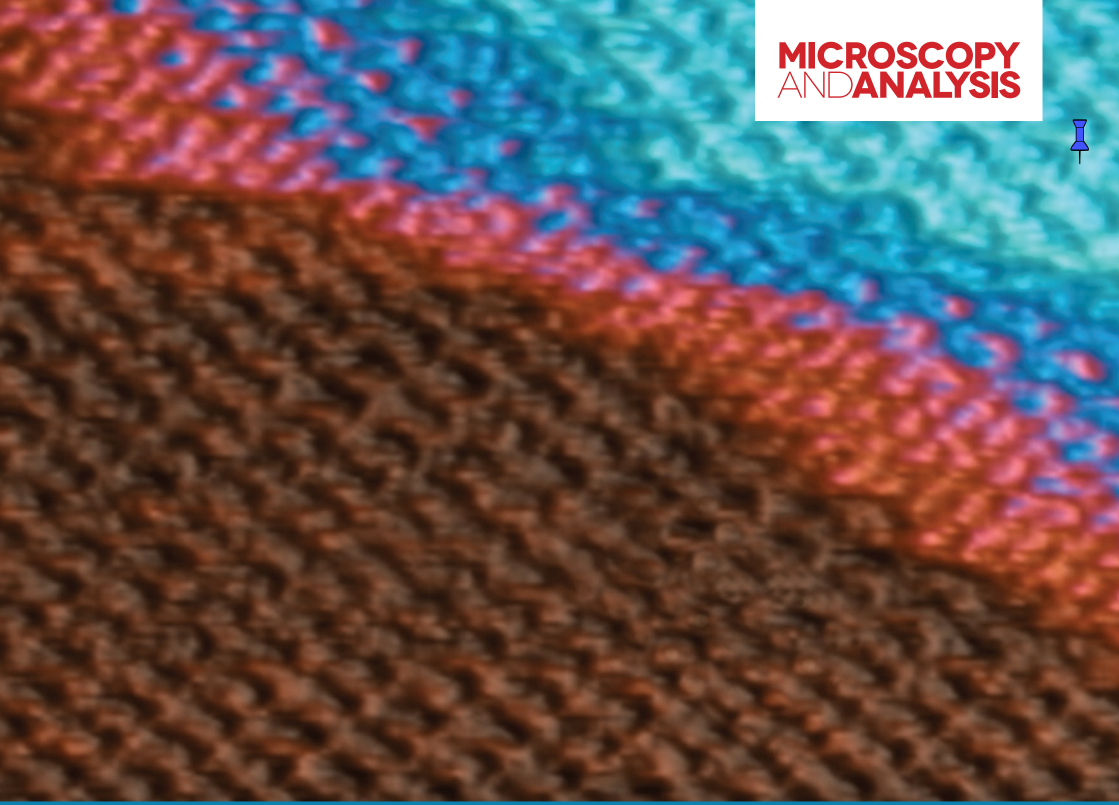
MICROSCOPY AND ANALYSIS



# Atomic Force Microscopy for Materials

Essential
Knowledge
Briefings

First Edition, 2017

BRUKER

Front cover image: atomic-resolution imaging of calcite in fluid using PeakForce Tapping and a Dimension FastScan atomic force microscope.

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## About Essential Knowledge Briefings

Essential Knowledge Briefings, published by John Wiley & Sons, comprise a series of short guides to the latest techniques, applications and equipment used in analytical science. Revised and updated annually, EKBs are an essential resource for scientists working in both academia and industry looking to update their understanding of key developments within each specialty. Free to download in a range of electronic formats, the EKB range is available at www.essentialknowledgebriefings.com

# INTRODUCTION

Atomic force microscopy (AFM) is a high-resolution analytical technique that dazzled the scientific world when it was first introduced in the 1980s. For the first time, researchers could capture images of surfaces at the atomic scale, with AFM able to resolve features less than 1nm in size. Since then, AFM has become a widely used technique for characterizing a variety of surface properties on biological, organic and inorganic materials.

