ADVANCED
MATERIALS

Surface Analysis I

Imaging Surfaces, Electric Charges and Magnetic Domains with the Atomic Force Microscope

By Jürgen P. Rabe*

The atomic force microscope (AFM) provides a means to record images of surfaces on the atomic length scale.[1,2] It is closely related to both the scanning tunneling microscope (STM) and the stylus profilometer, combining atomic resolution with the ability to image insulating materials. In the AFM an ultrafine tip is mounted on a small lever and brought into close proximity of the sample (Fig. 1). For high resolution imaging, the force between tip and sample is measured sensitively by the deflection of the lever, using either electron tunneling or some optical detection scheme. As the tip is scanned across the sample, a contour map of constant force can be recorded. For true non-contact imaging at lower lateral resolution, a shift in the resonance frequency of the lever is detected, giving contours of constant force gradient. The key feature of the AFM is its ability to measure extremely small forces. In order to achieve this, the lever has to be as soft as possible. At the same time, it should have a high resonance frequency in order to minimize its sensitivity to vibrational noise from the environment. The solution to this is miniaturization. Indeed, with microfabricated levers and an optical detection system, a force sensitivity of the order of 10^{-9} N in water and 10^{-7} N in air has been achieved.[3] The number of forces contributing to the net force are manyfold, ranging from hard core repulsion at very small distances through van der Waals attraction and capillary forces to long range electrostatic and magnetic forces. In practice there exists a balance of several contributions.

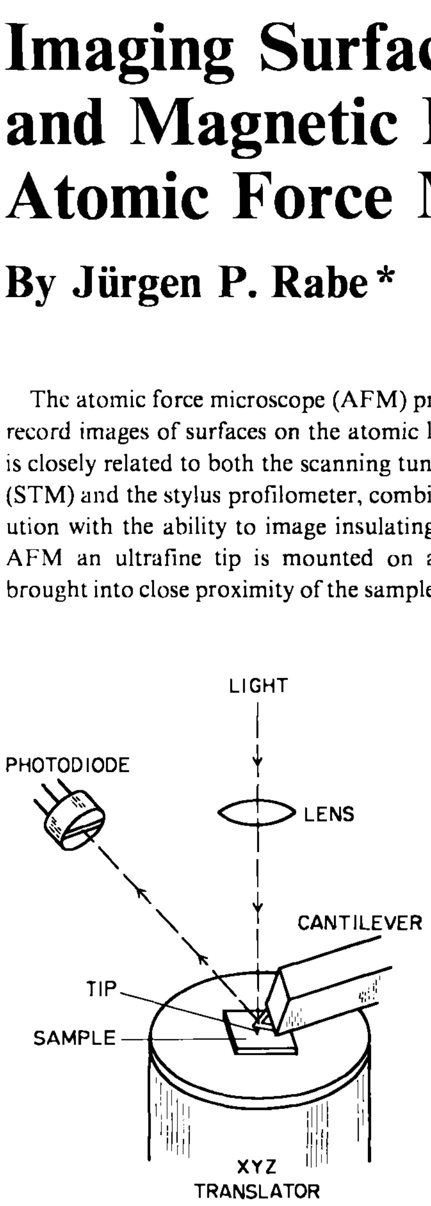

Fig. 1. The atomic force microscope (AFM) detects the vertical motion of the tip which is proportional to the force that the tip applies to the surface of the sample. The XYZ translator moves the sample in all three directions in space. In the particular detection scheme shown here the deflection of the laser beam, which is reflected from a cantilever, is measured sensitively by a two segment photodiode. The measurements can also be performed in fluid ambients like water [3].

Atomically resolved surface images have been obtained on both conducting and non-conducting materials like graphite,[2] boron nitride[4] or mica.[5] Also, the local step structure on some ionic crystal surfaces has been studied. For example, the (111) and (100) surfaces of chemically polished AgBr single crystals show some interesting differences.[6] While on the (111) surface, individual steps coinciding with both low index directions $\langle 0\bar{1}1\rangle$ and $\langle 1\bar{2}1\rangle$ were found, the (100) surface is dominated by crossing steps. These results may help to understand the different preferential J-aggregation of dyes occuring on these surfaces, a process which is of importance in photographic emulsion technology.

