ARTICLE

Direct Measurement of the Attractive Interaction Forces on F^0 Color Centers on MgO(001) by Dynamic Force Microscopy

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ABSTRACT Defect sites on oxide surfaces play a dominant role in surface chemistry. The direct atomistic study of these sites is important but very difficult. We have mimicked the adsorbate−defect interaction by a dynamic force microscope tip measuring the interaction with a color center (F^0) on the MgO(001) surface. The experimental findings, complemented by density functional theory calculations, show a highly attractive adsorbate−defect interaction and a charge transfer at a critical distance.

KEYWORDS: atomic force microscopy · dynamic force microscopy · scanning tunneling microscopy · density functional theory · magnesium oxide film · color centers · defect states · adsorption sites

Chemical reactions on oxide surfaces depend critically on electron transfer processes. In this respect, the interaction of adsorbates with electron trapping sites is of fundamental interest. Some of these trapping sites have been clearly identified,[1,2] particularly for well-characterized systems such as MgO surfaces where stable electron trapping sites exist, for instance, in the form of oxygen vacancies also known as F or color centers. Oxygen vacancies exists in three possible variants, depending on the charge of the defect.[3,4] The removal of a neutral oxygen leads to a F^0 color center, with two electrons trapped in the cavity; the removal of O^- or O^{2-} ions leads to F^+ or F^{2+} centers, with only one or no electrons trapped in the cavity, respectively. Theoretical considerations suggest[3,4] that color centers are directly involved in chemical reactions, for example, as adsorption sites due to a more attractive defect−adsorbate interaction compared to the clean surface. However, color centers could be less attractive than regular sites, forcing adsorbates into positions on the surface far from these defects. Up to now, no direct experimental proof has been given whether F centers act as attractive or repulsive sites with respect to the surrounding surface.[5,6] Here we provide evidence of a strong interaction of an adsorbate with a F^0 center by means of dynamic force microscope measurements corroborated by density functional theory (DFT) calculations. The dynamic force microscope is the appropriate tool to mimic the interaction of an adsorbate with a defect.

RESULTS AND DISCUSSION

The microscope employed in this study is a dual-mode frequency modulation dynamic force microscope (FM-DFM) and scanning tunneling microscope (STM) operating at low temperature (5 K).[7,8] The advantage of this setup is that it is possible to employ both techniques on the same surface area using the same tip.[9] The experiments have been performed on 3 and 6 monolayer thick MgO films with no significant difference. Figure 1 shows a FM-DFM image taken at a constant frequency shift of $\Delta f = -1.60$ Hz. The image shows a MgO terrace with a defect present at the terrace's step indicated by the circle. Point defects, and particularly oxygen vacancies, form preferentially at sites like steps, corners, and kinks because their formation energy is lower at low coordinated sites. This was predicted theoretically[10] and later confirmed experimentally.[11] The color centers have been created in the STM mode by scanning the previously checked clean surface at scanning parameters of $V_S = 7$ V and $I_T = 6$ nA. This is necessary because the defect density of pristine MgO is quite low. The protrusions appear only in the high voltage treated scan area. It should be noted that adsorbates would have desorbed at these scan conditions and therefore are not responsible for the observed images. The

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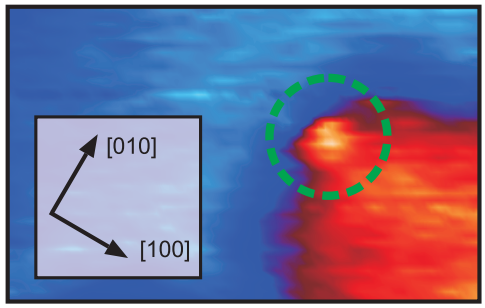

Figure 1. Constant frequency shift image showing a MgO terrace with a defect (indicated by the dashed circle). Scan range: 8.0 × 5.0 nm²; set point $\Delta f = -1.60$ Hz; bias voltage $V_S = -50$ mV; oscillation amplitude $A_{osc} = 350$ pm.

FM-DFM images are an ideal starting point for experimentally simulated adsorbate defect interaction studies. The tip, representing the adsorbate, scans laterally across the defect position at constant height.

This provides insight into the local surface potential and the local electronic structure at each surface position scanned by the tip. The result of such an experiment is presented in Figure 2. The three plots show the simultaneously recorded force sensor oscillation amplitude, tunneling current, and resonance frequency shift across the defect center. The object is a neutral oxygen vacancy, that is, a F^0 center. The proof that these constant height measurements have been performed on a F^0 center comes from applying a procedure described in ref 11, where dz/dV_S measurements in combination with DFT identified the electronic structure characteristics of this defect. The defect considered here gives rise to two peaks within the band gap of MgO, at around -1 and $+1$ V with respect to the Ag Fermi level. The peak at negative bias voltage originates from tunneling out of occupied defect states and is located in the middle between the valence band and the conduction band, whereas the peak at positive bias corresponds to tunneling into unoccupied defect states. Comparison with the Kohn–Sham energy levels derived from DFT calculations unambiguously identifies the defect as a F^0 center. Further details of this analysis can be found in refs 9 and 11.

