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Surface Science 470 (2000) L99–L103

SURFACE SCIENCE

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Surface Science Letters

Resolving ions and vacancies at step edges on insulating surfaces

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Received 10 August 2000; accepted for publication 10 October 2000

Abstract

Surfaces of BaF_2 and SrF_2 prepared by cleavage along (1 1 1) planes in ultra-high vacuum were investigated with a dynamic scanning force microscope operated in the constant frequency detuning mode. We observe an atomic corrugation of some 10 pm on terraces and demonstrate that individual ions and vacancies can be resolved at step edges. Step edges do not necessarily follow low index crystallographic directions but may exhibit significant roughness on the atomic scale.

Keywords: Atomic force microscopy; Step formation and bunching; Surface structure, morphology, roughness, and topography; Halides; Low index single crystal surfaces; Stepped single crystal surfaces; Surface defects

Step edges are simple atomic structures appearing on a surface upon cleavage of a single crystal what is often the most effective method to produce an insulating surface that is well ordered on the atomic scale. Many surface processes like diffusion of adatoms and/or growth of clusters are strongly influenced by the density and structure of steps and, therefore, an investigation of these features on the atomic scale is interesting for a general understanding of surface and interface phenomena and for many applications in nanoscience. The topography of cleaved insulating surfaces has been revealed on the nanometer scale by probe microscopy, however, until recently there was no experimental technique available that had the ability to explore structures on the atomic scale. The method of scanning force microscopy (SFM) has continuously been developed over the past years and was applied to this problem. As representative examples we mention results on fluorides, the class of insulating materials relevant in the context of this letter. The structure of their cleaved surfaces has first been investigated with force microscopy operated in the contact mode of operation [1]. In a recent study of this type, cleavage steps and regular protrusions appearing on the surface upon strong heating of CaF_2 have been imaged with highest resolution and the alignment of these features could be related to low-index directions on the (1 1 1) surface by imaging its atomic periodicity [2]. With SFM operated in the dynamic mode, on the other hand, it was possible to reveal surface modifications on the nanometer scale [3] and image ionic corrugation

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0039-6028/00/$ - see front matter
PII: S0039-6028(00)00916-X

and atomic size defects on flat terraces [4]. However, the apparent corrugations of some hundred picometers found in these images and the appearance of defects was influenced by the control loop of the force microscope and imaging was restricted to the perfect surface with minute elevations while any attempt to scan across a step of smallest possible height resulted in a loss of atomic resolution due to severe instability in scanning.

In the present letter we report about two major advancements in dynamic mode scanning force imaging of insulating surfaces with atomic resolution. We first demonstrate that with a well prepared tip and a suitable set of scanning parameters, it is possible to obtain atomic resolution on flat terraces not affected by peculiarities mentioned above. Secondly we explore the atomic structure of step edges on these surfaces and show that individual ions and vacancies can be resolved.

For our studies we used similar instrumentation and techniques than for previous SFM studies [3,4]. A silicon cantilever with a resonance frequency of about 80 kHz and a stiffness of 6 N/m was excited to oscillation with a peak-to-peak amplitude of 70 nm. This relatively high value was imposed by the requirements of our instrument rather than selected as an optimum value according to recently published criteria [5]. The amplitude of the cantilever oscillation as well as frequency detuning were kept constant by control loops providing a damping signal that is proportional to the energy input needed to maintain a constant oscillation amplitude and a topography signal proportional to a constant tip–surface interaction. As a new experimental component we introduced a lock-in detector recording residual amplitude variations. To accomplish this, the amplified output from the quadrant photodiode measuring the periodic cantilever deflection was directly fed into the input and reference channels of the lock-in detector. Care was taken to choose a lock in time constant large enough to avoid misreading due to the changing reference frequency and small enough to truly reproduce amplitude variations during scanning. We recorded topography and residual frequency detuning signals as well as a damping and residual amplitude variation signal simultaneously for forward and backward scan lines. Hence, we can characterize each point within the scanned frame by a complete set of eight numbers carrying information about local properties as well as scanning and direction related features.

The two critical parameters we took special care of in this study were the amplification in the feedback loop for distance regulation and the scanning speed. We raised the amplification of the feedback loop just before the onset of uncontrolled oscillation to obtain a fast re-adjustment to topographic features like scanning over a step edge. In all measurements we used the same amplification which was several times larger than in previous SFM studies [3,4]. To beat thermal drift that is unavoidable in our room temperature measurements we chose high scanning speeds. The specific choice of distance regulation parameters was determined by a trade-off between accuracy in following surface topography and the risk of instability in distance control.

