Atomic Resolution Imaging of the (001) Surface of UHV Cleaved MgO by Dynamic Scanning Force Microscopy

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The (001) surface of UHV cleaved single MgO crystals was imaged with dynamic mode scanning force microscopy. Large-scale images show various defects, like steps of mostly one atomic height, rectangular holes of nanometer size, and some complex adstructures. First time images with atomic resolution show one square ionic sublattice in its bulklike dimension with a corrugation of up to 40 pm along the ⟨001⟩ direction. Most images exhibit atomic point defects which appear as depressions including a few ionic lattice sites proving that point defects are stable on flat terraces.

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The (001) surface of MgO is one of the most studied oxide surfaces due to its simple structure, stable stoichiometry, and easy preparation by cleavage [1]. Further, it is largely used as a support for epitaxial growth of metals [2] and for model catalysts [3] as it has been demonstrated by experiments with palladium, silver, and gold clusters [3,4].

All experiments over the past years show that the clean (001) surface of ultrahigh vacuum (UHV) cleaved or annealed MgO is mostly characterized by atomically flat terraces separated and intersected by linear defects like steps and by holes and other unidentified localized features [1,5,6]. Further, it was found that the surface ions have a bulklike alignment exhibiting only a very small surface relaxation and rumpling [7–9].

Although these measurements deal with main features of this surface, they do not give direct access to atomic point defects which are, however, crucial for many surface processes like surface reactivity and heterogeneous nucleation of metals [3,10]. From the theoretical side considerable work has been undertaken introducing and predicting possible point defects [11]. Mainly oxygen vacancies in the form of F, F^+, and F^{++} centers [11,12] and neutral or charged divacancies on the surface [13–15] have been the main focus in numerical simulations. However, their experimental evidence has been provided only indirectly by different techniques [16–18], whereas the attribution to a specific type of defect is still controversial.

The scanning force microscope (SFM) in its dynamic mode is a very promising technique to investigate and characterize the (001) surface of MgO at atomic scale, especially with respect to the surface defects mentioned above. Although atomic resolution imaging has been successfully applied on a variety of surfaces of insulating materials [19,20] like on oxides [21,22], it has never been reached on MgO surfaces so far. Some years ago the periodic arrangement of the surface ions of an *in situ* cleaved crystal was imaged in dry atmosphere in the contact mode but without evidence of any point defects [23]. Much work was performed on surfaces of UHV and air cleaved MgO crystals to characterize the surface at nanometer scale but without any atomic resolution [5,6,24,25].

In this Letter we present dynamic mode SFM images with atomic resolution of the (001) surface of UHV cleaved MgO which reveal the ionic structure of the clean surface and the presence of single point defects on flat terraces.

Experiments were performed with a scanning force microscope (Omicron RT-STM/AFM) operated in the dynamic mode and in an UHV system with a base pressure in the low 10^{-10} mbar range. Dynamic mode scanning force microscopy measures the change in frequency (detuning Δf) of an oscillating cantilever due to the interaction of a tip at the end of the cantilever with the surface. A silicon cantilever (Nanosensors, P doped, 1.5 Ω/cm) with a spring constant of 30–50 N/m was excited to vibration at its resonance frequency of 293 kHz with a peak-to-peak amplitude (A_{pp}) stabilized to some nanometers. We did not sputter the tip. Before we took the images shown here the tip was first in contact with the surface. Therefore we assume that the apex of the tip was probably contaminated by material of the substrate. In order to measure the detuning of the cantilever oscillation with utmost precision and stability, the system is equipped with a digital demodulator (Nanosurf). All images have been recorded in the constant Δf mode in which the detuning Δf is always kept constant during scanning and in which the deflection of the z piezo is displayed in the images [26].

The samples were taken from commercial single crystals of highest available quality, 4 N pure MgO (Pi-Kem). The surfaces were prepared by cleavage parallel to the (001) cleavage plane of MgO at room temperature in the low 10^{-10} mbar region of the UHV in order to avoid immediate contamination. It has been previously shown that after cleavage under UHV no peak other than Mg and O can be seen by Auger spectroscopy [1].

We emphasize that one has to cleave precisely parallel to the (001) cleavage plane in order to obtain good quality

cleavages characterized by a low density of steps. We use a blade of tungsten carbide which edge is aligned and fixed parallel to the (001) cleavage plane within an error of 1° or less and which can move only along one direction. During cleavage the blade penetrates only 1 mm into the crystal in order to avoid damages by the blade on the remaining surface.

