ELSEVIER

Surface Science 380 (1997) 427–433

surface science

Enhanced surface atomic step motion observed in real time after nanoindentation of NaCl(100)

A. Folch [a,*], P. Gorostiza [b], J. Servat [b], J. Tejada [a], F. Sanz [b]

[a] *Departament de Física Fonamental, Universitat de Barcelona, 08027 Barcelona, Spain*
[b] *Departament de Química Física, Universitat de Barcelona, 08027 Barcelona, Spain*

Received 26 September 1996; accepted for publication 6 December 1996

Abstract

The nanometer-scale indentation of a crystalline surface produces nanostructures that evolve on a timescale that is inaccessible to existing imaging methods for the vast majority of surfaces. We have been able to observe the dynamic evolution of the freshly cleaved surface of a NaCl(100) crystal after indentation with an atomic force microscope (AFM) in air. Here we present sequential AFM images featuring vertical atomic resolution which show that atomic terrace motion is greatly enhanced by the AFM indentation. Moreover, some of the nanometric features generated by the indentation become reassimilated into the crystalline surface structure of the surroundings of the indentation over a period of time of the order of several minutes. © 1997 Elsevier Science B.V.

Keywords: Alkali halides; Atomic force microscopy; Surface diffusion; Surface relaxation and reconstruction; Surface structure, morphology, roughness, and topography; Tribology; Water

1. Introduction

The atomic force microscope (AFM) [1] is a powerful tool for nanotribology and the investigation of surface dynamics on a nanometer scale in real time. In this study, the AFM tip is used both to indent the surface of a NaCl(100) crystal and to image its evolution (namely, the atomic step motion) following indentation. The contact interaction between the tip and the sample during indentation causes displacement of material and its subsequent rearrangement or partial "damage healing". However, the evolution of a surface following AFM nanoindentation is elusive to observation because, for most materials, the rearrangement of material happens extremely fast, i.e. as the tip is being retracted. For metals, the timescale has been calculated to be of the order of a few picoseconds [2]. The rearrangement of self-assembled alkanethiol monolayers after compression with an AFM tip gives rise to viscoelastic forces between the tip and the monolayer which only take several tens of milliseconds to relax after load [3]. An exceptional example, presented here, is the rearrangement of the crystalline surface of NaCl after nanoindentation in air. We made nanometric indentations on NaCl(100) surfaces by pushing a cantilevered AFM silicon tip against the sample. A significant part of the surface rearrangement, as shown below, is slow enough to be observed with the AFM right after indentation.

*Corresponding author. Fax: +1 617 253 8806; e-mail: afolch@mit.edu

PII S0039-6028(97)00038-1

2. Experimental procedure

We used commercially available AFM microcantilevered tips [4] in a non-conventional way. Designed for tapping-mode AFM imaging [5], we also used them to perform the tip-to-sample mechanical contact. In the tapping mode, the tip is oscillated at resonance ($\sim$300 kHz) and strikes the surface gently on each oscillation cycle with a peak vertical force of the order of tenths of a nanonewton [6]. The amplitude of oscillation ($\sim$10–100 nm) is used as a proximity signal between the tip and the surface. For our application, tapping-mode imaging is superior to contact-mode imaging in the sense that shear forces between the tip and the sample, which could induce dragging of material as the tip scans the surface, are negligible. In contact mode and air ambient, on the other hand, the minimum applied force is determined by uncontrollable capillary forces between the tip and the sample. Furthermore, the high stiffness of the tapping-mode cantilevers ($\sim$300 N/m) makes them suitable for applying large indenting pressures when brought into contact with the sample. To do so we drive a tip-to-surface vertical approach (without scanning) beyond the "point of contact", which we arbitrarily define as the point where the oscillation magnitude drops to zero. An estimate of the applied force is computed as the cantilever stiffness times the distance traveled by the sample beyond the point of contact. Our indentation force values ($\sim 10\ \mu$N) depend upon the definition of the point of contact, but the latter is ambiguous in a range of only a few angstroms above the surface because the vibration amplitude drops dramatically within that range. The fact that the contact area is undetermined prevents the force values from being translated into pressure values but it does not affect our findings. Our vibration–isolation scheme allowed us to obtain images with vertical atomic resolution, i.e. monoatomic steps were visible.

