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Scanning Force Imaging of Atomic Size Defects on the $CaF_2(111)$ Surface

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Cleaved (111) surfaces on CaF_2 were imaged with scanning force microscopy operated in the dynamic mode in ultrahigh vacuum. Imaging the pristine surface reveals an atomic scale contrast with the structure expected for the fluorine terminated surface. We always reproduced the perfect surface periodicity never observing stable defects. However, after exposing the surface to 280 L of oxygen while constantly scanning, we detected stable atomically resolved defects that are assigned to OH^- groups incorporated into the surface. We could identify a jump of one of the groups from one atomic cell to the next. The observed contrast at regular lattice sites as well as at defects is discussed and qualitatively explained.

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Dynamic mode scanning force microscopy (SFM) is the only experimental method capable of direct imaging of poorly or nonconducting surfaces with atomic resolution. There is still only a very limited number of examples for successful atomic resolution SFM imaging on this class of materials available, e.g., high resolution imaging of the $TiO_2(110)$ surface [1] and studies on some alkali halide crystal surfaces [2]. The main experimental difficulty is to stabilize the tip during the scanning process and to keep an extremely subtle balance between several forces acting on the tip. This is specifically difficult since the end of the vibrating tip has to be kept in a distance of only a few angstroms from the sample surface atoms, i.e., in a region where chemical forces between tip and surface or an exchange of particles are relevant [3]. An important step forward in the development of scanning force microscopy is the development of low temperature techniques [4] allowing one to approach the utmost limits in high resolution imaging. Surface corrugations of several tens of picometers on InAs(110) have recently been reported for measurements performed at a temperature of 20 K [5].

In the present paper, atomic resolution scanning force imaging on the alkaline-earth fluoride surface $CaF_2(111)$ is presented for the first time. We first investigate the pristine surface yielding perfect atomic periodicity and then demonstrate that stable defects can be created on this surface by exposure to a few hundred langmuirs ($1\ \mathrm{L} = 10^{-6}$ Torr s) of oxygen and these defects appear as atomic size irregularities with a characteristic inverted contrast in the force micrographs. We interpret these features as OH^- molecules embedded into the surface in a first step of degradation starting at defective sites. The contrast formation for the pristine and degraded surface is discussed. The contrast is influenced and at defective sites may, in fact, be dominated by artifacts resulting from the control loop of the force microscope.

Our experiments were performed in an ultrahigh vacuum system with a base pressure in the low 10^{-10} mbar region with a commercial scanning force microscope. We used commercial p-doped (1.5 Ω cm) silicon cantilevers that were sputter cleaned with 1 keV argon ions for 10 min prior to each series of measurements. We operated the system in the dynamic mode [6] (amplitude 80 nm) where the cantilever (spring constant: 6 N/m) is excited to vibration at its resonance frequency (80 kHz) that varies due to the interaction with the surface. In our experiments this frequency detuning was typically fixed at -150 Hz by the SFM control loop. We scanned with about 1 Hz at low loop gain. As shown below, this is a relevant limitation for our measurements introducing scanning artifacts in situations where the corrugation rapidly changes on the atomic scale. Nonetheless, we kept these scanning parameters since all other combinations we tried resulted in considerable instability during scanning.

Samples were commercial single crystals of highest available quality CaF_2 that came as cylindrical rods with a diameter of 10 mm. Surfaces were prepared by cleavage along the (111) surface in the ultrahigh vacuum and heated to 400 K for 3 to 5 h to remove residual charges. For measurements we selected surface regions with a small density of macroscopic steps and waited several hours until the sample was in thermal equilibrium with the apparatus kept at room temperature. To remove the influence of electrostatic forces during scanning we applied a bias potential of typically 0.1 to 0.2 V between the tip and the metallic backing plate of the sample.

Figure 1 shows a section of the surface with high magnification revealing the periodic atomic structure on an area of $1.9 \times 2.0\ \mathrm{nm}^2$. The image exhibits perfect atomic periodicity, and there are no reproducible atomic size defects. We have taken several tens of images of this type of varying resolution and in different surface areas and never found another result; i.e., the surface appeared free of defects, although we expect a measurable concentration on a cleaved surface. We speculate that the expected vacancy or F center defects might be healed during the annealing procedure applied to the sample prior to the measurement or more probably that defects are, in fact, present but