Characterization at Different Tip–Sample Separations. The colored traces in Figure 2 indicate constant height scans at different tip–sample separations. The amplitude is constant for all tip–sample distances, a necessary condition to exclude an amplitude-induced effect in the frequency shift (the frequency shift scales with amplitude[12]). The tunneling current exponentially depends on tip–sample distance. At the largest tip–sample separation of 4.5 Å, the tunneling current vanishes and the frequency shift is an indicator of the long-range force background arising from electrostatic and van der Waals forces resulting in an average shift of $\Delta f = -0.52$ Hz. By decreasing the tip–sample separation by 0.5 Å, the modulus of the tunneling current and the frequency shift increase at the position of the defect. The tunneling current shows a value of $I_T = -0.5$ nA and a frequency shift of $\Delta f = -0.75$ Hz at the position of the defect. A further reduction of the tip–sample distance by 0.5 Å brings the tunneling current at the defect's position to $I_T = -9.9$ nA; the frequency shift results in $\Delta f = -1.13$ Hz. Despite the decrease by 1.0 Å in tip–sample distance, the average tunneling current on the regular terrace stays below $I_T = -0.05$ nA. The frequency shift background changes by about 0.15 Hz with decreasing tip–sample distance. This experiment demonstrates the highly attractive interaction with the point defect imaged. This is consistent with the results from previous DFT calculations[13] showing that F^0 color centers on MgO(001) are highly attractive sites and therefore represent preferred adsorption sites for adatoms or molecules.

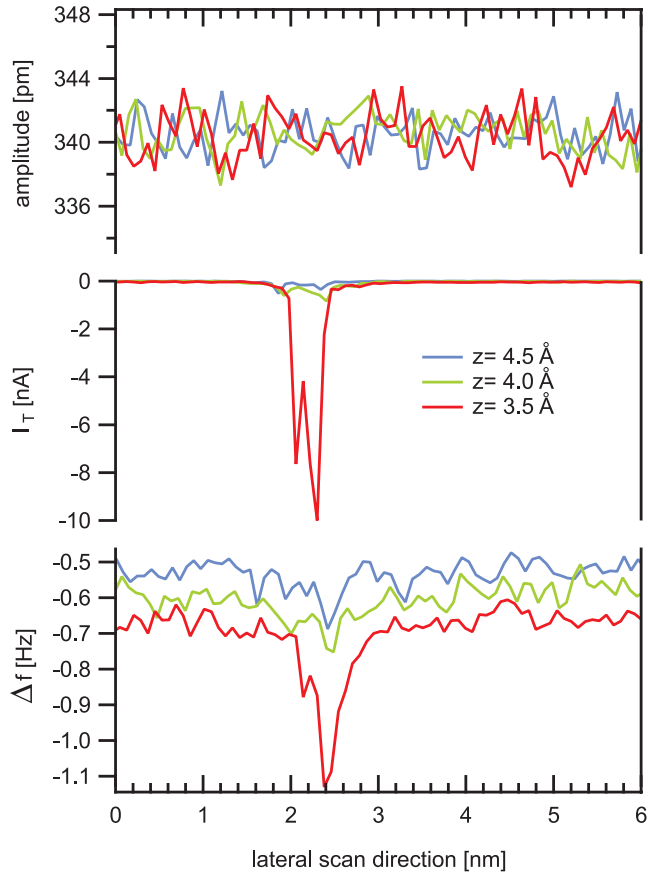

Figure 2. Constant height line scans across a F^0 defect situated at a step edge. The scan direction is along the step edge. The three presented channels have been simultaneously measured. The colors indicate different tip–sample distances. Note that the displacement of 4.5 Å has been arbitrarily chosen because absolute values are generally unknown in scanning probe microscopy. The top graph shows the oscillation amplitude. The amplitude is constant during scan process. This excludes artifacts in frequency shift. The graph in the middle presents the tunneling current, and the graph at the bottom shows the resonance frequency shift. Data have been taken at a bias voltage of $V_S = -50$ mV.