Previously, Hillner et al. [7] induced and observed the growth and dissolution of calcite under aqueous solution and Shluger et al. [8] observed that AFM-excavated grooves in NaCl widen and become refilled with time. Very recently, Shindo et al. [9] reported monoatomic step motion on NaCl(100) and found that it is highly dependent on ambient humidity and "frozen" below 50% humidity. We found, in addition, that it can be enhanced by local surface modification. We did not attempt to control the ambient humidity because our goal was to define an experimentally simple procedure to observe surface rearrangement of material at a given constant humidity. Therefore, only the relative step mobility before as compared to after the indentation is relevant to the purpose of this paper. For all practical purposes the ambient humidity in a closed room over the course of an experiment (typically less than 1 h long) can be assumed to be constant. Since we observe moderate step motion for the surfaces prior to indentation, from Ref. [9] we estimate our humidity values to be 50–60%. Similarly to Shindo et al., our experiments were done at room temperature ($\sim$25°C).

In a typical experiment, a NaCl crystal is freshly cleaved in air to expose the (100) facet and placed immediately onto the AFM sample stage for room-temperature air-ambient imaging. We start by imaging a $\sim 7\ \mu\text{m} \times 7\ \mu\text{m}$ flat portion of the surface so that several atomic steps are visible. Smaller scan areas do not reveal enough atomic terraces to provide a global picture of the motion and larger areas take too long to scan or yield noisy images, presumably from light tip crashes during scanning. Then one or more indentations are made at approximately the center of the image with the Si tip and the evolution of the surface is observed by taking a sequence of images (4 min frame acquisition time) with the same tip. Between each indentation and the actual start of image acquisition there is a lapse of $\sim$2–3 s. The indentation forces are typically three orders of magnitude larger than the peak forces applied during tapping mode imaging. We never observed a loss of resolution after indentation, which indicates that the indentation process does not damage the Si tip significantly.

3. Results and discussion

A representative example of an indentation experiment is shown in Fig. 1. The force constant

of the cantilever was 29 N/m [10]. Fig. 1a depicts the surface prior to indentation. Monoatomic as well as multiatomic steps are revealed. Images 1b, 1c and 1d are taken right after three consecutive indentations, each on the same location and at a greater indentation force F than the previous one: $F_1 = 9.2 \times 10^{-6}$ N, $F_2 = 1.1 \times 10^{-5}$ N, and $F_3 = 1.4 \times 10^{-5}$ N, respectively. After image d (i.e. after the third indentation), which we define as the time origin, the images show the temporal evolution of the surface with no further modification. An important observation is that, in general, repeated indentations at increasing depths on the same spot generate altogether lower and wider debris or mounds than one deep indentation. Since high debris or mounds must be avoided in order to visualize monoatomic steps, the penetration forces were optimized for each run by trial and error.

(We must point out first that there are two noise artifacts that could be mistaken as atomic steps. The faint diagonal line running from top to bottom of some images is due to electrical noise. The fact that it runs on top of the hole in image 1b is a rather unfortunate coincidence because it resembles a dislocation step. Also, the horizontal streaks along the scan direction arise from feedback instabilities at the beginning of the line scan.)

