MEASURING THE FORCE OF INDIVIDUAL SURFACE IONS

Adam S. Foster[1,2] Andrey Y. Gal[2] and <u>A. L. Shluger</u>[2]

[1]Laboratory of Physics, Helsinki University of Technology, FIN-02015, Helsinki, Finland

[2]Department of Physics and Astronomy, University College London, Gower St., London WC1E 6BT, UK, a.shluger@ucl.ac.uk

Recent experiments using dynamic force microscopy (DFM) demonstrate that the short-range interaction forces can be measured selectively above chemically identified sites on surfaces of insulators. These experiments and atomically resolved DFM imaging of insulators rely on advanced theoretical models for their interpretation [1]. We will discuss and compare different strategies for reliable interpretation of high resolution DFM images of insulating surfaces. The theoretical models available now are sufficiently refined to provide information not only about the surface, but also the probe tip, and the physical changes occurring during the scanning process. We will compare the mechanisms of image contrast formation on ionic and covalent surfaces, discuss the transferability of image interpretation between surfaces of similar structure, and DFM applications for probing spectroscopic and chemical properties of surface defects.

In spite of recent experimental advances in high resolution imaging details of the mechanism of contrast formation and chemical identities of observed image features often remain unresolved due to uncertainties in the tip structure. One can use several strategies to achieve further understanding of the various factors important in resolution and to provide unambiguous image interpretation.

One approach is to use a reference system, i.e. a surface which has a well understood image pattern, in order to characterize a tip, and then to use the same tip on another surface. One such a surface is Si(111), however, it has a well established image only in the case of a Si dangling bond tip. By combining experimental dynamic SFM images of the CaF_2 (111) surface with extensive theoretical modelling, we demonstrate that the two different contrast patterns obtained reproducibly on this surface can be clearly explained in terms of the change of the sign of the electrostatic potential at the tip end. We also present the first direct theoretical simulations of experimental dynamic SFM images of an ionic surface at different tip-surface distances. Experimental results demonstrate a qualitative transformation of the image pattern, which is fully reproduced by the theoretical modelling and is related to the character of tip-induced displacements of the surface atoms. Modelling of the image transformation upon a systematic reduction of the tip-surface distance with ionic tips allows an estimate of the tip-surface distance present in experiment, where 0.28 - 0.40 nm is found to be optimal for stable imaging with well-defined atomic contrast. While excellent agreement between theory and experiment is found for imaging with highly symmetric tips, irregularities in apparent contrast patterns can be used to identify tip asymmetries. This allows us to establish the CaF_2 (111) surface as a standard for characterization of tips with respect to their symmetry and ionic termination.

Another approach is to establish a standard tip. We used *ab initio* calculations and a pure silicon tip to study the tip-surface interaction with four characteristic insulating surfaces: (i) the narrow gap TiO_2 (110) surface, (ii) the classic oxide MgO (001) surface, (iii) the ionic solid $CaCO_3$ (10-14) surface with molecular anion, and (iv) the wide gap CaF_2 (111) surface [2]. Generally we find that the tip-surface interaction strongly depends on the surface electronic structure due to the dominance of covalent bond formation with the silicon tip. However, we also find that in every case the strongest interaction is with the highest anion of the surface. This result suggests that, if the original silicon tip can be carefully controlled, it should be possible to immediately identify the species seen as bright in images of insulating surfaces. In order to provide a more complete picture we also compare these results to those for contaminated tips and suggest how applied voltage can be used to probe chemical identity.

Yet another approach could be to use high precision measurements of force curves above well defined surface sites. Recent advances in the low temperature DFM facilitated the direct atomic precision measurements of forces between DFM tips and surfaces of binary compounds, such as NiO and KBr.

However, the measured force *vs*. distance curves are essentially "blind" as the chemical identity of the surface sites and tip atoms remained unknown. We used the CaF_2 (111) surface, where contrast formation in DFM imaging is well understood from theoretical modelling [1,3], to demonstrate that the short-range interaction forces can be measured selectively above *chemically identified* surface sites. This requires measuring interaction forces as low as a few pico-Newtons and interaction energies of about 0.5 eV. We used theoretical analysis and quantitative comparison between experiment and theory to define a credible chemical structure of the tip out of several possible options. This approach allows one to establish a tip used in measuring a particular image and thus to provide its interpretation.

Finally, one can "mark" a particular surface sub-lattice by adsorbing molecular species. In particular, it is well known that formate molecular ions adsorb on Ti sites on the TiO_2 (110) surface. Thus unambiguous imaging of individual formate ions on these surfaces should allow one to determine the chemical identity of the image features on the surface itself. We have studied the adsorption of formate ions on the TiO_2 (110) surface and calculated the DFM image using different tips. We compare these images with those of oxygen vacancies which are always present at reduced TiO_2 (110) surfaces. The results suggest that with oxide tips one should be able to distinguish these different species and thus identify the nature of ions imaged as bright.

Intuitively, one expects similar image patterns when imaging structurally similar surfaces with the same tip. This has been experimentally observed perhaps only on alkali halides. We consider three more complex materials, CaF_2, BaF_2 and CeO_2, with a very similar surface structure but different electronic structure. Our modelling of the CaF_2 (111) imaging predicted that at relatively large tip-surface distances (0.35 – 0.45 nm in theory) the "triangular" features observed in some experimental images could be attributed to the surface F^- ions imaged by a tip with positive polarity, and disc-like features correspond to the Ca^{2+} ions imaged by a tip with negative polarity. The triangular pattern is shown to be due to the tip interaction not only with the closest surface F^- ion but also with an F^- ion in the third surface layer. The question then is: i) whether the same image patterns should be expected for surfaces of other materials with similar structure; and ii) how the image pattern depends on the tip structure and surface electronic structure. It is well known from experiment that the clear image patterns described above are very rare and correspond to some very stable and sharp tips [3], which are apparently well-represented in our modelling by the MgO tip. We used this tip to model imaging of the BaF_2 (111) and CeO_2 (111) surfaces too. Both surfaces have the same structure as that of CaF_2, but BaF_2 has a much larger lattice constant, and CeO_2 has a very different electronic structure. Our modelling predicts qualitatively the same image pattern for all three materials, suggesting that the same image interpretation could be used when these patterns are observed experimentally. We then studied the dependence of the image on the tip structure using a Si tip model with an oxygen atom adsorbed at the apex Si atom (Si-O tip). Quantum-mechanical calculations performed for the CaF_2 and CeO_2 surfaces demonstrate that the image pattern is now different from that obtained with the MgO tip, but again similar for both materials. These results illustrate the mechanisms of image dependence on the tip structure and confirm that for tips with identical properties images of similar surfaces should also look qualitatively similar.

Finally, we discuss a more complex issue of DFM imaging of encapsulated systems. We modeled the imaging of KI nano-crystal encapsulated inside a single-wall carbon nanotube. The results demonstrate that the conductive nano-tube practically screens the electrostatic potential of the KI one-dimensional nano-structure with the square K_2I_2 cross-section encapsulated inside. However, one can image a dipole produced by a pair of charged K and I vacancies. These results clearly demonstrate the potential of DFM for probing very week interactions important in nano-science.

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