The ability of the AFM to image non-conductors enables it to be applied to organic materials, provided that the forces involved are small enough not to disrupt the sample. That this is indeed possible has been demonstrated for the surface of an amino acid crystal, DL-leucine,[7] and for a layer of polyalanine on glass.[5] Imaging an individual organic molecule, however, is even more demanding, since a single molecule can diffuse across the surface, particularly under the influence of the AFM tip. The adsorption energies must be particularly small if one wants to avoid a large distortion of the adsorbate on the surface. This, in turn, means that the forces applied by the AFM tip should be equally small. In this respect it is important to realize that surfaces in air are typically covered with an adsorbate layer of water and unknown contaminants causing a capillary force for small tip-

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to-sample gaps which can exceed the externally applied forces. An elegant way to eliminate this force, besides operating in ultra high vacuum, appears to be operation under water or other fluid ambients.[3] Figure 2 shows ten AFM images of the clotting of the human blood protein, fibrinogen, adsorbed on mica before (A) and after introduction of the clotting enzyme thrombin into the aqueous ambient (B through J).[5] The role of the thrombin is to unmask some polymerization sites on the fibrinogen. The resulting fibrin monomers polymerize to form larger aggregates. Attempts to obtain high resolution images of single fibrinogen molecules suffered from a commonly encountered problem in both STM and AFM, namely that the adsorbates did not adhere well enough to the mica. However, as the fibrin monomers polymerized into the larger aggregates, they were more reproducibly imaged (Fig. 2B). The aggregates could still move, growing larger and connecting to each other (Figs. 2C through F) until a single chain spanned the whole field of view (Fig. 2G). Next, a second chain grew adjacent to the first (Fig. 2H), then a third (Fig. 2I) and finally nearly the whole field of view was covered with a fibrin net (Fig. 2J). While the resolution in these images is considerably lower than in the examples mentioned above, the results demonstrate the potential of the AFM to study processes occurring at the interphase between a solid and a liquid at molecular resolution and in real time. Also, higher resolution images may be achievable with microfabricated tips which are currently under development. A more fundamental limitation, namely the motion of the adsorbate on the surface may be circumvented by imaging in more viscous fluids or by lowering the temperature.

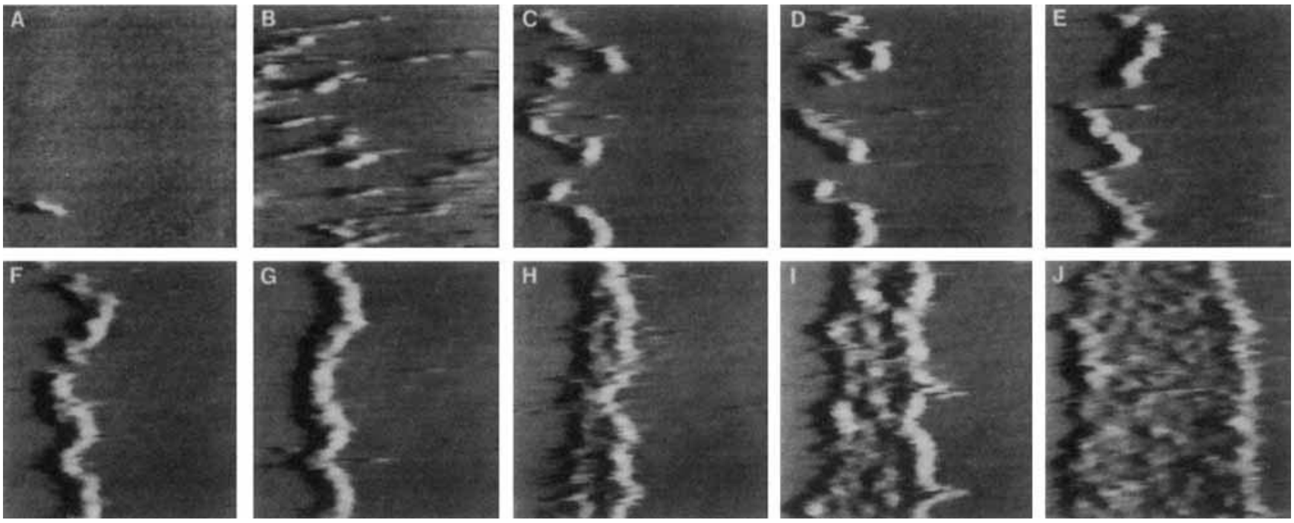

Fig. 2. Ten AFM images taken from a video tape that show clotting of the blood protein fibrinogen in real time. The images were selected from before introduction of the clotting enzyme thrombin (A), and at various times after its introduction between 9 min (B) through 33 min (J). Each image area is 450 nm x 450 nm [5].

