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Scanning Force Imaging of Colloids on CaF_2 (111) in the Ultra-High Vacuum

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Abstract. Scanning force imaging of dielectric surfaces in the ultra-high vacuum is a well established technique yielding images with a lateral resolution down to the atomic level. In contrast, scanning force images of metallic particles on dielectric surfaces are often obscured by artifacts resulting from strong metal/tip interactions. For the system $Ca/CaF_2(111)$ prepared by electron-induced metallization it is shown that imaging in the contact mode is strongly influenced by electrostatic and adhesive forces while the non-contact mode reveals differences in the van der Waals interaction of the tip with the metal and the dielectric surface. Both modes of operation are applied to study electron beam induced effects on the $CaF_2(111)$ surface ranging from the onset of erosion at step edges to the formation of nm-sized colloids.

INTRODUCTION

Scanning force microscopy (SFM) [1] involves a variety of interatomic forces [2] of different strength and range. The most commonly discussed long-range force is the van der Waals interaction that can be attractive as well as repulsive depending on the tip/sample system and is considered to be the main limiting factor for the lateral resolution of force microscopy [3]. When approaching the surface with the tip to distances less than approximately 3Å the "jump into contact" occurs and short range forces become dominant and enhance the strong hysteresis when retracting the tip. In particular, this phenomenon has been studied for metallic systems experimentally [4] and theoretically [5] and it has been shown that the presence of such adhesive forces involve a massive rearrangement of both tip and surface atoms. Often such rearrangement is not reversible and scanning results in a transfer of atoms from one lattice site to another [6]. Attempts for a realistic theoretical treatment of the consequences of scanning involve complicated models combining short and long range contributions. These simulations confirm that scanning leads to a strong instability of the surface which very sensitively depends on the local geometrical and chemical structure of the tip and its vicinity [7]. Experimentally many of these peculiarities limiting resolution can be overcome by introducing an "immersion" liquid between tip and surface that removes the instability and allows imaging with extremely low forces ($<10^{-10}$ N) acting on the surface [8].

For most applications, however, the introduction of a liquid is not a practical option but force microscopy in the ultra-high vacuum (UHV) [9,10] is desired. For simple ionic surfaces very high resolutions have been obtained [11], however, the significance of atomic features is still questionable and high resolution images are mostly discussed in terms of atomic periodicity rather than atomic resolution. Recently it has been shown that force imaging can favourably be influenced by introducing an electric field that allows a subtle control of tip/surface forces [12] and a discrimination of materials by their dielectric constant [13].

In the present paper we investigate a more complex situation than simple dielectric surfaces namely Ca colloids on a cleaved $CaF_2(111)$ surface. For this system we observed all of the mentioned interaction forces. The role of these forces for imaging the heterogeneous system is elucidated in some detail in the first section while the following sections show examples of imaging nm-sized metallic

particles in both, the contact as well as non-contact mode of operation. It will be demonstrated that imaging precipitates of a highly reactive metal on an inert surface is a challenging task for the conventional SFM technique but can be mastered with sufficient care.

TIP-SURFACE INTERACTION

In the following we present SFM results obtained in the UHV on the (111)-surfaces of CaF_2 crystals. Electron irradiation was done with a commercial low energy electron source operated at 800eV electron energy. Currents ranged from 1 to 100nA and were applied for some seconds or minutes while electrons were focused into a spot of approximately $0.25mm^2$. Since the SFM setup presently does not allow a precise determination of the sampled position within the irradiated spot, absolute values for the current density are hard to determine and unreliable. For the present purpose we only discriminate between weak and strong irradiations and present series of images showing qualitatively a progression in irradiation intensity. SFM scanning times were typically 60 seconds. Figure 1(a) shows a force distance curve obtained on a surface cleaved in air, transferred to the vacuum and measured after some days. The curve is typical for the interaction of a SiN cantilever with a dielectric surface. During approach the cantilever is bent only very gently until the jump into contact suddenly pulls the tip towards the surface. For a further approach and following retraction of the cantilever this is followed by the usual cycle through the repulsive force regime and a sudden lift off at a distance much larger than that for the jump into contact. The force curve is markedly different for the same surface when imaging some minutes after electron irradiation as shown in Fig. 1(b). There a long range attractive force is superimposed that can be measured even micrometers away from the surface. Similar phenomena have been observed during imaging of unirradiated surfaces where cleavage-induced charges acting on the tip were found to be stable even after days [11]. In our case we interpret this long range attractive force as an electrostatic interaction resulting from the charge that is accumulated during electron irradiation [14]. Since charging is found to be strongly inhomogeneous it often results in significant distortions of force images and has to be removed, e.g. by a heat treatment. However, heating is not an option when imaging colloids on surfaces since heating can drastically change the amount and topography of metallization.