AFM uses a cantilever with a sharp tip attached to the free end to detect the varying forces as the tip is scanned over a sample surface. Not only does this allow it to build up a detailed topographic map of the surface showing all the peaks and troughs, but it can also reveal information about a wide range of other surface properties, including adhesion, elasticity, conductivity and temperature.

This wide-ranging ability is primarily due to AFM being able to operate in a variety of different modes. These include several primary imaging modes, which differ in the way the tip interacts with the sample surface, and numerous secondary modes, which often involve specialized tips and cantilevers. It is these secondary modes that can reveal information about surface properties, which can usually be collected at the same time as the topographic information.

Thanks to its versatility, AFM has proved adept at the nanoscale study of many organic and inorganic materials, ranging from metals and polymers to hydrogels and powders. Furthermore, unlike other microscopy techniques, AFM isn't restricted to working under specific conditions: imaging can take place in air, vacuum or a liquid. This has allowed researchers to apply AFM to a wide range of materials applications, from analyzing failure in semiconductors and mapping the different components of composite materials to visualizing electrical and chemical processes in battery electrolytes.

This Essential Knowledge Briefing (EKB) introduces AFM and its materials characterization capabilities; it is one of a pair of EKBs on AFM, with its sister publication looking at life science capabilities. Beginning with a detailed explanation of the operation of a typical AFM instrument, including the role of the tip, cantilever and photodetector, the EKB also outlines how the technique evolved out of scanning tunneling microscopy in the 1980s.

It describes the primary imaging modes and gives a brief introduction to the main secondary modes, before moving on to explain some of the challenges involved in studying inorganic materials, including preparing samples for AFM scanning and selecting the right tip. Finally, it looks at how newer AFM instruments are providing faster imaging, a larger selection of modes and quantitative surface characterization of material samples. In addition, spread throughout the EKB are several case studies highlighting how materials researchers are using AFM in their work.

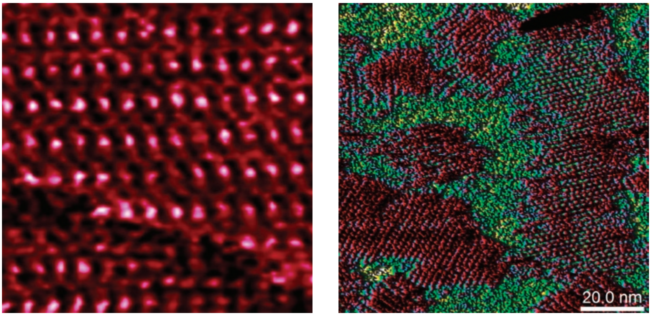


**Figure 1. Point defect resolution stiffness on (left) calcite (15nm image) and (right) molecular resolution adhesion on isotactic poly(methyl methacrylate) (iPMMA) (100nm image). iPMMA sample courtesy of Prof Dr Thurn-Albrecht, Martin-Luther-Universität Halle-Wittenberg**

## HISTORY AND BACKGROUND

AFM is a powerful and versatile method for studying sample surfaces at the atomic scale. Rather than produce a magnified optical image of a sample, it involves scanning a cantilever with a sharp tip across the surface of a material, and measuring the forces created by the interaction between the tip and the surface. Because the tip closely tracks the surface, AFM can create detailed maps of surface topography.

It is one of several related techniques for creating topographical maps at the atomic level, collectively termed scanning probe microscopy (SPM). The first type of SPM to be developed was scanning tunneling microscopy (STM), which uses quantum effects to create an electrical current that flows between the tip and surface. The size of this current is a function of the distance from the tip to the surface.

STM was invented by two researchers at IBM, Gerd Binnig and Heinrich Rohrer, and was one of the first microscopy techniques to allow scientists to 'see' the world at the level of individual atoms and molecules. With a background in semiconductors, these two researchers were fascinated by the electronic structure and imperfections of materials at the atomic scale. But their studies on semiconducting materials were constrained by existing technology. Optical microscopes were unable to resolve features below around 250nm in size, while electron microscopes were unable to visualize the surfaces of bulk materials at atomic-scale resolution.

