Noncontact Atomic Force and Kelvin Probe Force Microscopy on MgO(100) and MgO(100)-Supported Ba

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Abstract

Atomically-flat MgO(100) surfaces were prepared by sputtering and annealing. Noncontact atomic force microscopy (NC-AFM) and Kelvin probe force microscopy (KPFM) were used to characterize the MgO(100) surfaces. The NC-AFM images revealed the presence of point defects on an atomically-resolved surface. The surface potential at these point defects, as well as features such as step edges and deposited Ba nanoparticles were mapped using KPFM. The Kelvin images show that the surface potential increases at the point defects and at the step edges, suggestive of negativelycharged defects. On the other hand, a decrease in the potential was found over Ba nanoparticles which can be explained by electron charge transfer from the Ba to the MgO.

Introduction

Metal and metal oxide nanoparticles supported on metal oxide surfaces are a very important class of material that are employed, for example, as supports in catalysis and insulating platforms in electronics [1,2]. This has led to extensive study of their surface science. MgO(100) has long been employed as a model oxide surface due partly to the ease of sample preparation through cleaving [3]. More recently, alkaline earth oxides, especially BaO, have also received considerable attention because of their activity in NO_x storage [4-6]. For instance, alumina-supported BaO nanoparticles are employed in automobile catalysts [5].

Charge transfer between nanoparticles and their supports is thought to be important in catalysis [1,7]. Such charge transfer processes can be directly followed particle-by-particle using Kelvin probe force microscopy (KPFM) whereby the surface potential is measured simultaneously with non-contact atomic force microscopy (NC-AFM) [8-19].

It has proven difficult to image insulating oxides using NC-AFM and although several studies resolve steps or supported nanoparticles [20-31], only a few reach atomic resolution [21,23,27,29,31-35]. The difficulty in imaging these insulating oxides is probably related to strong surface charging [28,30]. Given that the technique is a modification of NC-AFM, it follows that there are only a handful of KPFM studies on insulating oxides [12,15-17].

In this article, we present NC-AFM and KPFM studies of MgO(100) and MgO(100)-supported Ba nanoparticles. Previously, MgO(100) surfaces have been formed by cleaving [3,12,16,25,28-30,35,36], annealing in air [37], preparation of thin films [17,38-41] or by the use of smokes and nanocubes [42,43], as well as by sputtering and annealing in UHV to 1600 K [20]. Here, we prepare our MgO(100)

surfaces by sputtering and annealing to a higher temperature of ~1700 K. Our preparation led to large, flat terraces, generally 100-1000 Å in width, that could be imaged with atomic resolution in NC-AFM, including the resolution of individual point defects. KPFM images reveal an increase in the surface potential at the point defects and at the step edges, suggestive of negatively-charged defects whereas a decrease in the potential was found over Ba nanoparticles which can be explained by electron charge transfer from the Ba to the MgO.

Experimental Details

The experiments were performed using a JSPM-4500A (*JEOL*) microscope operated at room temperature and housed in an ultra-high vacuum (UHV) chamber with a base pressure of ~2×10⁻¹⁰ mbar. NC-AFM images were recorded using conductive silicon cantilevers (*MikroMasch*) with resonant frequencies (f_0) of 280-365 kHz and force constants of ~14 Nm⁻¹. Peak-to-peak amplitudes (A_{p-p}) ranged from 70-135 Å. After approaching the tip to the sample, the apparent local contact potential difference (LCPD) between the two was found from a plot of the frequency shift (Δf) vs. applied bias [12,28], and a static compensating bias (V_{bias}) was applied to the sample during NC-AFM measurements.

KPFM measurements were conducted in the frequency modulation mode where an AC voltage, with a peak-to-peak amplitude $(A_{p,p})$ of 2 V and a frequency of 2 kHz, as well as a DC bias voltage (V_{CPD}) were additionally applied to the tip. The DC bias is the voltage applied to compensate the local contact potential difference (LCPD) at each point of the image. All KPFM images were recorded in the constant frequency shift (Δf) mode with a scanning speed of 1.7 sec/line. On an insulator, charged defects both at the surface or in the bulk can be detected as a modification of the LCPD [12,15,16,19,44].

