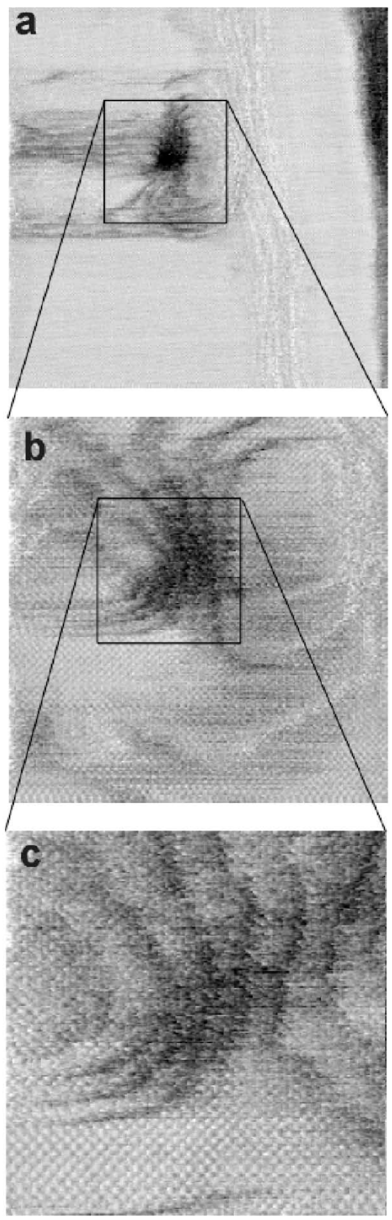

FIG. 2. Lateral force images acquired at the end of a groove produced by 256 scratches with $F_N = 20.9$ nN and $v = 300$ nm/s. Frame size: (a) 60 nm, (b) 25 nm, (c) 15 nm. The ordered structure of the debris is visible.

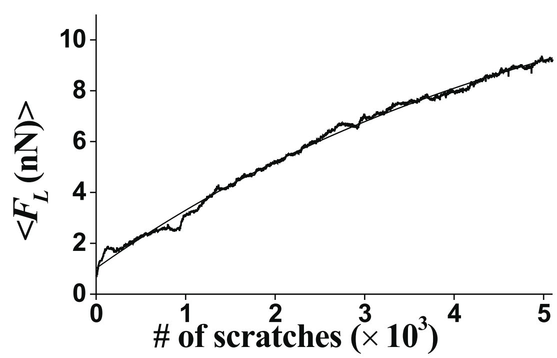

FIG. 3. Mean value of the lateral force on a 500 nm line during repeated scratching with $F_N = 11.2$ nN and $v = 2.5$ μm/s.

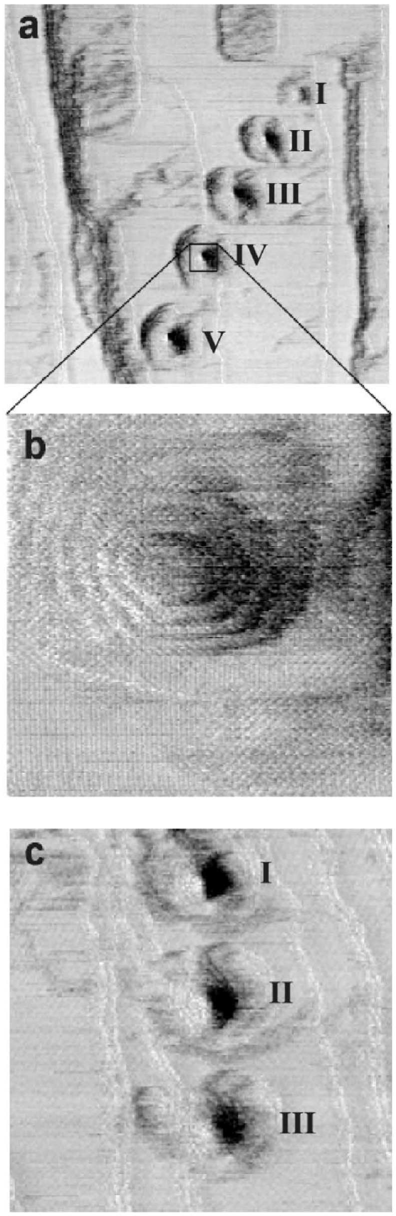

FIG. 4. (a) Lateral force images of pits and mounds produced by 256 scratches on 5×5 nm^2 areas with $F_N = 5.7$, 10.0, 14.3, 18.6, and 22.8 nN (up to down) and $v = 25$ nm/s. Frame size: 150 nm. (b) Lateral force image of the fourth pit. Frame size: 20 nm. (c) Lateral force images of pits and mounds produced by 256 scratches on 5×5 nm^2 areas with $v = 25$, 50, and 100 nm/s (upper to lower) and $F_N = 14.1$ nN. Frame size: 74 nm.

atomic stick-slip observed without wear [12]. The slope $k_{\text{eff}} = |dF_L/dx|$ increases for higher loads, as well as the contact radius, which is roughly proportional to k_{eff} [13]. A larger contact area is also responsible for the overall tilt of the friction loops at higher loads, due to the fact that the tip apex moves less than the 5 nm displacement of the cantilever end.