So the researchers decided to build their own instrument and began to experiment with quantum tunneling, a phenomenon by which electrons occasionally jump from one conducting material to another across an insulating barrier by borrowing energy from the environment. This process has been likened to a ball using kinetic energy from the environment to roll uphill.

By January 1979, Binnig and Rohrer had submitted their first patent for an STM. Over the next couple of years, they designed and built a working STM microscope, which used a heavy magnet floating in a tub of superconducting lead to reduce vibrations from the environment.

The STM revolutionized microscopy, but had its disadvantages. Because it relied on measuring a tunneling current, it could only be used on conducting materials such as metals. Then, in 1986, the same year that Binnig shared a Nobel Prize for inventing STM, he and colleagues replaced the fixed tunneling tip with a flexible cantilever to produce the first atomic force microscope.

Rather than measure changes in the tunneling current as the tip is scanned across the surface, AFM measures changes in the forces between the tip of the cantilever and the surface of the sample. These forces affect the position or movement of the cantilever, with the degree of deflection depending on the size of the forces, which increase as the tip gets closer to the sample surface. Because the deflection of the cantilever does not depend on an electrical current flowing between the tip and the sample, AFM can be used to produce maps of the surface of insulators, semiconductors and conductors.

In the first atomic force microscope, the tip comprised a tiny diamond glued onto the end of a cantilever made from a thin gold strip, while the deflection was measured using the tunneling current generated between the strip and a wire hanging above. Today, AFM cantilevers are usually made from silicon, with the cantilever and tip typically manufactured as a single unit. The tip can have a variety of coatings to allow additional surface properties to be measured; for example, a metal coating to detect conductivity. The tip is typically less than 5µm in height and 10nm in diameter at the apex, while the cantilever is 100–500µm in length.

The horizontal and vertical position of the tip over the sample surface is controlled by a scanner made from a piezoelectric ceramic that expands and contracts in a controlled way when a voltage is applied. This scanner is attached either to the cantilever, allowing it to control the position of the tip directly (tip scanning), or to the base the sample is placed on, moving the base under a fixed tip (sample scanning).

In either case, the tip is scanned over the surface of the sample in a raster pattern, a set of zig-zagged lines that cover a square or rectangle. Surface measurements are taken at equally spaced intervals along the scan lines to build up an image made of pixels, similar to the way an image is produced on a television screen. The zig-zag pattern means that data is collected as the scanner moves

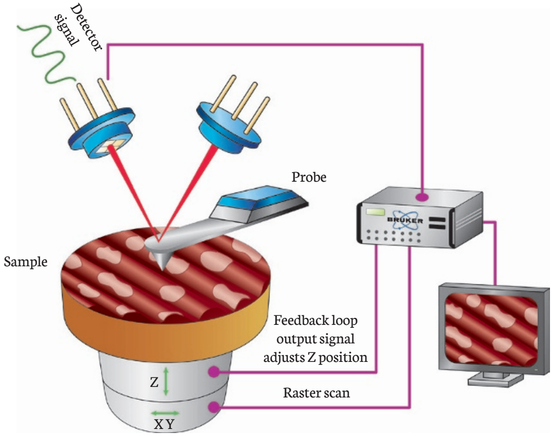


**Figure 2. Schematic of basic SPM operation**

both left to right (trace) and right to left (retrace). Collecting data in both directions helps to remove artifacts that don't accurately reflect the sample surface.

To begin a scan, the tip is brought close to the surface. As the tip is then scanned across the surface, forces between the tip and sample surface cause the cantilever to bend. When the tip begins to interact with the surface, these are attractive van der Waals forces; once the tip gets very close to the surface, they become repulsive electrostatic forces.