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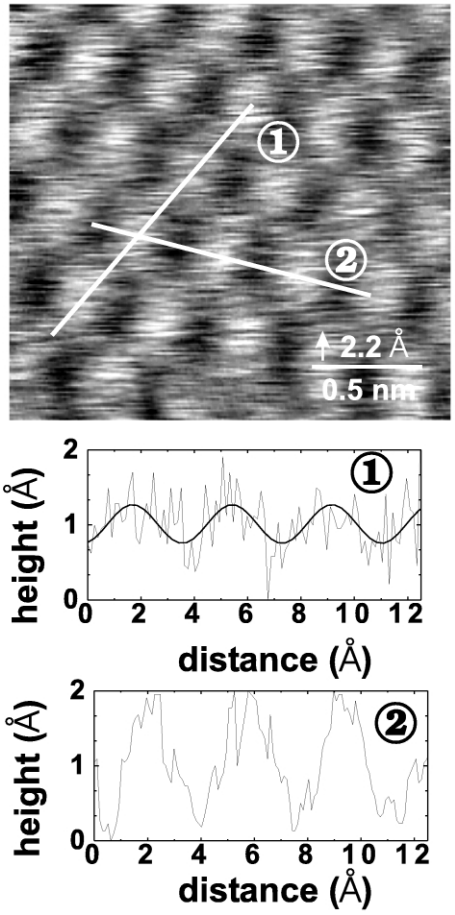

FIG. 1. Surface topography of a pristine $CaF_2(111)$ surface. The grey scale of the micrograph is linearly scaled from 0 (black) to 2.2 Å (white). Cross sections along two ionic rows with different direction were taken and fitted with a sinusoidal function [shown for trace (1) only] to obtain peak-to-peak corrugations along the lines of 0.5 and 1.4 Å, respectively.

mobile at room temperature and add to the noise rather than appearing as structures that are stable over a time elapsing between scanning consecutive lines.

The distance between nearest neighbor elevations is found to be 4.0 ± 0.5 Å which is in good agreement with the value of 3.86 Å expected for the (111) surface of CaF_2 [7]. From this observation it cannot *a priori* be concluded how the surface is terminated. However, in larger area SFM scans with less lateral resolution we find 3.5 ± 0.5 Å as the minimum step height, in good agreement with the 3.15 Å triple layer height of the CaF_2 structure [7]. Furthermore, knowing that the cohesive strength is smallest between adjacent fluorine (111) planes in the fluorite structure [8], we conclude that we always measured on fluorine terminated surfaces and associate the atomic scale elevations in the SFM micrographs with the positions of surface fluorine ions. From Fig. 1 it is immediately obvious that the apparent corrugation is different in different crystallographic directions. From a fit of sinusoidal functions to the cross sections shown we find a peak-to-peak corrugation of 0.5 Å for direction (1) but 1.4 Å for direction (2). Obviously this is related to the fact that the strongest contrast occurs in the direction of the scanning motion as has also been found in atomically resolved scans on alkali halide surfaces [2]. When changing the scanning direction in our measurements, images are well reproduced except for a weak additional contrast that is always found in the direction of the scan. We attribute this feature to an artifact generated by the combination of the strong electrostatic interaction between tip and surface ions and the response of the control loop stabilizing the frequency detuning. The mechanism is schematically depicted in Fig. 2(a) where we show both the assumed cantilever motion as a function of scanning position (left frame) and the associated changes in detuning Δf as a function of the tip-surface distance z (right frame). The dashed line in the right frame indicates the set point of the Δf control loop, i.e., the detuning fixed during normal operation. When the tip approaches an ionic elevation during rapid scanning (after passing A), the distance to the surface is decreased and at the same time the tip experiences a strong attractive force. Because of the low loop gain, the tip is not retracted fast enough to follow the contour and approaches the surface ion very closely (B). However, there is a strong error signal for the control loop that subsequently overcompensates the approach by a retraction from the surface that is larger than required to follow the true contour (C). In effect, this mechanism results in an enhanced contrast when compared to the true contour as well as to an almost 180° phase lag between the periodic tip movement and surface contour during scanning that is solely due to the action of the control loop and does not in a single way reflect the interaction of the tip with surface ions.