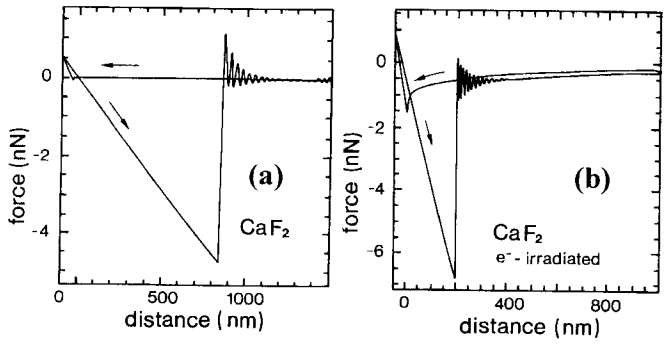

Fig. 1: Force distance curves with jump into contact for the unirradiated (a) and irradiated (b) $CaF_2(111)$ surface. The strong oscillations after retraction of the tip are a result of oscillations of the cantilever that are only weakly damped in the UHV.

We believe that the severe image distortions seen in Fig. 2 are a result of adhesion of the tip to the surface when scanning in the contact mode of operation. In this image, metal colloids form the background to an irregular pattern of stripes in the scan direction that do not correspond to any topographic features. Probably images are not distorted on CaF_2, however when the tip reaches a colloid it sticks to the metal and due to the scanning movement the adhesive force is converted into

a torsion of the cantilever that is so strong that it is seen as an artifact even in the "topography" image. When the torsional force exceeds the adhesion, the cantilever suddenly pulls off and after a short time of recovery resumes normal operation.

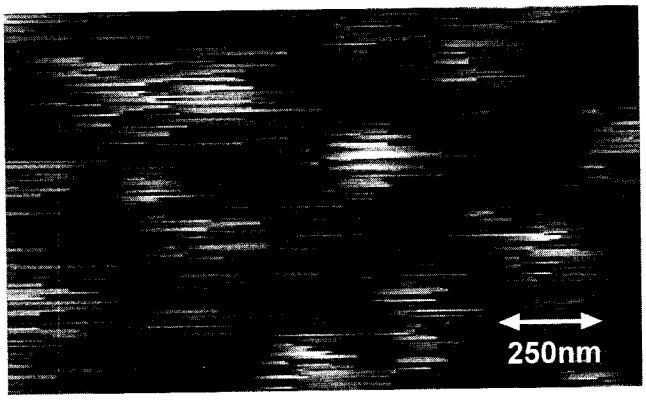

Fig. 2:
Contact mode image of colloids. The stripes are a result of the adhesion between tip and metal. The stripe starts when contact is established and ends when the cantilever torsional force exceeds adhesion. The strength of the adhesion can be inferred from the size of the stripes often acting far beyond the extension of the colloid.

Figure 3 is an image of a clean surface taken immediately after cleavage in vacuum and demonstrates that for high resolution an electrostatic force may be present as a constant background but does not result in image distortions since charge inhomogeneities are present only at a much larger scale. The image was obtained in the constant height mode; i.e. by positioning a Si tip at a fixed distance in contact to the surface and recording the normal forces acting on the cantilever during scanning. The observed periodicity results from subtle variations of the attractive force of the order of 0.01nN and reproduces the hexagonal structure of the (111)-surface. At some locations distinct irregularities are found as the one marked by the circle. We speculate that such deviations may represent point defects like surface H-centers that might be stable over the necessary fraction of the scanning time. Similar features have been observed in UHV on LiF(100) [15], however presently it cannot be decided whether the deviations from the regular grid are scanning artifacts or due to topography. So far it is impossible to reproduce such results and confirm the presence of defects by repetitive scanning. However, it should also be kept in mind that surface defects generally have a considerable surface mobility and evidence for a stable defect configuration could presumably only obtained by imaging at very low temperatures.