The deflection of the cantilever caused by these forces is recorded by bouncing a laser off the back of the cantilever onto a position-sensitive photodetector, with any deflection altering the position of the laser beam. Because the distance between the cantilever and the photodetector is much greater than the length of the cantilever, this set-up produces amplification, allowing the photodetector to detect tiny deflections at the sub-Ångstrom scale.

The map of surface topography can be built up directly from these recorded deflections, by comparing the deflected signal with a reference signal known as the setpoint. In general practice, it is produced from the voltage that needs to be applied to the scanner to correct these deflections by moving the tip such that the signal returns to the setpoint, with a higher voltage required for larger deflections. Building the map from the applied voltage, known as Z feedback, is slower, as the scanner needs to be moved up and down, but it is better at imaging irregular surfaces.

In addition to producing a visual representation of topography, AFM can also be used to reveal many chemical and mechanical features of the surface, including variations in composition, friction, magnetism, conductivity and temperature.

It can also be used as a spectroscopy tool to probe the forces at specific points on the surface. This produces a typical force–distance curve, plotting the force on the tip as a function of its distance from the surface, which can reveal information about the adhesion of surface contaminants and elastic properties.

# IN PRACTICE

AFM can be operated in several primary imaging modes, which differ in the way the tip physically interacts with the sample surface (Figure 3). There are also numerous secondary modes, which are generally specific applications of one or more of the primary modes, and are often developed by and proprietary to specific developers of AFM systems.

The simplest primary mode is known as contact mode, in which the probe is in permanent physical contact with the sample surface as it performs a raster scan, with changes in topography causing the cantilever to bend up and down. Although simple, fast and sensitive, contact mode has a major drawback: the lateral forces exerted on the sample as the tip is scanned across can be very high. For delicate material samples such as graphene or carbon nanotubes, these unwanted lateral forces can not only damage the sample, but they can also blur the image and lower the resolution.

An alternative option is non-contact mode, in which the cantilever is set to vibrate at its resonant frequency. As the tip is brought close to the surface of the sample, the forces between the tip and the surface alter this resonant frequency. The size of these forces, and thus the distance between the tip and the surface, can be determined by this change in resonant frequency, without the tip actually coming into contact with the surface.

The problem with non-contact mode is that the attractive forces that hold sway before the tip contacts the surface are smaller than the repulsive forces that hold sway when the tip contacts the surface. Furthermore, non-contact mode requires a stiffer cantilever than contact mode. Because of these factors, non-contact mode produces a smaller signal than contact mode.