In a second set of experiments we investigated defects induced by exposure of the surface to oxygen that was admitted in molecular form at a pressure of 1.5×10^{-7} mbar during repetitive scanning of the surface. For

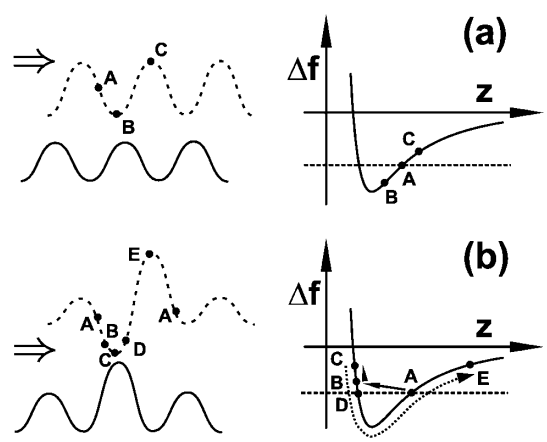

FIG. 2. Schematic illustration of the scanning force imaging process for noninverted contrast at regular ionic sites (a) and inverted contrast at defect sites (b). The left frames show the surface contour (solid line) together with the assumed cantilever movement (dashed line). The right frames illustrate the resonance frequency detuning Δf as a function of tip-surface distance z. The arrow (⇒) denotes the scan direction.

about one hour of measurements we did not observe any significant change in surface structure; however, image contrast and regularity improved constantly after oxygen exposure was started. We attribute this effect to an oxidation of the tip that in these measurements has also been exposed to several hundred langmuir of oxygen. Based on model calculations of the interaction of a silicon tip with an ionic surface, it has, in fact, been demonstrated recently that a tip with a polar group like oxygen at its end can be expected to yield a stronger interaction with an ionic surface than a clean silicon tip [9]. In all further scans we observed atomic size defects that were clearly related to oxygen exposure since not a single one of such defects had been observed in any micrograph of a pristine surface. We could follow a group of defects moving through the image for five consecutive frames that are shown in Fig. 3. Analyzing these frames we find that the whole group moved in a stable configuration along the dashed line shown in the figures. We anticipate that this movement is due to instrumental drift rather than a diffusive motion of the defects on the surface. However, one diffusive jump can be identified when comparing the last two frames. The expected position of the outmost defect on the left side is marked by a white circle and is displaced by one atomic row from the expected position.

Figure 4(a) shows another example of oxygen induced defects with higher magnification. The defects generally appear as pairs of bright and dark spots where the position of the defect is attributed to the dark spot for reasons outlined below. Counting the ionic elevation reveals that essentially one ionic position is occupied by a defect. This appears to be an important observation when discussing the possible stoichiometry and structure of the defects. In a recent theoretical study we dealt with oxide and hydroxide formation on $CaF_2(111)$ and found that there are only a few configurations that are likely to be stable [10]. As the stablest configuration we found a surface hydroxyl group where the oxygen essentially substitutes a fluorine and the hydrogen is on top with the molecular axis oriented normal to the surface. Hydroxyl formation on the surface appears to be a plausible process since hydrogen is an important fraction of the residual gas or may be provided by dissociation of water that is also present in the residual gas, and we propose that the atomic size defects observed in our SFM micrographs are, in fact, surface hydroxyl groups. This interpretation is supported by another observation that we made when investigating oxygen exposure related surface degradation with lower resolution force microscopy. There, surprisingly high oxygen dosages of the order of 10^6 L were needed for a degradation of a considerable fraction of the surface. An explanation for this finding might be that hydroxide formation is, in fact, the dominant surface reaction and its kinetics mainly limited by the available amount of hydrogen.

Although, Figs. 3 and 4 undoubtedly establish that we obtain atomic resolution, there remains the question of contrast formation on the atomic scale. On first sight, the contrast of defects seems to be the same as for regular lattice sites just strongly enhanced. A closer inspection reveals, however, that in this case the tip-surface interaction in combination with the control loop yields a more complicated cantilever movement than was found on the pristine surface. This becomes immediately evident when comparing Figs. 4(a) and 4(b) showing the cantilever movement for scanning in forward and backward directions, respectively. While forward and backward scanning results were essentially identical for measurements on a pristine surface, for the defects, only the dark spots appear at the same positions while the positions of the bright spots depend on the scanning direction. Our interpretation of this behavior is sketched in Fig. 2(b) where we again display the assumed tip movement as a function of the