Analyzing the Adsorbate–Defect Interaction. In the literature, it has been debated how color centers are imaged by FM-DFM.[5,6] However, detailed FM-DFM measurements (also referred to as noncontact atomic force

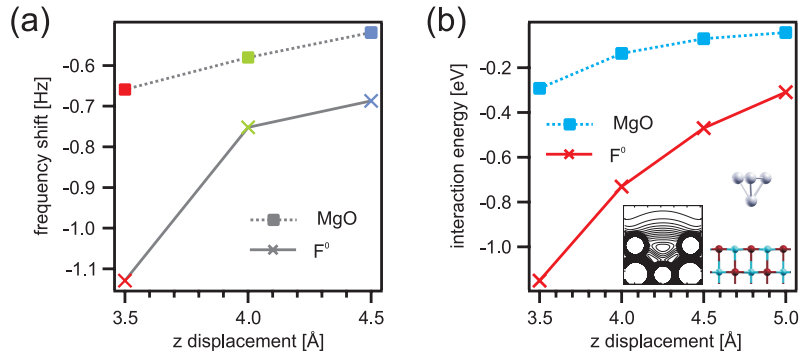

Figure 3. (a) Resonance frequency shift of a $Pt_{0.9}/Ir_{0.1}$ tip on a regular MgO surface (rectangles) and above a F^0 defect site (crosses). Experimental data are derived from the constant height measurements shown in Figure 2. The resonance frequency shift results from the potential gradients between tip and sample. The frequency shift is by integration related to the potential energy.[12] (b) Interaction energy of a Pt_4 cluster above the O site of a MgO surface (rectangles) and above a F^0 defect center (crosses) calculated by DFT. The insets show the spill over of the electron charge density of a F^0 center and the Pt_4 cluster above the MgO surface.

microscopy, NC-AFM) of well-defined color centers on MgO have not been reported so far. A missing oxygen atom in the lattice structure[14] is a "hole" and should be imaged in a similar manner in the topography signal. However, Figure 1 and the constant height data in Figure 2 definitely show that F^0 centers appear as clear protrusions in constant Δf FM-DFM images, resulting from a highly attractive interaction potential. Why are these defect sites so highly attractive? The attractive interaction is consistent with the electronic nature of this defect.[3,4] The charge density due to the two trapped electrons spills out of the surface such that there is a significant charge density above the surface plane compared to the surrounding MgO terraces (see inset of Figure 3b). This charge density is supposed to interact with the DFM tip, resulting in a strong attraction, as shown in Figure 2. Furthermore, the charge density accounts for the strong peak in the STM channel since the occupied F^0 gap states are close to the Fermi level in MgO/Ag(001) films.[11]

To further clarify the nature of the interaction between the tip and the surface defect, we have performed periodic supercell DFT calculations at the level of the generalized gradient approximation as implemented in the VASP code.[15,16] The Pt/Ir tip has been represented by a small tetrahedral Pt_4 cluster whose geometry has been optimized separately; the F^0 center has been generated by removing an O atom from a three-layer MgO slab and relaxing the structure. We computed the tip−surface interaction energy as a function of the distance of the apical atom of the Pt_4 unit from the MgO surface plane (see inset of Figure 3b). In these calculations, the Pt tip was not allowed to relax; the relaxation of the MgO surface under the effect of the tip is very small, at least for distances where no direct contact is formed between the tip and the surface (*e.g.*, at 3.5 Å from the surface the tip induces an outward relaxation of the O anion of 0.12 Å).

Figure 3 shows the interaction of a metal tip with the regular MgO surface and a F^0 color center with respect to the *z* displacement. The experimental data in Figure 3a, as derived from the results presented in Figure 2, show a significantly stronger interaction on top of the defect than on the regular MgO surface as already discussed; notice that the tip−sample distance is not known with precision in the experiment and is supposed to be around 4.0 Å since the tunneling current is fairly small on the terrace. In Figure 3a, the absolute *z* displacement has been assumed to be in the calculated range of Figure 3b. The comparison between measured and computed tip−sample interaction curves is necessarily qualitative since the exact shape and composition of the tip is not known, while this can have a substantial effect on the absolute value of the interaction energy.

Since the frequency shift *versus* distance behavior scales with energy, the qualitative agreement between the experimentally detected frequency shift (Figure 3a) and the theoretical calculations (Figure 3b) is well-established. Figure 3b shows that the interaction of Pt_4 with a F^0 color center and the oxygen site of the MgO surface are significantly different even at relatively long distance. We do not discuss explicitly the interaction of the Pt_4 tip with the Mg sites because here the interaction is significantly weaker. At a distance of 5.0 Å from the MgO surface, the interaction energy with the O site is nearly zero (0.04 eV, Figure 3b); when the tip is positioned above the F^0 center, however, already at this distance, there is an attractive interaction of 0.31 eV. By reducing the tip−surface distance, the interaction with the regular surface site and the F^0 center increases, but in this latter case, the potential is far more attractive (Figure 3b). At a distance of 3.5 Å, the interaction energy is 0.29 eV with the regular surface and 1.15 eV with the F^0 center. A further decrease of the distance leads to a very strong interaction: at 2.5 Å, when the tip and the surface are nearly in contact, the interaction energy with MgO is 1.26 eV, while that with the defect is 2.67 eV. At this distance, electron transfer occurs from the defect to the tip, which then becomes negatively