The crystals exhibit mostly a strong charging after cleavage in UHV which may even hamper stable scanning. In those cases we heat the crystals in UHV at high temperatures for some hours where we can reduce a large amount of charges. However, in all of our experiments we had to apply a negative bias voltage (U_{bias}) of mostly several volts at the rear side of the sample in order to minimize electrostatic forces due to residual charges. The measurements shown here have been done with a crystal which was annealed after cleavage at 350 °C for three nights. During annealing the pressure was kept in the middle 10^{-10} mbar pressure region. Since at those temperatures contamination is avoided or even removed [1] we are sure that the surface stayed clean after the annealing procedures.

Figure 1(a) shows a large-scale image of $250 \times 250\ \text{nm}^2$ size representing the main features of the surface after its preparation. Atomically flat terraces are intersected by steps of one monolayer height, rectangular holes of nanometer size, and some complex adstructures. The steps mostly run along the ⟨001⟩ direction but sometimes even along directions of higher lattice indices. In the latter case those steps are quite often composed by an alignment of small steps of ⟨001⟩ directions probably in order to reduce the total ledge energy [Fig. 1(c)]. One of the most striking observations of all large-scale images is the occurrence of nanometer-sized rectangular holes on flat terraces [Fig. 1(d)] as it has been observed before [5]. Independently, if the crystals were annealed or not after cleavage, holes of only one monolayer depth with smooth edges exclusively running along the ⟨001⟩ directions can be found. The holes have surface areas of up to 500 nm^2 (corresponds to a square hole with 22 nm side length), whereas the rectangular form may have different ratios of length to width. However, we could never find holes of much larger size nor did we observe the "negative cast" of the holes in the form of rectangular adislands of similar size one expects after the cleavage. The steps and holes are accompanied by some adstructures [Fig. 1(e)] which are rough and do not form compact objects like the holes exhibiting smooth rectangular shapes. They are composed by nanometer-sized spots with a height of up to 1 nm. The spots are mostly located in the vicinity of steps and holes and are sometimes connected to each other forming thin strings.

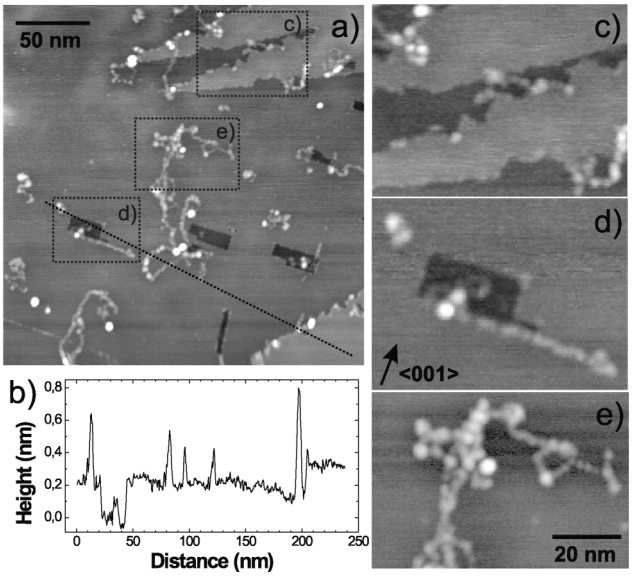

FIG. 1. (a) Large-scale topography image of the UHV cleaved (001) surface of MgO ($\Delta f = -12$ Hz, $A_{\text{pp}} = 12$ nm, $U_{\text{bias}} = -3.2$ V). (b) Profile taken at the position of the dark dotted line in image (a) exemplifying the height of steps, holes, and adstructures. (c)–(e) Parts taken from image (a) which show major features of steps, holes, and adstructures.

Steps and flat terraces are normal surface features which are created by cleavage and have been frequently observed on surfaces of many other insulating materials like on surfaces of fluorites [26] or alkali halides. However, the (001) surface of cleaved MgO is remarkable in that it exhibits a high density of nanometer-sized defects in an exceptional form of rectangular holes and adstructures which have not been found on surfaces of other UHV cleaved crystals.