The MgO(100) crystals (*Shinkosha*) were 7 mm \times 1 mm \times 0.3 mm in size and prepared with cycles of Ar-ion bombardment (2 keV) and annealing to ~1700 K by passing a current through a thin piece of Ta foil pressed against the back of the sample. Ba was vapor-deposited from a getter source (*SAES*) onto the as-prepared MgO(100) sample that was held at ~800-900 K in order to grow large clusters clearly attributable to Ba. Following evaporation, the sample was annealed for ~1 min at 1300 K to further increase the Ba particle size.

Results and Discussions

Figure 1a shows an NC-AFM image of the MgO(100) surface after several cleaning cycles. The height between terraces is ~ 2 Å, consistent with the minimum expected step height for MgO(100). Small bright features can be seen both on the terraces and decorating the step edges and some of these are circled in the figure.

Figure 1b shows a higher resolution NC-AFM image of the surface. Here, the features on the terraces have resolved into small protrusions with a density of ~0.01 monolayers (ML) where 1 ML is defined as the density of primitive surface unit cells. The widths (FWHM) of these protrusions is ~5 Å which is consistent with the size expected from individual point defects. There are several candidates for point defects on MgO(100), including O or Mg vacancies (vacs), ad-O atoms, ad-Mg atoms, segregated calcium and carbon, as well as adsorbates from the residual vacuum [20,45-48,49].

There are 88 bright point defects in Fig. 1b and of these 70 appear to be paired with only 18 isolated defects. The closest separation of these pairs is ~ 6 Å in the <110> directions. Such a separation is too long to originate from a direct bond.

One possible explanation for the pairing is that it results from water dissociation in surface O-vacs, the source of water being the residual vacuum. In such a scenario, the water would split with the -OH fragment filling the O-vac and the -H fragment adsorbing on a nearby O ion. Thus, two H-adatoms would be formed from each water molecule and given the relatively high barrier to diffusion for the H-adatoms (~1.2 eV) [50] we would expect to observe pairs of OH groups. Pairs of OH groups have been observed on $TiO_2(110)$ [51-55] but this is largely due to the high barrier calculated for the first hop (1.22 eV) [52]. STM measurements of subsequent hopping indicate a much lower barrier of ~0.8 eV [52]. Sequential images (e.g. that in Fig. 1b,c) confirm that the point defects are immobile at least on the timescale of several mins. Dissociation of other common impurities in the residual vacuum such as CO and CO₂ would not give rise to two equivalent fragments. While this explanation of the paired defects being hydroxyl is feasible, a more definitive assignment would require further study. For example, the proposed dissociation of water at the vacancies could be directly visualized with atomically-resolved imaging before and after active dosing of water. This pairing is not apparent in Fig. 1a because of the lower resolution of the image.

Fig. 2 shows two sequential images taken from the same surface as those in Fig. 1. Between the two images, there is an adventitious tip change that leads to an inversion in the contrast of the point defects from bright to dark. Similar contrast inversions have been explained by a change in the nature of the tip apex [36,54-58], the most simple of which involves a change in the potential. If the tip apex has a negative potential, it will be attracted for example to a positive H adatom which will therefore appear bright in the NC-AFM images. On the other hand, changing the

polarity at the tip apex to a positive potential means the tip apex will be repelled by the H adatom so that it will appear dark in the NC-AFM images instead.

Previous sample preparations of MgO(100) by sputtering/annealing did not lead to atomically-resolved images, presumably because the annealing temperature (1600 K) was not sufficient to form a well-ordered atomically flat surface [20]. We found that samples annealed only to 1300 K were rough and contained large particles over 100 Å in height. On the other hand, after sputter/annealing cycles to ~1700 K, several different MgO(100) samples were imaged with atomic resolution images. Figure 3 shows one such example. The separation between the bright spots in the <001> directions is ~4 Å, consistent with NC-AFM images from UHV-cleaved and thin film MgO(100) [29,39], as well as STM images of the film [38,40,41]. A line profile in Fig. 3b highlights the atomic corrugation in the image. This periodicity is twice the separation between Mg and O ions along <001> (i.e. 2.1 Å), suggesting that only one sub-lattice, the Mg or the O sub-lattice, is imaged bright. However, we cannot identify which sub-lattice appears bright from our NC-AFM images alone. Definitive identification of similar sub-lattices in ionic surfaces is difficult in NC-AFM and usually only possible by using molecular markers, by careful comparison between experimental and theoretical simulations of NC-AFM images, analysis of force spectra, or a combination of the three [36,54-58]. As in Fig. 1,2, there are also several point defects present that appear as small protrusions (one of which is circled). The point defects have a coverage of ~ 0.04 ML and have a streaky appearance. While such streakiness is often an indication of a fast-moving adsorbate, sequential images of the same area indicate that there is no movement of the adsorbate on the timescale of several minutes. Instead, the streakiness presumably arises from some imaging instability.