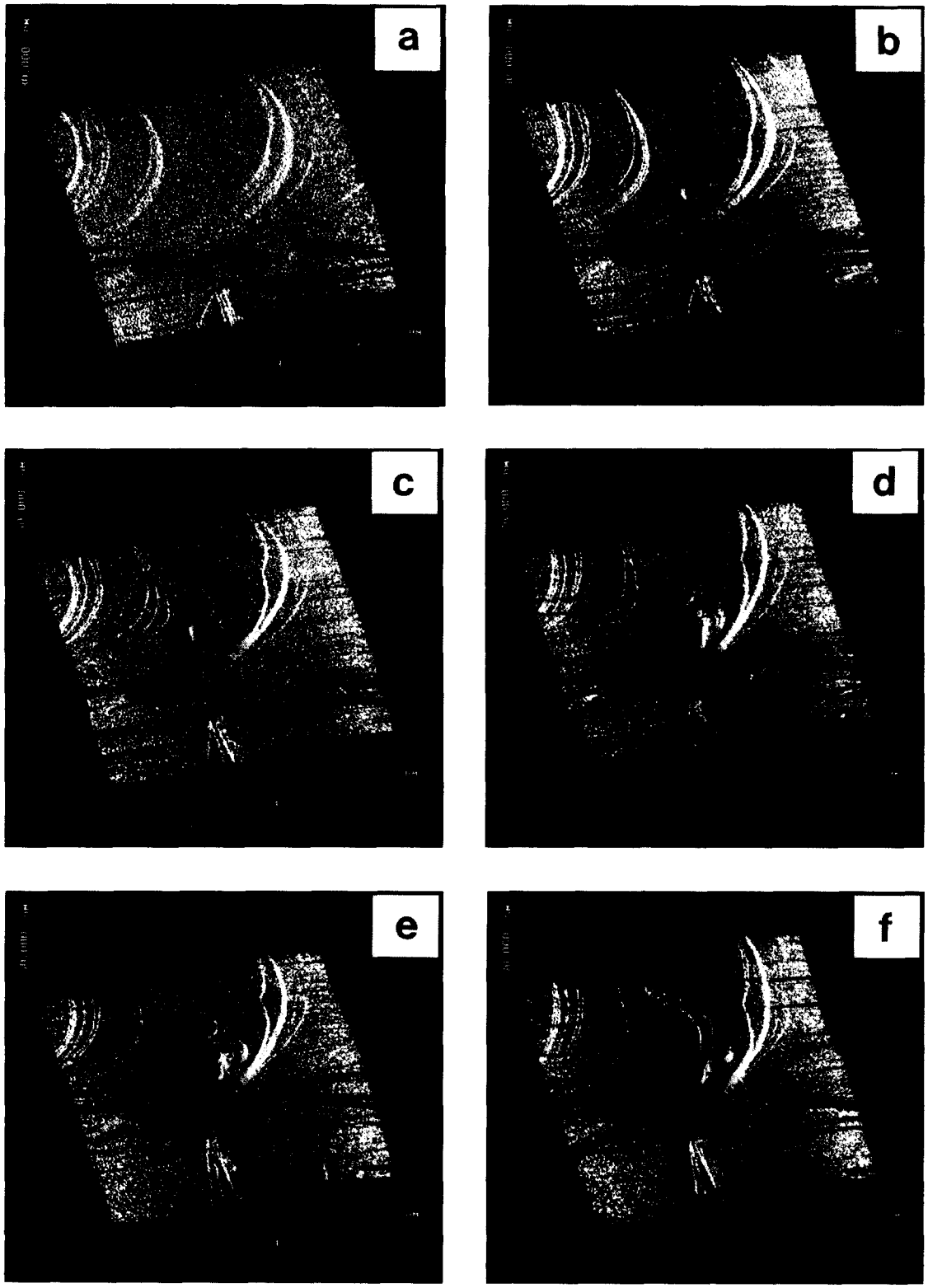
Some steps are pinned at certain locations. These pinning sites, probably due to a defect or an impurity, appear not to follow the motion of the terraces around them and are thus a good reference point to visualize the changes on the surface. The terrace motion is slow enough that, at this scale, terraces do not advance noticeably in the time scale of a line scan, which results in the observed smooth steps.

A global look at the sequence of images straightforwardly reveals three trends in the evolution of the surface: (1) the activity of the surface, albeit difficult to quantify, increases remarkably right after the third and deepest indentation (i.e. from image 1d onward); (2) it is highest around the indentation whereas a few microns away from it step motion proceeds relatively slowly; and (3) that it gradually slows down. Note, in particular, that images 1d and 1e, taken right after the third indentation, show dramatic differences around the hole and are separated by only 5 min, whereas the last two images are separated by 19 min (see figure caption) and show very few changes at random spots. At the end of the sequence, the activity of the surface is back to normal and, even within the proximity of the indentation, it is no longer characterized by intense rearrangement but instead by slow and apparently random drifting of the terrace steps.

