Imaging surface defects using Atomic Force Microscopy: An ultimate frontier for chemical resolution

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We present the results of calculations performed to simulate the process of atomic scale imaging with the noncontact atomic force microscope (NC-AFM) that explicitly take into account thermally induced dynamical processes occurring at the surface in real time, using a multiscale simulation method. AFM is a striking example of dynamic formation of an interface between two surfaces: a tip and a substrate. The dynamic atomic force microscope, operated in the frequency modulation or "noncontact" mode (NC-AFM), is now a well established tool in surface science that is capable of imaging insulating as well as conducting surfaces with true atomic resolution. However, chemically identifying image features still remains a challenge and requires detailed and accurate theoretical simulations. In this presentation we discuss several recent examples of application of NC-AFM both in UHV and in liquid environment. These include imaging and manipulation of oxygen vacancies and Pd atoms at the MgO (001) surface, manipulation and control of an electron transfer between surface defects, and modeling of AFM imaging of the CaF_2 (111) surface in water. Dynamic processes are evolved in real time using a kinetic Monte Carlo method, while simultaneously being imaged using a virtual atomic force microscope, which performs a simulation of the entire instrumentation. The results of these simulations establish different mechanisms of contrast formation in NC-AFM imaging and show how dynamical processes can significantly change the contrast seen in images.

In the NC-AFM, an atomically sharp tip attached to the end of a cantilever is oscillated perpendicular to the surface at its resonant frequency and at a constant amplitude, so that the tip apex comes close to the surface at one of its turning points. The attractive force acting on the tip over its oscillation cycle due to its interaction with the surface has the effect of reducing the resonant frequency of the oscillations, which can be precisely measured and used as an imaging signal as the surface is scanned. In this way, the NC-AFM can produce an image of frequency shift at a constant height of closest approach; however, it is also common for the surface height to be modulated in order to maintain a constant frequency shift set point, which results in the microscope producing a topography of constant frequency shift.

We present the results of the multiscale modeling of the process of lateral manipulation of a Pd adatom adsorbed on the MgO (001) surface using NC-AFM at finite temperature and in real time as a tip moves above the surface [1,2]. We show that the stochastic thermal motion of Pd adatoms can be controlled by localized forces from an oscillating tip and demonstrate how this can be achieved in practice. The energy barriers for manipulation as a function of tip position in three dimensions above the surface are determined from atomistic calculations and then used in a kinetic Monte Carlo algorithm to determine the evolution of the system at a finite temperature and in real time for a realistic trajectory of the tip, which is in turn governed by a complete

numerical simulation of the instrument including the response of the feedback loops. We can then predict the probability of a successful manipulation event for a given procedure.

Electron transfer is an essential process in molecular electronics, as well as in many other areas, such as in electrochemistry, biology, catalysis, information storage, and solar energy conversion. Therefore, understanding fundamental mechanisms of electron transfer between molecules and electrodes, and their dynamics at the molecular level, is important fundamentally as well as for technological applications. Using ab inito calculations we propose how to control and image single electron transfer between surface defects individual atoms using an NC-AFM tip.

Our DFT calculations demonstrate that on perfect and stepped ultrathin MgO/Ag(100) films the doubly occupied F^0 centre transforms spontaneously into the paramagnetic F^+ centre by losing one of its electrons to the metal support [3]. On the MgO/Mo(100) films, where the Fermi level is at higher energy, F^0 centers are stable but F^+ centres are unstable and capture one electron from the Mo metal to generate the corresponding doubly occupied vacancy. We demonstrate that this process can be reversed by applying an electric field of NC-AFM tip allowing studying the electron transfer rate between the metal substrate and individual surface defects as a function of oxide thickness. We also demonstrate that in a system, which consists of both a neutral F-centre and Pd adatom some distance apart on the MgO (001) surface, the transfer of an electron from the vacancy to the Pd adatom could be induced by the electric field from the NC-AFM tip [4]. Both the rate of the electron transfer and the relative energies of the two states depend on the distance between the vacancy and the metal adatom due to the Coulomb interaction between the charged defects. Therefore in addition one can control the relative energies of the final and initial states through the separation of the two defects. Simulation of NC-AFM images of surface oxygen vacancies and Pd atoms in different charge states demonstrated that the transfer of an electron between the vacancy and metal adatom could be detected by a change in the NC-AFM image contrast.

Finally we consider the mechanism of contrast formation in the NC-AFM imaging of the CaF_2 (111) surface in water. These simulations are carried out using classical molecular dynamics methods. Potentials of mean force are calculated using the free energy perturbation method. Our simulations demonstrate that in this case the cause of the lateral contrast is rather complex and is determined by a convolution of the direct interaction between tip and surface and forces entirely due to the water structure around the tip and surface [5].

References

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