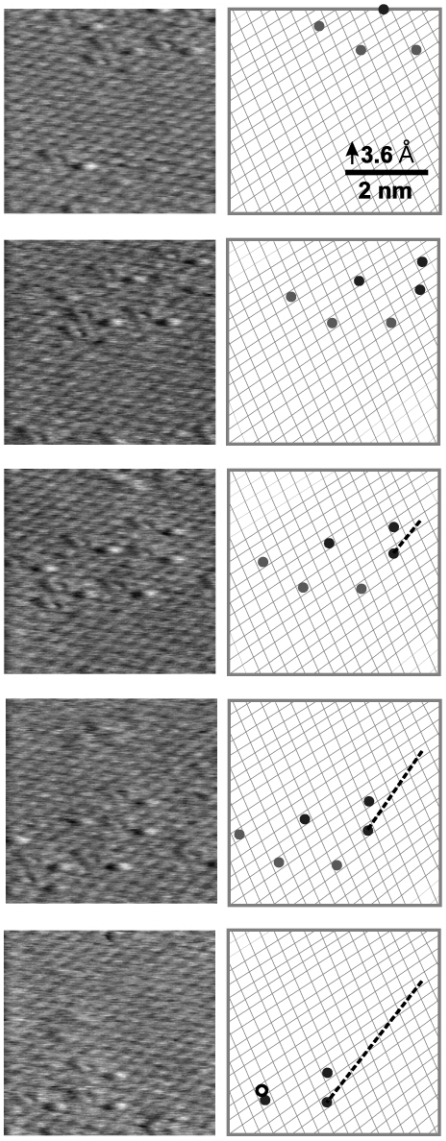

FIG. 3. Oxygen exposure related defects on the $CaF_2(111)$ surface. The frames show consecutive scans of 5 min duration. The O_2 dosage was 280 L for the first and 440 L for the last frame.

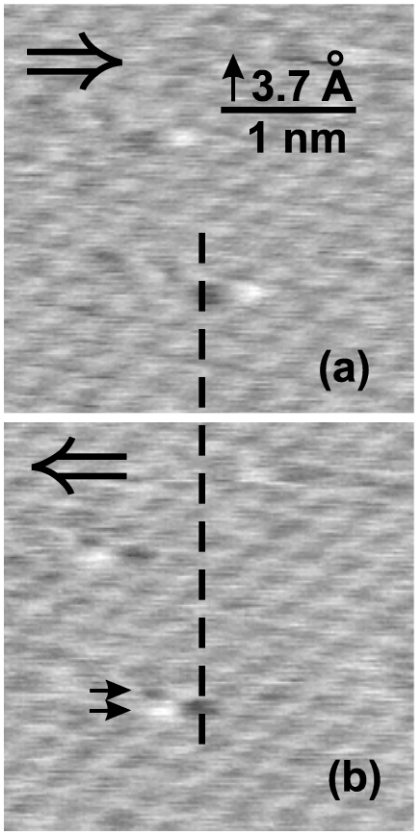

FIG. 4. Enlarged images of surface defects obtained from forward (⇒) and backward (⇐) scans of the same measurements. The dashed line marks the position of a defect occurring at the same position for forward and backward scanning.

scanning position (left frame) and the associated frequency detuning curve (right frame). At point A the tip approaches a defect sticking farther out of the surface than a regular ion. We anticipate that during approach the tip is not retracted fast enough by the action of the slow control loop so that the minimum of the frequency-distance curve is passed into a region where the response of the control loop is inverted (B). Consequently, the tip is further pushed towards the surface (C) but due to the fast scanning and low loop gain this does not result in a surface crash but the pronounced dark spot associated with each defect. When the defect is passed, the system returns to the other side of the minimum of the frequency detuning curve. During most of this way ($D \rightarrow A$) there is an error signal yielding a retraction of the tip, and overcompensating this signal results in the bright spot of the defect structure (E). This tip movement over a defect effectively results in a stronger attraction as experienced at regular ionic sites [B in Fig. 2(a) and C in Fig. 2(b)] and in a contrast inversion in the sense that the elevation of the defect is marked by a dark spot indicating attraction while the adjacent valley appears bright indicating repulsion. Recently we observed a similar inversion phenomenon also for atomic resolution imaging of Si(111)-(7 × 7) when selecting a slow feedback. A close look at Fig. 4(b) reveals that one defect might, in fact, yield both an inverted behavior in the center of the defect and a noninverted behavior in a region of reduced elevation at the periphery as indicated by the two arrows pointing to the respective scan lines.

In summary, we have shown that atomic resolution can be achieved in dynamic mode scanning force imaging on pristine $CaF_2(111)$ and one obtains the perfect structure of the fluorine terminated surface. In a large number of room temperature measurements we were not able to detect any surface defects. Admitting oxygen to the surface at a dosage of some hundred langmuir, however, results in the formation of defects, each occupying one ionic site that we interpret as hydroxyl groups substituting surface fluorine ions. These defects can be located with the scanning force microscope with atomic resolution; however, their apparent surface contour is mainly determined by a cantilever motion induced by the scanning control loop. So far, we believe that a perfect fluoride surface is chemically inert and will not be degraded by exposure to oxygen or water, but preexisting surface defects in the form of vacancies or F centers play an important role for the surface reaction. Further measurements at low temperatures are needed to identify such defects on an atomic scale and directly show their chemical reactivity.

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