The ability of the AFM to measure minute forces cannot only be used to image surface structure but also to elucidate other surface properties, for example, friction on an atomic scale.[8] Also intriguing is the imaging of electromagnetic forces at surfaces. Compared to the van der Waals force, electromagnetic forces are long range, i.e. they are dominating for large tip-to-sample separations. This makes imaging

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possible in a true non-contact mode. Recently it has been demonstrated that the AFM can be used to deposit and image localized charge on an insulator with a lateral resolution surpassing that of other currently available techniques.[9] A lever is oscillated near its resonance frequency at a tip-to-sample distance of the order of 100 nm. As the tip is scanned across the sample, variations in the tip-to-surface force gradient will alter the effective spring constant of the lever. The resulting change of its resonance frequency is detected as a change in the amplitude of the tip oscillation. If local charge is present on the surface, the tip will feel an additional force due to the coulomb attraction of the charge to its image charge in the tip. The measured force gradient contour will have a peak at the location of the charge. Moreover, by applying a voltage to an electrode behind the sample it is possible to determine the sign of the charge present. The amount of charge can be estimated by measuring the force as a function of distance. Initial experiments[9] have demonstrated the ability of the AFM to deposit and detect low charge levels on insulator surfaces with a lateral resolution of the order of 1 µm. The sensitivity was estimated to be about 100 electrons. The charge had been deposited by applying a voltage pulse to the tip. Interestingly, while charge on polymethylmethacrylate (PMMA) and sapphire samples was observed to decay over approximately 1 h in air, charge on mica and quartz appeared to dissipate so rapidly that it was impossible to obtain an image of a locally charged region.[9] An improved technique, employing a modulation of the bias of the back electrode on the sample[10] resulted in a further increase in resolution to 0.2 µm with an estimated sensitivity of 6 ± 3 electrons. With this, bipolar charging after contact charging has been observed in an area of about 10 µm diameter.[10] This is a surprising result, which could not be observed in previous tribocharging experiments with the lower lateral resolution. It may, however, help us to understand the spot-to-spot variations found in these earlier experiments. The above mentioned high resolution data may be complicated by the fact that they were obtained in air, with water possibly contributing to charge mobility at the surface. However, they demonstrate the ability of AFM to address very old but still unresolved problems on the underlying mechanisms in contact- or tribo-charging.

Magnetic forces can also be measured with a very similar setup, provided a magnetic tip of, for example, iron or nickel is used. Figure 3a shows an image of magnetic domains in a 2.5 µm thick NiFe film and Figure 3b shows the corresponding Kerr image, giving essentially the same structure.[11] Clearly, entire domains and domain walls are imaged with the AFM with submicron resolution. The inset in Figure 3 shows the direction of magnetization in each domain inferred from the images. The tip was scanned at a constant height of 150 nm above the surface, and it was concluded that the field of the tip did not move the walls significantly in this comparatively thick film. The image contrast at the wall is attributed to the sense of the rotation of the magnetization across the wall. However, a detailed interpretation of the complicated magnetic structure of domain walls in soft magnetic materials is still difficult. For a thinner film (30 nm), domain walls appeared to be narrower and more susceptible to stray magnetic fields. Therefore, the tip could induce wall motion when brought sufficiently close to the surface.[11] While this may be disadvantageous in some cases, it is anticipated, that it will provide a means for studying magnetic properties such as wall motion coercivity on a microscopic scale. As far as resolution is concerned, a magnetic image of the domain pattern on a TbFeCo thin film on silicon has been obtained with a resolution of approximately 25 nm.[12] Clearly, a better understanding of the magnetic domain structure is of great fundamental and also technological interest as performance in magnetic recording devices depends on the detailed micromagnetic structure of the recording medium.