The tip was a commercially available etched Si tip that was sputtered prior to experiments. We anticipate, however, that the tip that created the images presented here was mostly not a pure silicon tip but modified by chemical interactions with constituents of the residual gas in our ultra-high vacuum system. We conclude this from observations made over many series of measurements that best results have routinely not been obtained shortly after tip preparation but after the tips had rested in vacuum at a total pressure in the low 10^{-10} mbar range for several days. Without having yet investigated this finding in detail, we speculate that the improvement in imaging quality is a result of oxide or hydroxide formation at the very end of the tip as has recently been predicted for ionic systems on the basis of theoretical calculations [6]. Samples were commercial highest purity single crystals prepared by cleavage in ultra-high vacuum to obtain clean (1 1 1)-surfaces.

One of the first examples where we obtained atomic resolution on BaF_2 at step edges of one Ba–F–Ba triple layer height is shown in Fig. 1. The atomic corrugation is clearly seen on the terraces including the two step edges forming a cleavage tip. The step edge on the left side is aligned along the [1 2 1] direction while the one on the right side

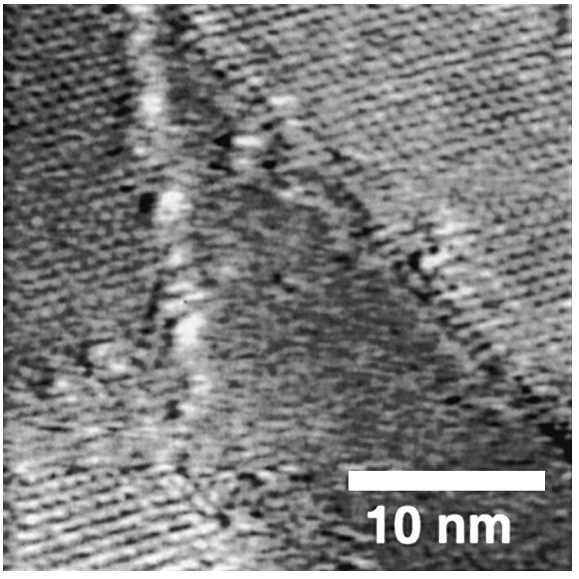
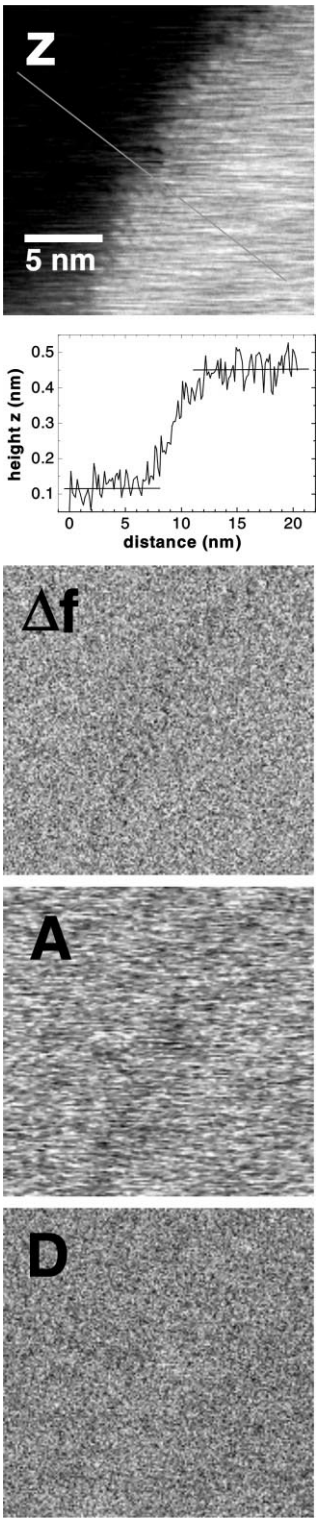


Fig. 1. Scanning force image of a cleavage tip on BaF_2(1 1 1). The image was obtained in the dynamic mode at a frequency detuning pre-set of −160 Hz and a scanning speed of 30 nm/s. The image was slightly Fourier filtered to remove stripes from fast scanning.