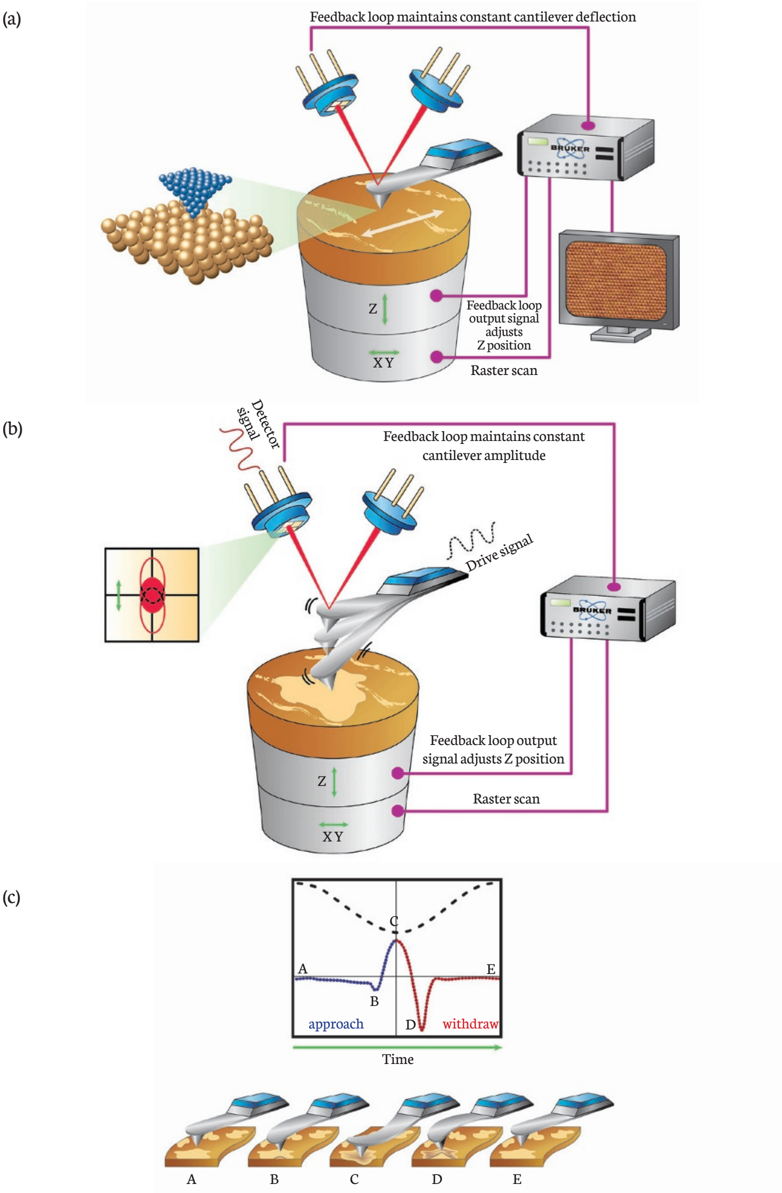


**Figure 3. Schematics of primary AFM modes: (a) contact mode, (b) tapping mode, (c) PeakForce Tapping mode**

So, in 1992, engineers at Digital Instruments (now Bruker) essentially combined the contact and non-contact modes to produce tapping mode. Like non-contact mode, the cantilever oscillates at or near its resonance frequency, but with a large enough amplitude (10–100nm) that the tip regularly touches the surface with a tapping action. Tapping considerably reduces the damage inflicted to samples. It also generates a much higher signal, as it is affected by both attractive and repulsive forces.

Another benefit of the tapping motion is that it prevents the tip from being trapped by the thin layer of water that can form on samples when studied under ambient conditions, which can be a major problem in non-contact mode. Because of all these advantages, tapping mode is now the most widely used AFM primary mode.

Nevertheless, in 2009 Bruker introduced a new mode called PeakForce Tapping. In PeakForce Tapping, the cantilever is oscillated in a sine wave pattern at a frequency that can be an order of magnitude less than the resonant frequency; typical frequencies are 2kHz compared to 60–500kHz for tapping mode.

As the tip approaches the surface, the attractive van der Waal forces increase until the tip jumps into contact. At this point, the tip experiences repulsive forces, which eventually dominate the attractive ones. PeakForce Tapping uses an intelligent algorithm to determine the peak force experienced by the tip, which occurs at the point where the tip begins to withdraw from the surface. As a consequence, PeakForce Tapping can produce a quantifiable measurement of the peak force during each oscillatory cycle. In contrast, tapping mode measures the average oscillatory amplitude while the tip is in contact with the surface. This makes

PeakForce Tapping less susceptible to noise caused by the tip moving through electric and magnetic fields.

A wide range of secondary modes have been derived from these primary modes, often by employing functionalized tips or specialized cantilevers. While the primary modes focus on producing three-dimensional (3D) images of surface topography, measuring surface roughness or calculating peak–valley distances, the secondary modes can probe various chemical, mechanical and electrical features of the surface of materials. These include conductivity, surface hardness, friction and elasticity, adhesion, permittivity, magnetism, surface potential and temperature.

Two of the most important secondary modes are conductive AFM (C-AFM) and PeakForce Tunneling AFM (TUNA), which both utilize a conductive tip to map conductivity variations over the surface of conducting and semiconducting materials. C-AFM is a secondary contact mode, while PeakForce TUNA is a secondary mode of PeakForce Tapping. Both modes are useful for studying conductive polymers, semiconductors and certain organic materials, as well as analyzing electrical defects, while PeakForce TUNA is particularly appropriate for fragile samples such as organic photovoltaics, lithium-ion cathodes and carbon nanotubes (Figure 4).