The energy dissipated when the pits were drilled, E_{diss}, is given by the area of the friction loops (Fig. 6). The total dissipation increases with load up to $F_N \approx 18$ nN and it slightly decreases with velocity; the saturation of the dissipated energy at high load is due to the reduction of the length scanned by the tip. The number of ions extracted from the pits can be estimated from the lateral force images. For example, about 850 couples of ions were removed to drill the second pit in Fig. 4. A similar number of ions forms the corresponding mound, and we conclude that the debris did not diffuse far away during the scratch. The dissipated energy is $E_{\text{diss}} = 19.7$ keV, which, assuming a binding energy $E_{\text{bond}} = 6.87$ eV [14], corresponds to the removal of about 2850 atomic bonds. Thus, if all the ions are removed pair by pair, only a minor part of the dissipated energy went into wear (about 30%). However, in case of partial recovering of the damaged surface, the number of displaced ions observed is certainly less than the number removed while scratching. The slight variation of the mound shape in the series of frames in Fig. 2 suggests that such a process is possible.

The abrasive character of the wear process is clearly demonstrated by the continuous time evolution of the lateral force under scratching (Fig. 3). The hypothesis that the ions are removed and released by pairs or by small clusters of ion pairs is supported by the following observations: (i) No dramatic crack events were observed in thousands of scans, and (ii) the regular arrangement of the deposited material resembles the epitaxial growth of thin ionic films, where the ions are piled up pair by pair [15]. The ion removal can also be recognized in the irregularity of the friction loops in Fig. 5, where the number of displaced ion pairs is comparable to the number of slip events, as the ions were detached when the tip jumps from one stick position to the next one. The adsorption of ion pairs from an ionic surface to a sharp tip was observed by Shluger *et al.* by molecular dynamics (MD) in the case of a MgO tip sliding on the NaCl(001) surface [16]. The transfer, due to the local charge at the tip end, occurs in both directions, leading to a redistribution of the ions on the surface.

Although the ions are reasonably detached pair by pair, they must be dragged collectively by the SFM tip to get the result in Fig. 1, for example, which was realized with only one scratch. A recent MD simulation by Komanduri *et al.* considered an infinitely hard tool sliding along the [100] direction of the Al(001) surface [17]. Even at very low penetration depth (0.1 nm), several aluminum atoms are adsorbed and dragged by the indenter at the same time, which makes possible the transfer of a large amount of debris over distances of several lattice constants. The material adsorbed on the tip does not reveal any structure; the release of the debris is not considered in these simulations.

In conclusion, we have observed abrasion of KBr(001) down to the atomic scale. The damaged surface is smoothly modified by the tip pressure and the debris is rearranged in an epitaxylike process, which leads to the creation of mounds with the same structure as

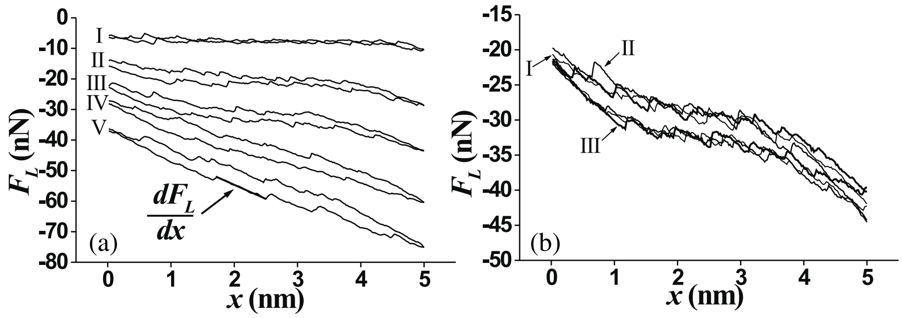

FIG. 5. Friction loops acquired during the 100th scan to produce the pits (a) with $F_N = 5.7$ to 22.8 nN and $v = 25$ nm/s, (b) with $v = 25$ to 100 nm/s and $F_N = 14.1$ nN.

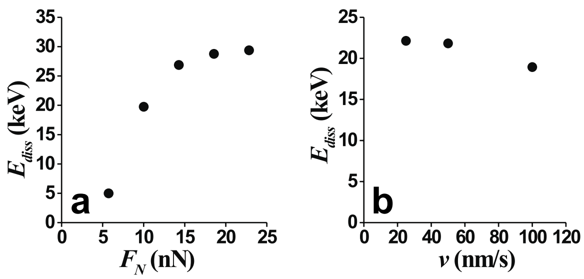

FIG. 6. Total energy dissipated to drill the pits (a) with $F_N = 5.7$ to 22.8 nN and $v = 25$ nm/s, (b) with $v = 25$ to 100 nm/s and $F_N = 14.1$ nN.

the underlying surface. The depth of grooves and pits increases at high load, whereas the velocity does not affect significantly the scratching process. A comparison between the experimental data and the few theoretical studies available on this topic suggests that the KBr ions are detached pair by pair, and moved by the tip to form ordered structures. Local epitaxial growth of debris material may become a valuable tool for future nanotechnological device fabrication, e.g., local growth of an insulator.

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