is aligned along the [0 1 1] direction. From the line profile taken along an ionic row across one of the step edges we extract an apparent step height of 50 pm that is way below the expected triple layer height of 358 pm. This is clearly an effect of the finite tip asperity that does not allow the tip to follow the true topography. Consequently, atomic resolution is mostly lost when scanning on the bottom terrace between the steps. This image also well exemplifies effects of instability in the tip structure when scanning across topographic features at very small tip–surface distances. Both, variation and loss of atomic contrast observed over several scan lines as well as spots of extremely high contrast appearing at the step edges indicate changes in the atomic structure at the end of the tip determining atomic scale contrast. The bright spots at the edges of both terraces are attributed to an intensified interaction between low coordinated edge ions and the outermost tip atom. This feature is similar to recent observations of an enhanced contrast for step edges of a NaCl film evaporated on a copper substrate [7]. Note that for the instance of the scan presented in Fig. 1 this effect does not appear evenly at all step ions but preferentially at the left step what we attribute to the stronger interaction between the tip and the step edge forming ions along the [1 2 1] direction. This demonstrates the extremely high sensitivity of the balance of forces sensed by the cantilever on subtle variations of the local configuration of tip and surface ions.

When aiming for experimental parameters allowing most stable atomic resolution imaging of a step edge on SrF_2 we obtained results shown in Fig. 2. These images have been obtained with the same tip used for the measurement displayed in Fig. 1 and shortly after the first measurement. Hence, we expect that there occurred only minor changes in tip geometry between the two measurements. In the series of four images and one cross-section, we present data recorded simultaneously during scanning in forward direction where results did not differ significantly for scanning backwards. The scanning speed was four times faster than in the measurement of Fig. 1. For this measurement we optimised parameters for best contrast at the step edge on cost of atomic resolution on terraces. The uppermost frame displaying the topography signal reveals that we had a very stable tip configuration allowing to sense individual ions without any enhanced interaction at low coordinated sites. Having a stable, compact cluster of atoms at the end of the tip is presumably also the cause of the low atomic peak-to-peak corrugation of only 30 pm found on the upper terrace. In other images on terraces obtained under similar experimental conditions we had found corrugation values about twice as high. The apparent gradient in atomic contrast extending from the step edge into the interior of the upper terrace as well as a faint appearance of atomic corrugation on the lower terrace (that can be extracted from the original data but cannot be seen in the topmost frame of Fig. 2 due to the limited dynamic range of the grey scale representation) is due to a variation in tip–surface distance due to the inclination between the sample surface and the plane of the scan.

We find that the step is not simply aligned parallel to any of the low-index planes intersecting the surface as we found in other measurements but



exhibits a curved shape with rather arbitrary directions over straight segments. The excellent resolution at the rim allows the identification of single ionic vacancies and protruding ions along the step edge. The line profile shown below the topography image reveals a perfect reproduction of the triple layer height for the step but also convolution effects of the tip asperity with the step extending over a range of about 4 nm.

The lower frames displaying amplitude, damping and detuning signals are testament of the validity of topographic information. These images mainly show instrumental noise and exhibit only an extremely weak contrast in the vicinity of the step edge. Especially the absence of any contrast in the amplitude and damping signals is a clear-cut proof that there is not the slightest enhanced interaction when probing low coordinated step sites. This is a most remarkable finding suggesting that the observed enhancement in other measurements is a result of very specific atomic configurations at the end of the tip and can principally be avoided. We speculate that this happens when having a compact tip configuration and suggest such tips as ideal for atomic resolution imaging.

In summary we have demonstrated the basic features of atomic resolution imaging on stepped fluoride surfaces as prototype insulating materials. We found lowest ionic corrugations of 30 pm on terraces and resolved individual ions and vacancies at step edges with a tip of suitable and stable atomic configuration at its end.

Fig. 2. Scanning force results of a step edge on $SrF_2(1\,1\,1)$. The series of images was obtained simultaneously during one scan performed at a frequency detuning pre-set of −100 Hz and a scanning speed of 110 nm/s. The upper frame represents the topography z while the graph shows a cross-section along the indicated line. Horizontal stripe patterns are due to noise that cannot be suppressed when scanning at high speed requiring large detection bandwith. The other frames represent the residual frequency detuning Δf (mean: −100 Hz, deviation: 4 Hz), the cantilever oscillation amplitude A (mean: 5.229 a.u., deviation: 0.013 a.u.) and the damping signal D (mean: 1.54 a.u., deviation 0.13 a.u) of the oscillation, respectively. The numbers for mean and deviation denote the mean values and full width at half mean of the distributions taken over the respective frame.

Acknowledgements

The authors are grateful to A.S. Foster and A.L. Shluger for most stimulating discussions.

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