PeakForce scanning microwave impedance microscopy (sMIM) is a secondary mode of PeakForce Tapping that offers nanoscale mapping of the permittivity and conductivity of a variety of inorganic materials, including graphene and carbon nanotubes. This secondary mode applies a low-power microwave signal to a shielded AFM tip, which possesses insulating layers surrounding a central metal trace that delivers the microwave

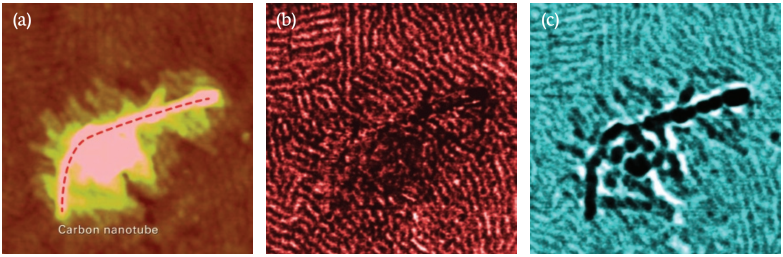


**Figure 4. PeakForce TUNA: (a) topography, (b) current, and (c) adhesion maps of a semi-conducting polymer composite, poly(3-hexylthiophene) (P3HT) with embedded carbon nanotubes. Image courtesy of Philippe Leclère *et al*, University of Mons (UMONS), Belgium**

signal to the tip apex. The reflected microwaves are affected by variations in sample permittivity and conductivity. Many of these secondary modes can be combined with each other to investigate several surface properties in a single analysis. For example, PeakForce sMIM can be combined with a secondary mode called PeakForce Quantitative Nanomechanical Mapping (QNM) to produce simultaneous mechanical measurements of adhesion, modulus and deformation. PeakForce QNM uses a proprietary algorithm to analyze the force curves created during each tap in real time, and can also be combined with PeakForce TUNA for the simultaneous measurement of nanomechanical and nano-electrical properties.

Other secondary modes commonly used to analyze inorganic materials include scanning thermal microscopy, which uses a cantilever made of two metals that respond differently to thermal conductivity to measure temperature variations across the sample surface. Another example is magnetic force microscopy (MFM), which uses a tip coated in a ferromagnetic thin film to measure the magnetic force gradient over the surface of a sample (see Case Study 2 for a specific application).

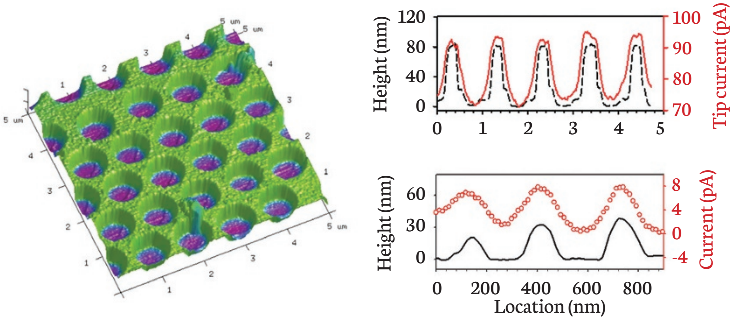


**Figure 5. (Left) 3D topography of a nanomesh electrode (Au-SiO2 ) covered by electrochemical (EC) current skin; (top right) line profiles of the topographic and EC variations on the Au-SiO2 surface; and (bottom right) line profiles of the topographic and EC variations from a nanoelectrode array. Nanomesh electrode sample courtesy of C Stelling and M Retsch, University of Bayreuth. Image courtesy of A Mark, S Gödrich and G Papastavrou, University of Bayreuth. Nanoelectrode array sample courtesy of M Nellist and Prof S Boettcher, University of Oregon**

