

Probing adsorption sites on thin oxide films by dynamic force microscopy

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Site specific atomically resolved dynamic force spectroscopy measurements were performed on a thin MgO film grown on Ag(001). The microscope is operated in ultrahigh vacuum at low temperature to ensure defined imaging condition, high stability, and drift reduction. Atomically resolved dynamic force microscopy images have been combined with site specific frequency shift versus distance measurements. The frequency shift is measured as a function of z and the lateral displacement. With these measurement characteristics the authors are currently probing inequivalent surface sites on thin MgO films to extract atomic-scale information on surface chemical reactivity and possible adsorption sites for metal atoms and small clusters. © 2006 American Institute of Physics. [DOI: 10.1063/1.2424432]

The interaction among metal atoms and clusters with metal oxide supports plays a key role in catalysis and microelectronics. Understanding the mechanisms of growth and parameters the geometric and electronic structures is important for a large number of technological applications.¹

The structure of metal/oxide interfaces is often complex and not well understood, in particular, the initial stages of the metal adsorption and the nature of the metal adsorption sites and of bonding to these sites. In order to gain further insights into these phenomena, we present site-specific atomically resolved dynamic force spectroscopy measurements performed on a thin MgO film grown on Ag(001).

Atomically resolved dynamic force microscopy (DFM) images obtained under ultrahigh vacuum conditions at constant frequency shift have been well established. However, precise measurements at 5 K where the frequency shift is measured as function of z and lateral displacement have not been presented in detail. From these spatially resolved frequency shift spectra the interaction force and energy can be directly derived. For the analysis and interpretation of DFM images it is important to measure the full interaction potential between the probe and the sample surface. Instead of keeping the frequency shift constant over the sample surface, it becomes necessary to map the frequency shift at different z displacements over the sample surface. Such type of measurement allows to search for the largest interaction potential and an analysis of the variation of the interaction potential at specific surface sites.

Frequency shift versus distance curves can be measured at specific lattice sites or can be acquired in every point corresponding to a pixel of a DFM image. Different types of modes for the force mapping have already been discussed in the literature for atomic force microscopes under ambient conditions operated in a static mode.²⁻⁴ Measurements of site-dependent frequency shift curves on an atomic scale as a function of the tip-sample surface distance have been reported by Morita *et al.*⁵ as well as distance dependent DFM images,⁶ where the possibility to acquire three-dimensional force-related maps by DFM has been presented. Complete three-dimensional force fields with atomic resolution by DFM have been shown by Schwarz and co-workers,^{7,8} where

the force fields have been derived from frequency shift curves aligned at the previously acquired topography image.

In this letter the presented measurements have been obtained by utilizing a single quartz tuning fork sensor (Fig. 1) driven at small oscillation amplitudes in the range of about 0.4 nm. All experiments have been performed in ultrahigh vacuum at a temperature of 5 K using a custom-built instrument. Details of the sensor electronics have been described in detail in Ref. 9. The sensor used in the presented measurements has a resonance frequency $f_0=17\,866.7$ Hz, a Q factor of 25 000, and a stiffness of about $k=22\,000$ N/m. A cut Pt/Ir wire with a diameter of 0.25 mm has been used as a tip. The tip is electrically connected by a thin Pt/Rh wire with a diameter of 50 μm . Both the tip and Pt/Rh wire are insulated from the tuning fork and its electrodes. The single tuning fork assembly is operated by the sensor controller/FM detector easyPLLplus from Nanosurf¹⁰ in the self-exciting oscillation mode in combination with a custom made FM detector. The principle of frequency detection was described by Albrecht *et al.*¹¹ A unit by Nanotech Electronics¹² has been used for scan control and data acquisition.

The model catalyst used in these experiments is a thin MgO film grown on Ag(001). The study of thin metal oxide films pursues several goals. The use of thin films is a way of circumventing the problems associated with charging of insulating materials. Ultrathin films allow comparison between

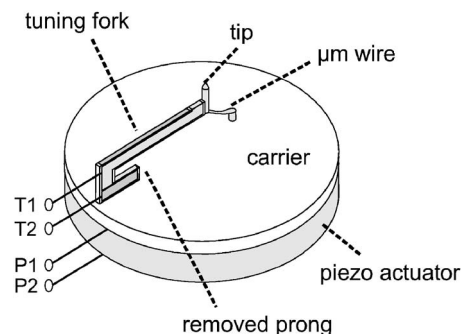


FIG. 1. Schematic setup of the single quartz tuning fork sensor for DFM and scanning tunneling microscopy measurements. The lower prong of the quartz tuning fork has been partially removed. The quartz tuning fork has been tuned to a carrier support. The tip is separately connected by a thin wire.