In principle, the tip interacts with the sample not only during indentation but during imaging as well. However, we did not observe any effect of the imaging parameters (scan speed and interval between images) on terrace motion. This is expected from the low tip-to-sample interaction during imaging in the tapping mode.

Images 1a, 1b and 1c deserve close attention. By comparing images 1a and 1b we note that the surface atomic steps are virtually unaffected by the first indentation ($F_1 = 9.2 \times 10^{-6}$ N). The few slight differences may well be attributed to random terrace motion caused by surface diffusion. This is surprising, since the indented hole occupies a significant portion of the area of a terrace. On the other hand, the second indentation, made at a slightly larger force ($F_2 = 1.1 \times 10^{-5}$ N), has a distinct effect. Special attention must be paid to the set of four atomic steps right above and to the left of the first indentation in image 1b. In image 1c we note that these four terraces have been attracted towards the hole and that the closest one has even

Fig. 1. Set of 12 AFM images showing the evolution of a NaCl(100) surface following three nanoindentations with the AFM tip on the center of the scan area. All images are projected in stereoscopic view and low-angle simulated illumination in order to better reveal the atomic steps. The straight edge-to-edge lines are noise artifacts. Imaging parameters: scan size 7 μm × 7 μm, "tapping" mode, 4 min frame acquisition time. The images show: (a) surface prior to indentation; (b) after first indentation, applied force $F_1 = 9.2 \times 10^{-6}$ N; (c) after second indentation, $F_2 = 1.1 \times 10^{-5}$ N; (d) after third indentation, $F_3 = 1.4 \times 10^{-5}$ N; this image defines $t = 0$. and subsequent images show the evolution of the surface as a function of time t: (e) $t = 5$ min; (f) $t = 9$ min; (g) $t = 19$ min; (h) $t = 24$ min; (i) $t = 35$ min; (j) $t = 41$ min; (k) $t = 55$ min; (l) $t = 74$ min.