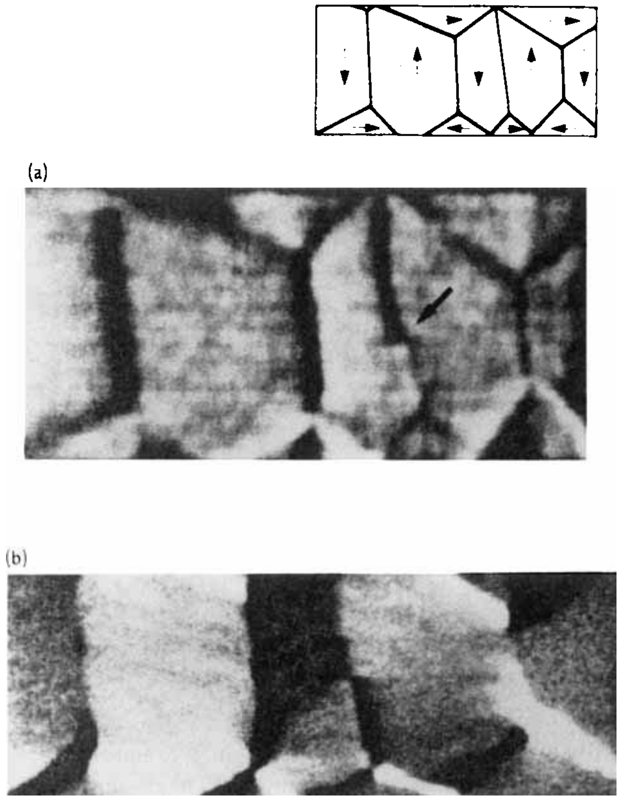

Fig. 3. (a) Magnetic force microscopy image and (b) Kerr image of domains in permalloy film. The imaged region is 50 µm x 30 µm; magnifications differ in horizontal and vertical directions. Arrow marks the location of a Bloch line [11].

The results given above demonstrate the wide variety of forces which can be measured by the AFM on small lateral length scales. For high resolution surface imaging the advantage of AFM over STM is the ability of the former to image insulators. While this appears particularly promising for organic systems, a further reduction of the forces applied during scanning is desirable.

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Low Temperature Deposition of a CaF_2 Insulator Layer on GaAs*

Over recent years there has been widespread interest in the development of alternative insulators for silicon and GaAs, especially where these might be obtained in epitaxial layer form to permit the production of multilayer semiconductor-insulator structures.[1-3] Several workers have reported the growth of epitaxial CaF_2 on silicon[4-6] and GaAs.[7-9] The major problems in obtaining good quality films lie in the lattice mismatch between the layer and substrate (0.6% for Si; 3% for GaAs) and the thermal conductivity mismatch (α $CaF_2 = 1.9 \times 10^{-5}$ K^{-1}; α Si $= 4 \times 10^{-6}$ K^{-1}; α GaAs $= 6.9 \times 10^{-6}$ K^{-1}). For GaAs applications the former has been overcome, partially at least, by the use of solid solutions of CaF_2–SrF_2, the composition $Ca_{0.44}Sr_{0.56}F_2$ being perfectly lattice-matched to GaAs at 25 °C.[10] The thermal expansion coefficient differences between GaAs, CaF_2, and SrF_2 produce strain at the film/substrate interface during cooling from the growth temperature. In the case of high elastic modulus material such as CaF_2 and CaF_2-rich alloys this leads to cracking, whilst the more plastic SrF_2 and SrF_2-rich alloys deform by dislocation generation, so that the layer becomes a poor substrate for subsequent semiconductor overgrowth. The best solution to this problem lies in a reduction of a growth temperature to minimize cooling strains. This demands a growth system which permits transport and low temperature decomposition of a suitable precursor, which must nevertheless remain sufficiently stable to withstand premature thermal decomposition.

Benac et al.[11] have recently reported polycrystalline growth by pyrolytic decomposition of bis(pentamethylcyclopentadienyl)calcium $(C_5Me_5)_2Ca$ in either SiF_4 or NF_3 at 150 °C. This low decomposition temperature may, however, lead to handling problems. At the observed growth rates of 10–100 µm/hr the product is polycrystalline CaF_2 with a grain size of 20–50 µm but X-ray photoelectron (XPS) studies show relatively high impurity levels (approximately 18% carbon and 7% oxygen) in these films.

Recent work at RSRE Malvern and Queen Mary College London has led to the development of a new approach to the deposition of CaF_2 on GaAs at low temperatures, which combines the advantages of the organometallic approach with those of photochemically-induced precursor decomposition. This permits the use of thermally stable precursors, thus reducing the risk of premature reaction outside the required deposition zone, and of gas phase reactions which generally result in poor epitaxy. Careful design of the photochemical reactor and the use of suitable projection masking in the incident photon beam can then be used to promote selected-area deposition.

The process is based on the photochemical decomposition of bis(1,1,1,5,5,5-hexafluoro-2,4-pentanedionato)calcium(II), $Ca(hfac)_2$, (Fig. 1) using xenon lamp radiation in the 180–300 nm waveband. The precursor compound was developed and synthesized at Queen Mary College, London.[12]

The material is obtained in the form of a pale yellow powder which sublimes at approximately 100 °C. It is impor-

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