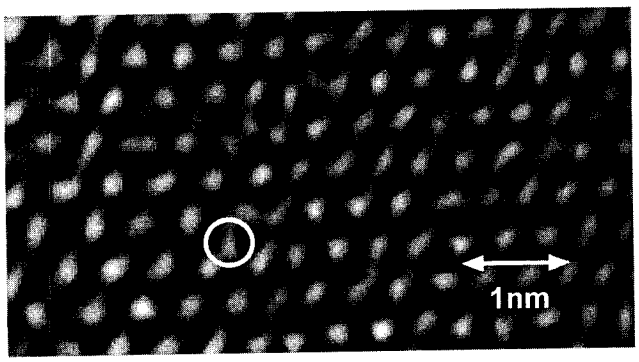

Fig. 3: Normal force image (constant height mode) obtained on a freshly cleaved CaF_2(111) surface. Since the forces observed were close to the detection limit, the S/N-ratio was poor and the image was Fourier filtered to better visualize the atomic periodicity.

In the non-contact mode of operation the SFM signal is proportional to the force gradient and, therefore, can be used to determine intermolecular potential curves. This offers the possibility to measure subtle differences in the interaction between the tip and different materials. An example exploiting

this is shown in Fig. 4 where similar to the procedure used in the measurement of Fig. 1 tip/surface interactions of unirradiated and irradiated surfaces are compared to each other. This time, however, the measurement was performed days after irradiation and charging was completely eliminated. Figure 4 demonstrates that there is a significant difference between the surfaces also for the long range van der Waals or polarization interaction and the SFM is able to detect the different chemical nature of surface constituents.

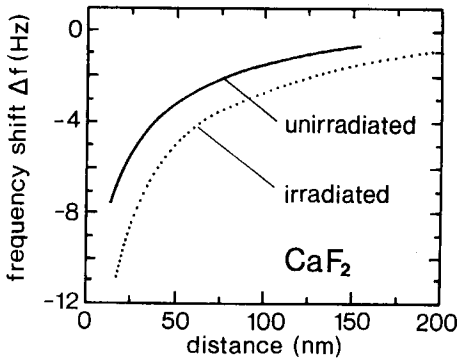

Fig. 4: Comparison of forces acting on the tip during an approach towards an unirradiated and irradiated spot of the surface, respectively. The second measurement was taken some minutes after the first one.
Shown is the detuning of the cantilever vibration in the non-contact mode as a function of the tip/surface distance.

CONTACT MODE IMAGING

Due to the signal distortions arising from adhesion it is generally extremely difficult to obtain undisturbed images of colloids in the contact imaging mode. Even after successfully taking one image, a second scan will most times fail even when performed immediately after the first under identical conditions. The reasons for this behaviour are not yet clear but a possible explanation is a temporary chemical passivation of the tip by a pick up of surface contaminants. Also a partial oxidation of the colloids may account for increased stability. This argument is supported by the observation that very small colloids are found to be the most stable and we rarely experienced adhesion problems during imaging in air [16]. In both cases, a considerably large fraction of the colloid is expected to be oxidized in contrast to the weak oxidation of a larger colloid in the UHV.