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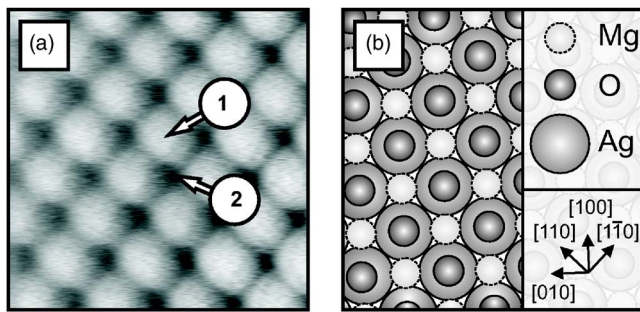


FIG. 2. (a) DFM image of MgO on Ag(001) with atomic resolution. Scan area of $1.5 \times 1.5 \text{ nm}^2$, $\Delta f = -8.5 \text{ Hz}$, oscillation amplitude $A = 0.35 \text{ nm}$, $T = 5 \text{ K}$, and approximately 30 pm corrugation. The labels 1 and 2 indicate the position of frequency-distance measurements (see text). (b) The MgO/Ag(001) growth model, schematic illustration of the configuration: Mg atoms occupy hollow sites, i.e., they continue the Ag fcc lattice ($a = 0.409 \text{ nm}$), while O atoms occupy top sites.

force microscopy and simultaneously performed tunneling microscopy. The single crystal Ag(001) surface was cleaned by several cycles of ion sputtering (Ar^+ , $10 \mu\text{A}/\text{cm}^2$, 800 V) and annealing (700 K). The MgO/Ag(001) films were prepared by e-beam evaporating Mg in an oxygen background pressure of $5 \times 10^{-7} \text{ mbar}$ using deposition rates of 0.75 ML min^{-1} . Usually MgO films between 2 and 8 ML have been prepared.

Figure 2(a) shows an image with atomic resolution which has been obtained on a flat terrace of the MgO film. The direction of largest differences in contrast corresponds to the distance of next-neighbor ions in the (010) direction. After acquisition of the DFM image, frequency-distance measurements were performed above the center of the two inequivalent labeled sites (1, 2), which will be discussed later on in more detail. A schematic illustration of the MgO/Ag(001) growth model is provided in Fig. 2(b).

For the acquisition of two- or three-dimensional force or energy maps, the frequency shift needs to be measured, while moving the oscillating tip in the x , y , and z directions over a selected scan field. In principle it does not matter in which direction one first moves the tip over the scan field. The order is defined by the needed precision in the spatial resolution and drift aspects of the scanner unit. A schematic view of this method is provided in Fig. 3(a). The three dimensions in the x , y , and z , directions can be independently addressed. The movement of the tip is adjusted by time synchronized triangular voltage cycles for the different scan directions. Here we have chosen to acquire the data set in the sequence of x , z , and y direction, where x has the fastest and y the lowest scan speed. A single x , z scan is marked by a