a
b
c
d
e
f

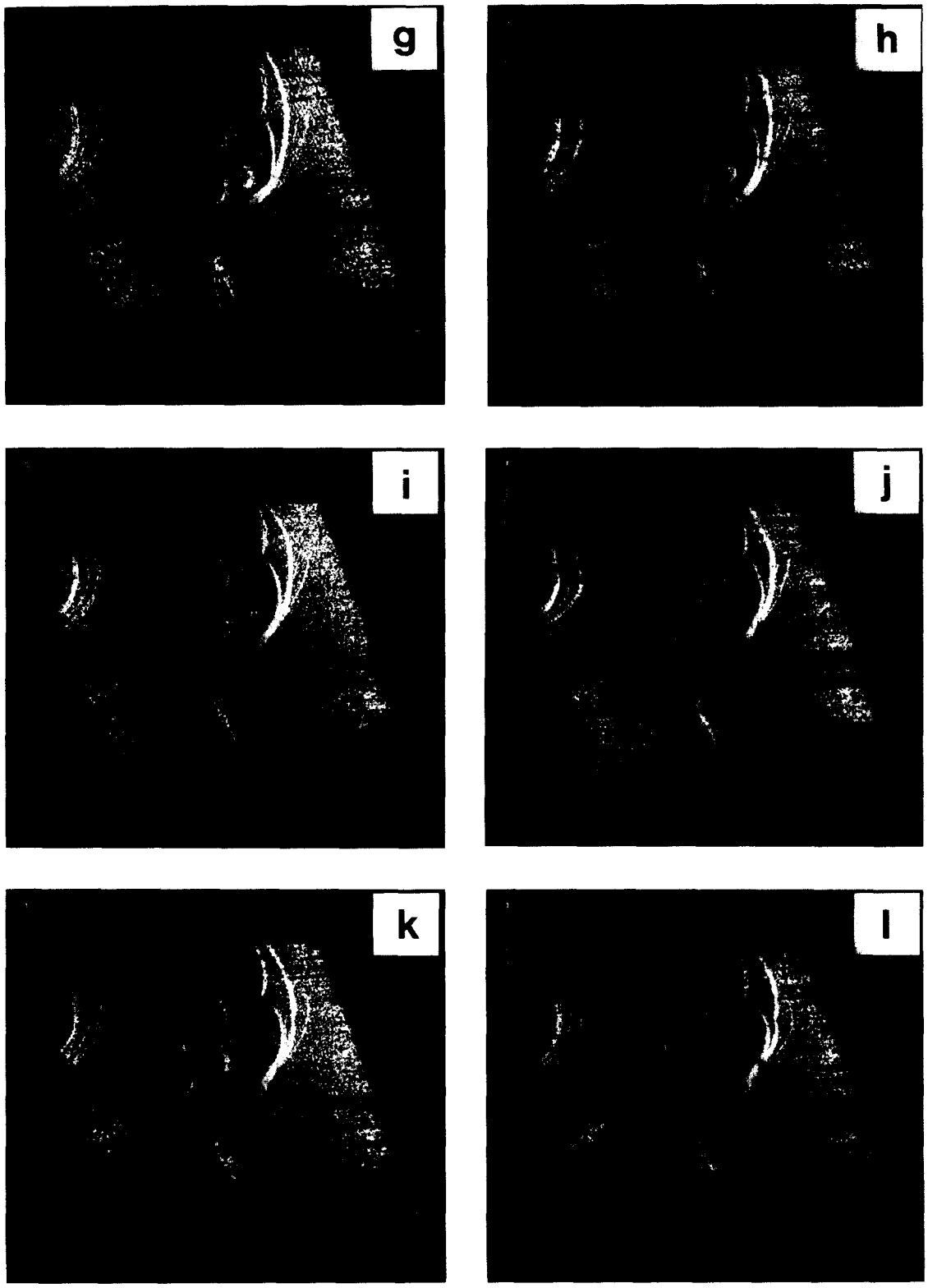


Fig. 1. (*continued*)

been pinned or "captured" by the hole. This change, contrary to the changes observed after image 1d, is very sudden and it could probably be explained by a stress-relief mechanism (resulting from the indentation) alone [11], even in the absence of adsorbed water-assisted transport (see discussion below).

Perhaps the most striking feature is the mound or hillock created around the hole in image 1d, right after the third indentation ($F_3 = 1.4 \times 10^{-5}$ N). No trace of crystalline organization is visible in the mound surface, which means that either the displaced material is amorphous or that it is formed of nanocrystallites too small to be resolved due to the large ($\sim 7\ \mu$m) scan size or due to convolution with the AFM tip. In any case, in the subsequent images the mound "gives birth" to a set of highly active crystalline terraces, in particular to the left and to the right of the hole. This observation is unique in the sense that it shows formation of crystalline structures on a nanometer scale and in real time. By the time image 1h is completed, the hole has captured all four terraces that were right above and to the left of the hole in image 1b. As the last of them is captured, we also witness at the same time its fusion with one of the new-born terraces at the left of the hole.

In general, as the features flatten and the surface energy becomes lower the step motion slows down. Furthermore, as exemplified in this sequence of AFM images, we have consistently observed that holes tend to widen over time. Plausible explanations could be that the material from the rim is attracted towards the lower surface energy location at the bottom of the hole, dragged by water-assisted transport into the hole and/or simply pushed into the hole by the tapping tip.