This huge variety of modes allows researchers to use AFM for a wide range of applications. PeakForce sMIM can be used to characterize the electrical properties of the semiconducting iron oxide nanoparticles used in devices such as photovoltaics, solar-fuels generators and storage devices. PeakForce QNM has applications in locating contaminants and mapping the different components of composite materials such as plastic packaging. Scanning thermal microscopy is commonly used for analyzing semiconductor failure, mapping material distribution in composites and characterizing magnetoresistive heads. PeakForce scanning electrochemical microscopy (SECM), meanwhile, allows the nanoscale visualization of electrical and chemical processes *in situ* in many materials systems relevant to energy research, such as battery electrodes, fuel cells, and solar fuel catalysis (Figure 5).

## CASE STUDY 1. Developing higher energy density batteries

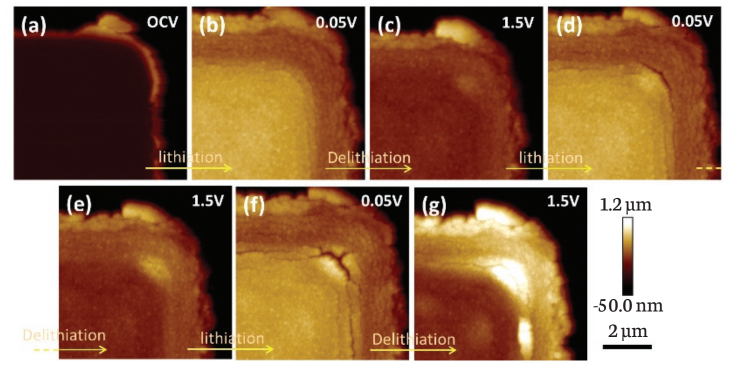
*Helping the automotive industry move from gasoline to electric vehicles is one long-term aim of AFM research being conducted by Ravi Kumar at Brown University, USA. ‘That means developing higher energy density batteries,’ he explains. ‘These will include silicon so that electric vehicles can travel further.’*

*Compared to the graphite electrodes used in today’s state-of-the-art lithium-ion batteries, silicon electrodes have an almost 10-times higher capacity and a higher energy density. However, silicon also expands and contracts more than graphite as the battery is charged and discharged. This puts strain on the solid electrolyte interphase (SEI), a protective film that forms on the negative electrode during battery operation. If the SEI cracks, the silicon electrode becomes exposed to the surrounding electrolyte, leading to additional electrolyte breakdown and lithium consumption, which causes the battery to lose capacity over time.*

*Kumar and his colleagues used a Dimension Icon atomic force microscope to make the first ever observations of real-time cracking of the SEI layer on silicon. These studies provided important new information about the degradation of SEI films. ‘People have speculated about the failure mechanisms,’ he says. ‘Our study provides input for future mathematical models and improved design of SEI layers.’*

*Imaging the fragile SEI layer in real time over multiple charging cycles is challenging in liquid electrolytes. So the team employed PeakForce Tapping because it exerts less shear force on the fragile SEI layer.*

*They also simultaneously measured the mechanical response of the SEI layer with PeakForce QNM. 'We wanted to investigate the elasticity of the material that forms to understand the stresses that develop in these layers due to expansion and contraction of underlying silicon,' says Kumar. 'A highly compliant SEI layer can better withstand expansion and contraction.' PeakForce QNM allows quantitative high-resolution nanomechanical data to be collected at the same time as standard AFM images, without compromising imaging rates.*



**AFM images showing opening and closing of SEI cracks that formed during (a–c) the first cycle, (c–e) the second cycle and (e–g) the third cycle. Reprinted from Kumar R, Tokranov A, Sheldon BW, *et al.* In situ and operando investigations of failure mechanisms of the solid electrolyte interphase on silicon electrodes. *ACS Energy Letters* 2016;1:689–97. Copyright 2016 American Chemical Society**

Kumar R, Tokranov A, Sheldon BW, *et al.* In situ and operando investigations of failure mechanisms of the solid electrolyte interphase on silicon electrodes. *ACS Energy Lett* 2016;1:689–97. (http://dx.doi.org/10.1021/acsenergylett.6b00284)