Figure 4 shows a topographic image of MgO(100) together with the simultaneously acquired Kelvin image. In the topography, a number of nanoparticles with heights of ~4 Å can be observed, several of which are circled. Given that the main contaminant on MgO(100) crystals annealed beyond ~1300 K in UHV [20] as well as in O_2 [45,46] is calcium, we tentatively assign these nanoparticles to CaO_x . Even after several tens of sputter/anneal cycles, we were not able to remove the CaO_x nanoparticles entirely, although their density varies from sample to sample and with each set of sputter/anneal cycles. The circles that are drawn in the topography image in Fig. 4a are mapped onto the Kelvin image in Fig. 4b, indicating that the nanoparticles are not strongly correlated with any variation in the surface potential.

On the other hand, there is a very clear increase in potential at the step edges. Surface potential increases over step edges have been reported previously [8,9,12,16], and have been explained by the presence of negatively-charged defects at the steps. Indeed an increase in the potential at the step edges was observed for UHV cleaved MgO(100) [12,16]. The increase in the surface potential we observe in Fig. 4b is ~1.2 V which compares well to the value of 1.5 V reported by Barth *et al.* [16] However, a direct comparison of the surface potential change with the earlier work cannot be made because the exact value of the potential increase will depend on the tip and sample condition. For instance, in other images that we recorded using a different tip and MgO(100) sample we observe a smaller potential increase of ~0.5 V. Likewise, in a separate measurement by Barth *et al.* [12] on another UHV-cleaved MgO(100) sample, a lower value of 0.5 V was found.

O-vacs on MgO(100) can be neutral or positively charged. An accumulation of positively-charged O-vacs at the step edges would lead to a decrease of the surface potential, contrary to the observation. In contrast, Mg-vacs can be neutral or

negatively charged. An accumulation of negatively-charged Mg-vacs at the step edges could therefore lead to an increase in the surface potential, as observed. However, even though the Kelvin contrast suggests that the steps are negatively charged, a definitive assignment is not possible because it has been shown that the Kelvin contrast can also be inverted depending on the nature of the tip apex [17,18]. This means that we cannot rule out the presence of positively-charged O-vacs at the step edges. Moreover, due to the expectation that water dissociates at step and corner sites [48,49], positively-charged H adatoms may also decorate the step edges and this would be consistent with the step edge decoration observed in Fig. 1a and recent observations on MgO(100) films [41].

Figure 5 shows another topographic image of MgO(100) together with the simultaneously acquired Kelvin image at a higher resolution. The image in Fig. 5a has three main features: a step edge, a number of CaO_x nanoparticles, and point defects that appear as small depressions.

As in Fig. 4, the step edge clearly corresponds to an increase in surface potential. As for the nanoparticles, in Fig. 5b their outlines are drawn on the topographic image and duplicated over the Kelvin map in Fig. 5c. There is no clear correlation between the nanoparticles and the Kelvin map, although a vague increase of surface potential is observed over 8 of the 12 particles outlined. There is, however, a rather clear correlation between the point defects and the Kelvin map. In Fig. 5b, the point defects are indicated with crosses and an identical array of crosses is superimposed on the Kelvin map. 102 of the 121 (84%) crosses lie on areas of increased surface potential. This correlation is also apparent in the line profiles shown in Fig. 5d. The line profiles show that the potential over the point defects have FWHM widths of ~20 Å compared with ~10 Å in the topographic image. The

magnitude of the increased potential over the step edges (~ 1.2 V) is about three times the size of the increase over the point defects (~ 0.4 V).

Fig. 6 shows higher resolution topography and Kelvin images where the point defects are again clearly observable as depressions. Of the 64 such point defects marked in Fig. 6, 60 correspond to regions of increased potential (i.e. 94%) and only four (red crosses) do not correspond to regions of increased potential in the Kelvin image. An uneven background in the Kelvin image, possibly originating from charged subsurface defects [14], may be responsible for the minority of defects, both here and in Fig. 5, that do not correspond with increases in the surface potential or it may simply be that these minority point defects are different to the others.