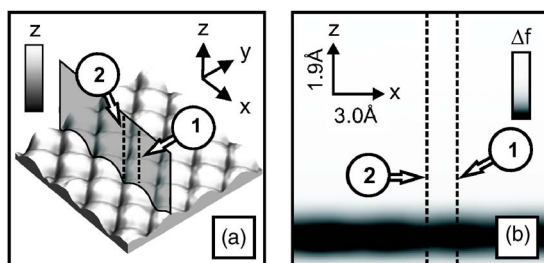


FIG. 3. Schematic of the DFM spectroscopy method. (a) During the data acquisition the oscillating tip is moved in the x , z , and y directions over the selected scan field. A single x , z scan is marked by a gray shaded area. (b) Frequency shift image map of the selected x , z plane ($1.5 \times 0.95 \text{ nm}^2$).
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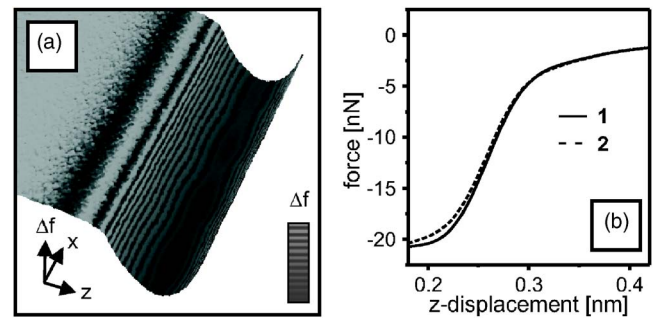


FIG. 4. (a) Pseudo-three-dimensional view of the frequency shift measured in the x , z direction. (b) Selected force vs distance curve calculated by the given formula (1) from the frequency shift image map at specific lattice sites marked in Fig. 3(b).

gray shaded area in Fig. 3(a). With this setup we achieve a very high spatial resolution of the frequency shift in the x , z direction. Such a frequency shift map is provided in Fig. 3(b), where the frequency shift is color coded and plotted across the x , z direction. The onset of atomic resolution can be seen by the lateral variation of the potential. In Fig. 4(a) a pseudo-three-dimensional view of such a data set is plotted in order to illustrate the measured interaction potential in more detail. The atomically resolved contour lines show the variation in the interaction strength of the tip-sample surface potential.

From these data sets it is possible to derive the interaction force $F(z)$ between the tip and the sample as well as the according energy $U(z)$ by using formulas (1) and (2).¹³ The expression for the force in terms of the frequency shift is given by

$$F(D) = \frac{2k}{f_0} \int_D^\infty \Delta f(z) \left(\left(1 + \frac{A^{1/2}}{8\sqrt{\pi(z-D)}} \right) - \frac{A^{3/2}}{\sqrt{2(z-D)}} \frac{d}{dz} \right) dz, \quad (1)$$

where D is the distance of closest approach between the tip and the sample, A is the oscillation amplitude, z is the tip-sample distance, and F is the interaction force between the tip and the sample. Integrating Eq. (1) gives the corresponding expression for the interaction energy $U(D)$ between the tip and the sample,

$$U(D) = \frac{2k}{f_0} \int_D^\infty \Delta f(z) \left((z-D) + \frac{A^{1/2}}{4} \sqrt{\frac{z-D}{\pi}} + \frac{A^{2/3}}{\sqrt{2(z-D)}} \right) dz. \quad (2)$$

Figure 4(b) displays two site specific force-distance curves calculated from the frequency shift map in Fig. 3(b) (labeled by 1 and 2). The selected curves are equivalent and in full agreement with single frequency shift curves taken at the corresponding surface sites. Besides further quantification we can now compare the features of the image obtained at a constant frequency shift [Fig. 2(a)] with the site specific

frequency shift curves [Fig. 3(b)]. The analysis reveals that one type of ion is imaged as a protrusion, while the other one is imaged as a depression, which is a typical finding for ionic surfaces imaged by DFM.^{14,15} Here, the tip seems to prefer one atomic species. The comparison of the two force-distance curves calculated from frequency shift versus distance curves [Fig. 4(b)] clarifies that the deepest minimum occurs at the protrusion, which corresponds to the largest tip-sample interaction. Since the electron density on the MgO surface is maximal above the oxygen atoms,¹⁶ it is likely that the maxima in the DFM image correspond to the position of the oxygen atoms. Moreover, electron paramagnetic resonance (EPR) spectra have shown the possibility to determine the adsorption site of Au atoms, namely, adsorption on top of oxygen ions on the terrace of the MgO surface.¹⁷ The hyperfine coupling constants measured by EPR spectroscopy are compared to density functional theory calculations, indicating a good qualitative agreement of the theory with the experimental results. We can now connect a metallic tip apex to correspond to a metal atom or cluster, which probes the sample surface for adsorption sites of equilibrium force or energy interaction. With these measurement characteristics we have an additional tool that probes inequivalent surface sites to extract atomic-scale information on surface chemical reactivity and possible adsorption sites for metal atoms and small clusters. The combination with the highly resolved interaction potential in the x and z directions allows to derive the full shape of the interaction potential for further comparison with theoretical calculations.

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