charged (as shown by the values of the Bader charges); this indicates that for distances below 3.0 Å there is a strong overlap between the wave function of the tip/metal cluster and that of the F^0 center. Therefore, 3.0 Å seems to be the critical distance necessary for a defect−tip charge transfer while the cluster senses already the attractive interaction at a distance of about 5.0 Å. The minima of the potential energy curves computed for the surface−tip interaction perpendicular to the surface are located at about 2.0 and 1.4 Å, respectively, from the O ion in the surface and the F^0 center, with interaction energies of 1.7 and 4.1 eV, respectively. Below these distances, the potential rapidly becomes strongly repulsive.

Very similar results have been obtained with two completely different models of the tip, that is, a single Pd atom and an extended two-layer Pt surface, providing a proper representation of the metallic character of a large "flat" tip. The Pd atom was chosen because of the low electron affinity, ≈0.6 eV,[17] compared to that of a Pt_4 cluster, ≈2.5 eV.[18] While the details of the interaction are obviously different, the strong interaction with the defect is always pronounced and is therefore a general feature of F^0 centers.[19] Also in these two cases, there is an electron transfer from the defect to the tip at distances of about 2.5 Å. So, the qualitative features are confirmed also with rather different models of the metal tip. Of course, the DFT approach used does not account for the van der Waals interactions of the defect with a macroscopic tip, but we have seen that the chemical forces on the F^0 center are clearly dominant over the dispersion forces.

The large difference in gradient between the vacancy and the perfect surface (0.39 eV/Å as computed with the Pt_4 tip in the interval 3.5−5.0 Å) is the reason for the detection of the protrusion in the experimental image. This possibility has been recently predicted theoretically using an oxide tip.[5] It should be noted, however, that in those calculations the computed differences in gradient between the regular and the defective surface (0.1 eV/Å) is much smaller than with a metal tip. A possible reason, other than the obviously different nature of the tip, oxide covered or pure metal, is the representation of the tip in ref 5 by a classical potential, which does only account for electrostatic interactions while the present results show the occurrence of chemical forces already at 5.0 Å from the surface in the case of the point defect.

CONCLUSION

A highly attractive tip−defect interaction has been investigated experimentally by FM-DFM and theoretically by supercell DFT calculations. Since FM-DFM is a local technique sensitive to local potentials, the attractive interaction has been detected in a direct manner for a surface defect on a MgO(001) surface, specifically the F^0 color center. This direct method allows one to probe electron trapping sites as preferred adsorption sites. The proven attractive interaction with metal adsorbates results from trapped electrons in the oxygen vacancy. The range of the attraction is a consequence of the charge density protruding from the surface and extends rather far from the surface. This reveals the role of trapped charges in important surface processes such as adsorption, nucleation, and growth.

EXPERIMENT AND THEORY

Setup: Our instrument is optimized for high-resolution imaging in both dynamic force microscopy (DFM) and scanning tunneling microscopy (STM). The microscope operates in ultrahigh vacuum (UHV) at cryogenic temperature (5 K), which reduces damping of the force sensor and enhances it with respect to tip stability as well as to reduction of thermal drift, piezo creep, and piezo hysteresis. The setup ultimately enables atomic resolution imaging and ultrastable spectroscopy of conducting and insulating surfaces by recording tunneling current and frequency shift with the same microscopic tip and if desired at the same time. The probe is a cut $Pt_{0.9}/Ir_{0.1}$ wire. In addition to detailed investigation of surface structures, the high stability allows site-specific spectroscopy measurements to be performed. All measurements presented in this article were performed in UHV at 5 K. More details on the particular equipment can be found in refs 7 and 8. The MgO surface has been prepared by reactive deposition of Mg evaporated from a Knudsen cell in an oxygen background pressure of 1×10^{-6} mbar onto a Ag(001) single-crystal support. The MgO growth rate was 1 monolayer per minute. During the reactive deposition, the Ag(001) single crystal was heated to
550 K.

DFT Calculations: The periodic supercell DFT calculations were performed at the level of generalized gradient approximation as implemented in the VASP code.[15,16] We used the PW91 exchange-correlation functional[20] and a plane wave basis set (energy cutoff of 400 eV). The electron−ion interaction was described by the projector augmented wave method.[21]

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