The observation that both step edges and point defects correspond to regions of increased surface potential suggests that the defects are negatively charged. This is in agreement with measurements on UHV-cleaved MgO(100) [12,16], although in the earlier work, individual point defects were not resolved. Negatively-charged Mg vacs may therefore be the origin of the point defects, although there are other candidates such as negatively-charged radicals (e.g. CO⁻ and O²⁻) that could form from gases in the residual vacuum [16,59]. However, we note again that the Kelvin contrast can be inverted depending on the nature of the tip so that positively-charged point defects cannot be ruled out. As such, it is possible that these point defects are H adatoms which would be in line with the tentative assignment of the point defects in Fig. 1b,c.

The distinctive pairing of the defects of Fig. 1b,c and Fig. 2 is not apparent in Figs. 5 and 6. One explanation for this could be the lower resolution in Figs. 5 and 6. In Fig. 7, we show line profiles both for a pair of defects and a single defect taken from Fig. 2b and labelled (i, ii) respectively. Plotted alongside these are line profiles from the pair of depressions circled in Fig. 6a, as well as a single depression, labelled

(*iii*, *iv*) respectively. The pair of defects from Fig. 2 have a combined lateral extent of ~20 Å which is about the same as the extent of the single depression in Fig. 6. The pair of depressions from Fig. 6 only have a slightly greater lateral extent. Thus, the apparently single defects in Fig. 6 may be unresolved pairs of defects. In addition, there seems to be two different types of single depressions: the profile (*iv*) has a depth of ~2 Å while a line profile taken from an adjacent depression (*v*) has a depth of only ~1 Å and it may be that the ones with greater depths are pairs. Similar size differences were observed in NC-AFM images of single H and paired H on TiO₂(110) [54,55].

Figure 8 shows the topography and Kelvin images of Ba nanoparticles on the MgO(100) surface. On the as-prepared surface, nanoparticles are already present up to a height of ~ 4 Å and these have already been tentatively assigned to CaO_x. Thus, only nanoparticles that exceed this height are assigned to Ba and most have heights between 8-20 Å. The contrast of the topographic image in Fig. 8a is adjusted so that the nanoparticles assigned to Ba appear yellow. The amount of Ba estimated from the NC-AFM images at this coverage corresponds to a hypothetical, uniform, continuous film with a thickness of ~2.1 Å. Figure 8b shows the corresponding Kelvin map. Some of the smaller particles, lower than ~4 Å in height, show an increase in potential of ~0.1-0.2 V and can be assigned to point defects and/or nanoparticles that were already present on the as-prepared surface. On the other hand, a decrease in the surface potential of ~0.1-0.2 V is found over nearly all the Ba nanoparticles as also shown in the line profile in Fig. 8c. This is similar to what has been reported for Na atoms adsorbed on TiO₂(110) [10], and this was interpreted as electron transfer from Na to $TiO_2(110)$. We interpret the present results in a similar way, as an electron transfer from the Ba to the MgO(100). This is consistent with the much lower work function of 2.7 eV for Ba [60] (and about 2 eV for BaO [61]) compared with 4.94 eV

for MgO(100) [62]. Tracking the changes in the charge distribution of such particles following exposure to automobile gases, such as oxygen and nitrogen oxides may shed light on the role of charge transfer.

Summary

In summary, NC-AFM and KPFM were used to characterize MgO(100) surfaces prepared by sputtering and annealing to ~1700 K. Surfaces prepared in this way are atomically-flat with wide terraces (100-1000 Å) that could be imaged with atomic resolution, including the resolution of point defects. The surface potential of these point defects, as well as features such as step edges, and deposited Ba nanoparticles were mapped using KPFM. The surface potential at the point defects increases relative to the terrace sites suggesting that they are negatively charged. An increase in surface potential was also found over step edges but a decrease in the potential was found over Ba clusters suggestive of an electron charge transfer from Ba to the MgO.