Since these experiments were not carried in a controlled environment, we can only conjecture why the surface activity is increased by indentation. Although surface diffusion and the stress field created by the nanoindentation must surely be taken into account in an exact description, the findings by Shindo et al. (see Ref. [9]) suggest that adsorbed ambient moisture plays a dominant role in the rearrangement dynamics after the third nanoindentation (images 1d and following). Indeed, previous surface science studies on NaCl [12] and recent AFM imaging on mica [13] have shown that surfaces exposed to air are readily covered with a thin film of water on a nanometer scale. We hypothesize that a water film on the NaCl surface dissolves some debris or mounds generated by the indentation and act as a medium for the transport of material by diffusion to other parts of the surface. The indentation disrupts both the water film and the NaCl surface underneath, which effectively creates in the film a radial gradient of salt concentration around the hole in the surface plane. Indeed, terraces "born" around the hole drift away from it, which reveals transport of material away from the hole. Thus we explain that the motion slows down as the water film reaches a uniform salt concentration in equilibrium with the NaCl surface underneath. We predict that AFM nanoindentations in a dry environment will result in a much lower increase in surface activity because of the absence of a water layer acting as a NaCl-material transport medium. Experiments to perform AFM nanoindentations on NaCl in controlled-temperature/humidity ambient are underway.

In conclusion, we have demonstrated the observation of monoatomic step motion on a NaCl(100) surface in real time by means of low-interaction tapping-mode AFM imaging. The step motion activity is greatly enhanced after "disturbing" the surface by means of nanometric indentation with the same AFM tip. The fact that the increase in surface activity is locally induced opens exciting new possibilities in surface dynamics studies, such as comparing the effect of the same disturbance in different locations or at different humidities. We reproducibly witnessed the real-time formation of crystalline nanostructures, namely monoatomic steps not present on the surface before the indentation. Even in a dry ambient, the AFM indentation should prove a valuable method for testing stress-induced motion of surface atomic steps. We expect to clarify in the near future the degree to which the dynamics of the rearrangement of NaCl nanoindentation debris are enhanced by the presence of a water thin film. Similar indentation experiments under water could well reveal the

dynamics of dissolution of salt in water on a nanometer scale.

Acknowledgements

We are grateful to Lourdes Miralles for providing the NaCl samples and indebted to Sylvain Cantin (Instrumat, S.A.) for the free loan of the AFM system. This work has been supported by the Ministerio de Educación y Ciencia, Spain.

References

[1] G. Binnig, C.F. Quate and Ch. Gerber, Phys. Rev. Lett. 56 (1986) 930.
[2] U. Landman, W.D. Luedtke, N.A. Burnham and R.J. Colton, Science 248 (1990) 454.
[3] S.A. Joyce, R.C. Thomas, J.E. Houston, T.A. Michalske and R.M. Crooks, Phys. Rev. Lett. 68 (1992) 2790; M. Salmeron, G. Neubauer, A. Folch, M. Tomitori, D.F. Ogletree and P. Sautet, Langmuir 9 (1993) 3600.
[4] We used "tapping mode" tips and a Nanoscope III AFM by Digital Instruments, Inc.
[5] Q. Zhong, D. Inniss, K. Kjoller and V.B. Elings, Surf. Sci. 290 (1993) L668.
[6] J.P. Spatz, S. Sheiko, M. Möller, R.G. Winkler, P. Reineker and O. Marti, Nanotechnology 6 (1995) 40.
[7] P.E. Hillner, S. Manne, A.J. Gratz and P.K. Hansma, Ultramicroscopy 42–44 (1992) 1387.
[8] A.L. Shluger, R. Mark Wilson and R.T. Williams, Phys. Rev. B 49 (1994) 1915; Ultramicroscopy 42–44 (1992) 1387.
[9] H. Shindo, M. Ohashi, K. Baba and A. Seo, Surf. Sci. 357–358 (1996) 111.
[10] The stiffness was calculated from the specified dimensions of the cantilever and the measurement of its resonance frequency.
[11] U. Landman and W.D. Luedtke, J. Vac. Sci. Technol. B 9 (1991) 414.
[12] J. Estel, H. Hoinkes, H. Kaarman, H. Nahr and H. Wilsch, Surf. Sci. 54 (1976) 393; P. Tepper, J.C. Zink, J. Reif and E. Matthias, Phys. Rev. B 42 (1990) 9685.
[13] J. Hu, X.-D. Xiao, D.F. Ogletree and M. Salmeron, Science 268 (1995) 267.