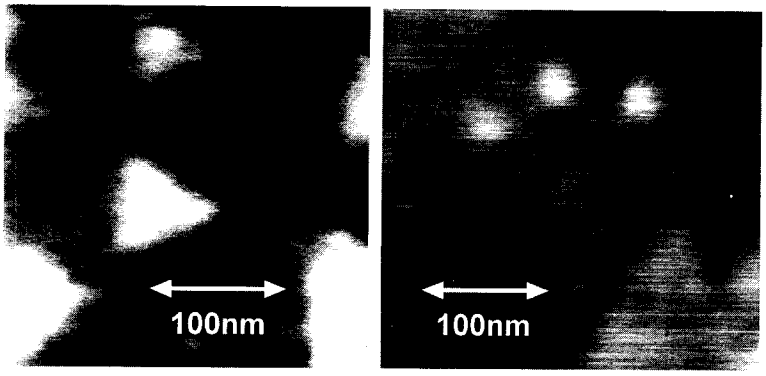

Fig. 5: Images of small Ca colloids obtained in the contact mode of operation. The vertical scales (maximum height) are 2.3nm for the left image and 0.6nm for the right image, respectively.

Examples for the formation of small colloids are shown in Fig. 5. The left image is a striking example for the alignment of colloids along crystallographic directions that we found also for ionic crystals with a simple cubic symmetry (NaCl, LiF). The straight lines intersecting the image are step

edges of monoatomic height. Apparently, colloids are not aligned along these edges but along parallel lines without any topographic signature. We speculate that these lines represent dislocations along the crystallographic directions providing nucleation sites for surface metal in the early stages of colloid formation and later the colloid is formed by a pick up of diffusing material, thereby preserving the triangular shape of the initial nucleation. The ability of dislocation lines in halide crystals to collect surface metal has been shown previously by metal decoration experiments [17]. The right image represents the state-of-the-art in detection of smallest precipitates imaged in the contact mode. The observed colloids have a lateral extensions below 20nm and their height of 0.7nm is equal to twice the height of a F-Ca-F triple-layer of the CaF_2 lattice.

NON-CONTACT MODE IMAGING

The non-contact mode of operation allows imaging with a large tip/sample distance and thus avoids adhesion-related artifacts. Nonetheless imaging is not at all straightforward and free from features difficult to interpret. However, for several scans we at least succeeded in precisely reproducing surface topography during repetitive scanning of the same region. The main problems still arise from the inhomogeneous chemical composition of the surface. As outlined in the above discussion about force gradients, the tip responds differently to metal colloids and the CaF_2 matrix. Sudden changes in the interaction force can strongly disturb the sensitive balance of the vibrating cantilever and introduce considerable instability. In some instances this even results in a temporary jump into contact. Non-contact imaging of oxidized replica of the colloids, however, is not affected by such phenomena confirming the role of the tip/metal-interaction for the instability. As shown in Fig. 6, imaging of larger colloids can be performed with a quality and resolution that is comparable to that obtained by imaging in air [18]. The set of images represents a cross-sectional selection through an irradiated spot where the irradiation intensity was increased from the left to the right image. As found previously [18] the number density of colloids increases with electron intensity for the lower intensities and for high intensities, large colloids created by diffusion [19] form the background for a large number of small colloids resulting from direct surface metallization.

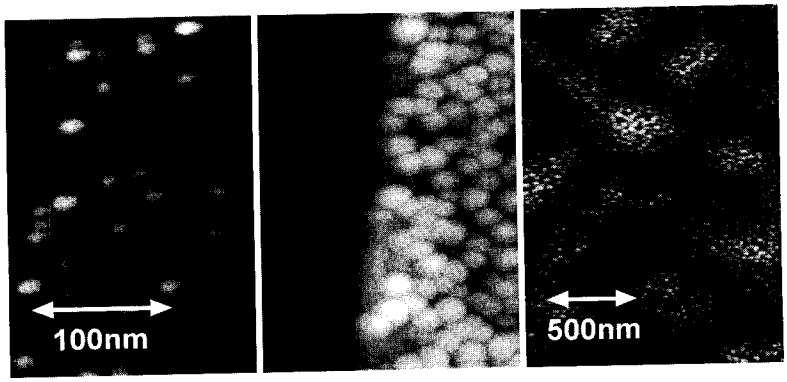

Fig. 6
Colloids prepared by electron irradiation in UHV and imaged in UHV after three days of oxidation in air. The series represents a progression from the periphery (left) to the center (right) of the irradiated spot.