Since all structures have been created by the cleavage one can anticipate that the adstructures are adsorbed fragments of MgO-like species, e.g., Mg adatoms, MgO molecules or clusters, which resulted from its cleavage, either neutral or charged. We could not find any change of their position and shape after taking several images so that they seem to be stable, which is in agreement with recent calculations [27]. However, the detailed process of the creation of the holes and adstructures and the detailed composition of the adstructures still remains speculative.

In order to obtain information about other defects such as atomic point defects on the flat surface, we imaged the surface with atomic resolution. Figure 2 shows an image with atomic resolution which was gained on a flat terrace of the MgO surface after cleavage and annealing of the crystal. In the lower part of the image the surface ions were imaged by an asymmetric tip in the form of ionic rows. After a tip change they have been imaged by a more symmetric tip exhibiting a square lattice. Those tip changes occur quite frequently on the (001) surface of MgO during scanning and exhibit same characteristics as it has been observed on surfaces of other materials as well [28]. As a consequence, scanning with high resolution is most difficult since the resolution can be lost during recording of an image.

Along the direction of largest differences in contrast, which corresponds to the ⟨001⟩ direction, we found a

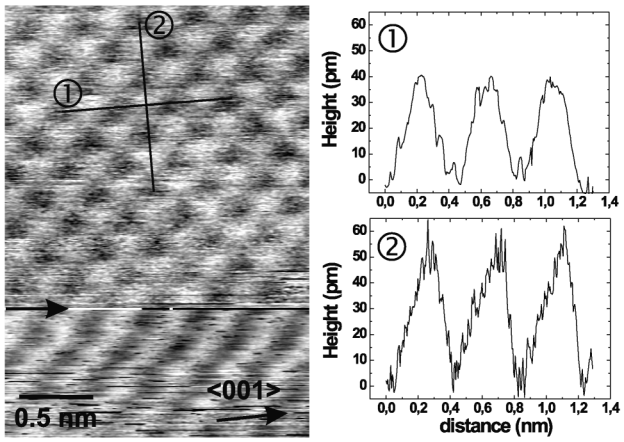

FIG. 2. Image with atomic resolution representing a surface area of 3.2×2.2 nm^2 on a flat terrace ($\Delta f = -139$ Hz, $A_{pp} = 8$ nm, $U_{bias} = -1.4$ V). The black arrow (left) points to a tip change that occurred during scanning within one single scanning line. Two profiles on the right-hand side show maximum contrast along the $\langle 001 \rangle$ directions. They have been gained by a superposition of nine profiles along equivalent ionic rows of the $\langle 001 \rangle$ direction for each orientation (1) and (2). The differences in profile shape are due to the tip apex which was still slightly asymmetric after the tip change.

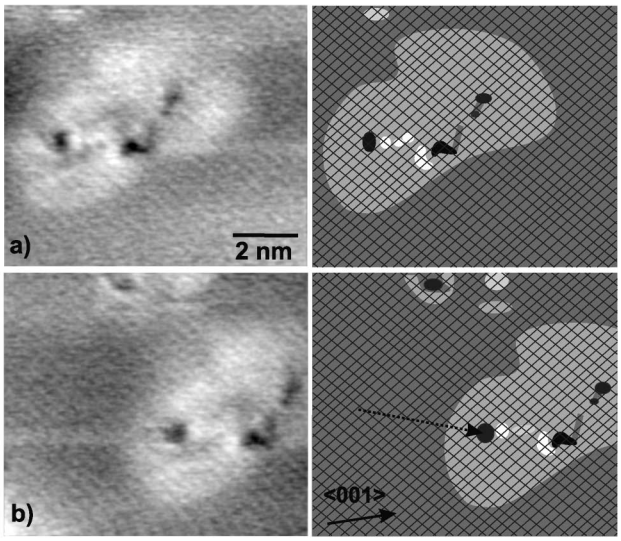

FIG. 3. Single point defects on a flat terrace imaged with atomic resolution in two consecutive measurements (a) and (b) (9.1×9.1 nm^2, $\Delta f = -46.6$ Hz, $A_{pp} = 12$ nm, $U_{bias} = -6.0$ V, height range 70 pm). Each of the two images is a result of a superposition of images recorded simultaneously in forward and backward scanning direction in one measurement. They have been slightly Fourier filtered afterwards. The panels on the right-hand side depict the major features of the images. Since the tip apex was asymmetric only one ionic row of the sublattice was imaged. With the help of the drift vector, the second ensemble of ionic rows could have been reconstructed but was adjusted arbitrarily since no information of the real position can be extracted from the images.