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Figures



Fig. 1 NC-AFM images of the same sputtered and annealed MgO(100) surface recorded with $f_0 = -340$ kHz. (a) $(1000 \text{ Å})^2$ image with $\Delta f = -17$ Hz, $A_{p-p} = -70$ Å, and $V_{\text{bias}} = -2.0$ V. Some bright features at the steps and terraces are circled red. (b) $(250 \text{ Å})^2$ image with $\Delta f = -58$ Hz, $A_{p-p} = -70$ Å, $V_{\text{bias}} = -6.0$ V. Examples of paired and single bright defects are circled green and red, respectively and a light-blue square is drawn round a dark defect. The black square indicates where the image in (c) was taken from. (c) $(150 \text{ Å})^2$ image with $\Delta f = -61$ Hz, $A_{p-p} = -70$ Å, $V_{\text{bias}} = -6.0$ V. The markers are the same as in (b). Note that in (b) and (c), there is a slight elongation of the defects in the $[01\overline{1}]$ direction due to the tip shape. In (b) and (c), a small number of dark regions are also present, one of which is highlighted with a light-blue square. These dark regions have rather abrupt changes in the contrast and we attribute this to some imaging artefact perhaps due to the slow response of feedback loop.



Fig. 2 Sequential $(70 \text{ Å})^2$ NC-AFM images $(f_0 = ~340 \text{ kHz}, \Delta f = -78 \text{ Hz}, A_{p-p} = ~100 \text{ Å}, V_{bias} = -6 \text{ V})$ of MgO(100) between which a tip change occurs. (a) The point defects appear as protrusions. (b) The point defects appear as depressions. A rectangle marks the same area in (a) and (b). Line profiles are taken from the indicated lines. The light-purple and light-blue lines in (b) correspond to the line profiles in Fig. 7.



Fig. 3 (a) Atomically resolved $(50 \text{ Å})^2$ constant height image ($f_0 = \sim 310 \text{ kHz}$, average $\Delta f = -127 \text{ Hz}$, $A_{p-p} = \sim 70 \text{ Å}$, $V_{\text{bias}} = -1.5 \text{ V}$). One of the point defects is circled red. (**b**) Line profile taken along the red line indicated in (a) showing the atomic corrugation and periodicity.



Fig. 4 Simultaneously recorded (2000 Å)² images of MgO(100) with parameters $f_0 = ~280$ kHz, $\Delta f = -56$ Hz, and $A_{p-p} = ~70$ Å. (a) Topographic image (z). (b) Kelvin image. Red circles mark the position of the CaO_x nanoparticles.



Fig. 5 Simultaneously recorded (500 Å)² images of MgO(100) with parameters $f_0 = ~280$ kHz, $\Delta f = -36$ Hz, and $A_{p-p} = ~70$ Å. (a) Topographic image (z). (b) As (a) but with with nanoparticles outlined in yellow and point defects indicated with green crosses. (c) Kelvin image. The outlines and crosses in (b) are superimposed on the Kelvin image. Almost all the crosses lie over areas of increased surface potential. (d) Red line profile taken from the topography image and light-blue profile taken from the topography image and light-blue profile taken from the topography (z) which clearly coincide with increases in the Kelvin contrast.



Fig. 6 Simultaneously recorded $(250 \text{ Å})^2$ images of MgO(100) with parameters $f_0 = ~280 \text{ kHz}$, $\Delta f = -39 \text{ Hz}$, and $A_{p-p} = ~70 \text{ Å}$. (a) Topographic image (z). (b) As (a) but with green and red crosses marking the point defects. (c) Kelvin image. The crosses in (b) are superimposed on the Kelvin image. 60 crosses are green and these indicate the point defects that lie over areas of increased surface potential. Four crosses are red and these indicate the point defects that do not lie over areas of increased surface potential. The pink, green and red lines in (a) correspond to the line profiles in Fig. 7.



Fig. 7 Line profiles over defects taken from the indicated lines in Fig. 2b and Fig. 6a.



Fig. 8 Simultaneously recorded $(1000 \text{ Å})^2$ images of Ba on MgO(100) with parameters, $f_0 = \sim 365$ kHz, $\Delta f = -91$ Hz, and $A_{p-p} = \sim 135$ Å. (a) Topographic image. (b) Kelvin image. Green arrowheads in (b) point at areas of increased potential. When superimposed on (a) the arrowheads point at some of the smaller particles in (a) which we attribute to point defects/nanoparticles already present on the as-prepared surface. Purple crosses in (b) are drawn over the areas of decreased potential. When superimposed on (a), nearly all the crosses appear over the large particles in (a) which we attribute to Ba. (c) Green line profile taken from the topography image and lightblue profile taken from the Kelvin image as indicated in (a) and (b). The Ba nanoparticles clearly correspond to decreases in the Kelvin contrast.