An example for non-contact imaging in UHV without any exposure of the surface to air is shown in Fig. 7. The series again is a progression towards higher irradiation intensity from left to right, however, intensities were much smaller than those used to obtain images from Fig. 6. The left hand frame represents the unirradiated surface and demonstrates the unexpectedly high lateral resolution that can be obtained in the non-contact mode. The other frames exhibit only few indications for colloids but an increasing tendency of erosion at step edges

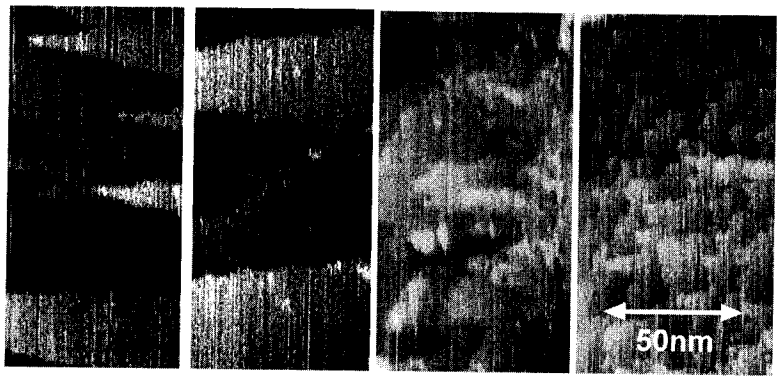

Fig. 7
Surface erosion due to weak electron irradiation. The left image represents the unirradiated surface while the others have been irradiated with progressively increased intensity.

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REFERENCES

1 C.F. Quate, Surf. Sci. **299/300**, 980 (1994)
2 J.N. Israelachvili, *Intermolecular and Surface Forces*, Academic Press, London 1985
3 W. Zhong, G. Overney, D. Tománek, Europhys. Lett. **15**(1), 49 (1991)
4 U. Dürig, O. Züger, D.W. Pohl, Phys. Rev. Lett. **65**(3), 349 (1990)
5 O. Tomagnini, F. Ercolessi, E. Tosatti, Surf. Sci. **287/288**, 1041 (1993)
6 S. Ciraci, E. Tekman, A. Baratoff, I.P. Batra, Phys. Bev. **B46**(16), 10411 (1992)
7 A.L.Shluger, A.L. Rohl, R.T. Williams, R.M. Wilson, Phys. Rev. **B52**(15), 11398 (1995)
8 F. Ohnesorge, G. Binnig, Science **260**, 1451 (1993)
9 L. Howald, E. Meyer, R. Lüthi, H. Haefke, R. Overney, H. Rudin, H.-J. Güntherodt, Appl. Phys. Lett. **63**(1), 117 (1993)
10 F.J. Giessibl, Jpn. J. Appl. Phys. **33**, 3726 (1994)
11 L. Howald, H. Haefke, R. Lüthi, E. Meyer, G. Gerth, H. Rudin, H.-J. Güntherodt, Phys. Rev. **B49**(8), 5651 (1994)
12 L. Howald, R. Lüthi, E. Meyer, H.-J. Güntherodt, Phys. Rev. **51**(8), 5484 (1995)
13 J. Hu, X.-D. Xiao, M. Salmeron, Appl. Phys. Lett. **67**(4), 476 (1995)
14 R. Bennewitz, D. Smith, M. Reichling, E. Matthias, N. Itoh, R.M. Wilson, Nucl. Inst. Meth. **B101**, 118 (1995)
15 M. Ohta, T. Konishi, Y. Sugawara, S. Morita, M. Suzuki, Y. Enomoto, Jpn. J. Appl. Phys. **32**, 2980 (1993)
16 R. Bennewitz, M. Reichling, R.M. Wilson, R.T. Williams, K. Holldack, M. Grunze, E. Matthias, Nucl. Instr. Meth. **B91**, 623 (1994)
17 H. Bethge, phys. stat. sol **2**, 755 (1962)
18 M. Reichling, R.M. Wilson, R. Bennewitz, R.T. Williams, S. Gogoll, E. Stenzel, E. Matthias, Surf. Sci. **366**(3), 531 (1996)
19 M. Reichling, Nucl. Inst. Meth. **B101**, 108 (1995)