distance of next-neighbor ions of (4.2 ± 0.4) Å which is in perfect agreement with the value of 4.21 Å expected for ions of one sublattice. The two profiles in Fig. 2 present the contrast of equivalent $\langle 001 \rangle$ directions. They exhibit a corrugation of 40 pm, which is comparable with values found for surfaces of other insulating oxides, such as NiO [22], and with values of numerical simulations which have been recently done on MgO(001) [29]. The imaging process of ionic tip-surface systems has been already characterized and successfully used for identifying sublattices of surfaces [30]. However, the bright ions in the image of Fig. 2 cannot be identified, so far, since it does not seem possible to identify sublattices of high symmetric surfaces which exhibit a cubic ionic structure as shown recently on the (001) surface of NaCl [31].

The majority of our images with atomic resolution contain several point defects on the flat surface that have been mostly imaged in the form of depressions. Figure 3 shows two typical images which have been consecutively recorded with the same scanning parameters. We did not approach the tip too close to the surface in order to avoid instabilities of the tip oscillation which mostly occur above defects for closer distances. The atomic contrast in the images is therefore rather faint but sufficient for the interpretation. Because of the thermal drift of the piezo scanner the defects seem to move from the left side to the right side. This effect is depicted by the drift vector in the panels on the right-hand side representing the major details of each image.

The images show a group of three single dark point defects which seem to cover up to four single lattice sites whereas the exact lateral extension of the defects is unknown. A fluffy bright region with a size of 6×4 nm^2 surrounds those defects and exhibits a less pronounced contrast. We could not find any movement of the defects within their interior arrangement in the series of images. In images of larger scale (not shown here) we could observe several of such groups of point defects which exhibit a similar appearance. We estimate the density of point defects to be roughly 10^{12}–10^{13} defects/cm^2 on flat terraces, which scales with the maximum density of metal clusters on MgO(001) which are expected to grow at point defects [3].

An identification of the defects is, so far, not possible. Moreover, we have no information about the composition of the tip's apex and therefore it is even not possible to verify that the dark defects reflect on real topographical depressions of 40 pm. Namely, on the (111) surface of CaF_2 it has been shown that the atomic contrast becomes inverted as soon as the tip's last atom changes the sign of its electrical potential [30]. The same phenomenon can occur here as well as in the case of charged defects.

However, we find strong evidence from literature that possible candidates for the defects could be vacancies [11,12] or rather divacancies, either neutral [14] or charged [13], since the defects in the images take more than one lattice site. It has been shown that those defects need large energies of several electron volts for their

formation [11–15] so we anticipate that they are created by cleavage. In order to interpret unambiguously the defects in our images, a comparison of systematic measurements and numerical simulations must be done as it has been successfully applied for surfaces of other insulating materials [30].

It is obvious that the defects are probably responsible for several surface features we found in our images. For instance, the defects may play an important role with respect to the strong charging of the surface we often observed after cleavage and annealing of the crystal. If the defects are charged they may also explain the fluffy bright regions in the images of Fig. 3. We believe that in those cases Kelvin probe force microscopy can give access to relating answers. Further, other mechanisms, such as a pinning of the adstructures by the defects or especially the creation of the holes by mobile defects, must be taken into account as well for a future characterization of the surface.

In this Letter we have shown large-scale images and, for the first time, images with atomic resolution of the UHV cleaved (001) surface of MgO. Large-scale images present a high density of nanometer-sized defects in an exceptional form of rectangular holes and adstructures on the surface which must be taken into account for a complete characterization of the (001) surface of cleaved MgO. Further, we have shown dynamic mode SFM images with atomic resolution of MgO(001) which show one ionic sublattice of the (001) surface in its bulklike dimension. We proved the existence of stable single point defects on flat terraces which appear mostly as depressions in the images and cover a few lattice sites. From the literature we anticipate that they are probably divacancies; however, more systematic measurements in combination with numerical simulations must be done. We regard our results as a promising access for further experimental investigations at atomic scale and we will focus on the nucleation process of metal clusters and on the hydroxylation of the MgO(001) surface in the near future.

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