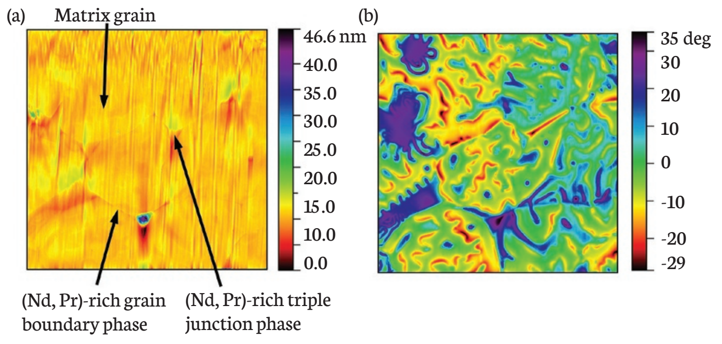
## CASE STUDY 2. Rare earth magnets

*Yin Yao at the University of New South Wales in Australia uses AFM to study the magnetic properties of rare earth (RE) magnets, which are an essential component of advanced electric motors such as the direct-drive generators in wind turbines. However, the correlation between the microstructure, magnetic properties and performance of RE magnets remains poorly understood.*

*'Better understanding of the microstructure of these magnetic materials is the key to improving their properties,' says Yao. 'The grain size, grain boundary and elemental composition are very important as they can have a major influence on the material's performance.'*

*In a recent study, Yao and his collaborators Hansheng Chen and Rongkun Zheng used MFM, a secondary AFM mode, to study the magnetic domains of neodymium, iron and boron magnets. MFM is a variant of tapping mode that employs a magnetized tip, which first taps on the sample surface to obtain topographic information before being lifted off to obtain information about the magnetic field above the surface. This way, the localized microstructure, topography and magnetic information can all be obtained at the same time. Moreover, the typical resolution of the magnetic domain images is less than 100nm, allowing very small features to be captured.*

*'MFM is one of the few techniques available to study the domain structures at different regions of the sample,' explains Yao. 'We can then analyze the elemental composition of these regions using other microscopy techniques, such as energy-dispersive X-ray spectroscopy (EDX).' The MFM and EDX data can be combined to understand the link between the sample microstructure and magnetic properties.*



**Surface topography and magnetic domain structures of the (Nd,Pr)-Fe-B RE magnet: (a) topological image, (b) corresponding MFM image. The scan area for Figures (a) and (b) is 15×15μm². Image from R Zheng's group at the University of Sydney, Australia**

Chen H, Yao Y, Warner, *et al.* Grain size quantification by optical microscopy, electron backscatter diffraction and magnetic force microscopy. *Micron* 2017;101:41–7. (http://dx.doi/org/10.1016/j.micron.2017.06.001 )

## PROBLEMS AND SOLUTIONS

As with any analytical technique, AFM has some limitations. Although inorganic samples generally don't need much preparation prior to AFM, they do need to be fairly flat. The typical vertical range of an AFM scanner is around 10µm, but the horizontal range may be 2mm or more. Thicker samples may need cutting to size with a microtome or a focused ion beam.

The type of sample is also important. Dry powders need to be fixed before imaging by, for example, dispersing the powder onto glue; otherwise, it will be dislodged by the tip during AFM. The ambient conditions in the lab also need to be considered. The humidity will affect the thickness of the nanoscale layer of water that forms on hydrophilic samples when imaged in air and, if the tip is also hydrophilic, this layer can provide a strong adhesive force that binds the tip to the surface.

In general, sample preparation and measurements are best carried out in a glove box or clean room. Because AFM is a surface characterization method, any dirt or dust will be measured as part of the sample. In addition, the presence of water can cause some samples to swell.

The primary imaging mode should be chosen carefully. Contact mode in air exerts high tip-sample forces and offers the fastest scan rates. This makes it suitable for imaging hard materials that are less prone to deformation and damage, or samples where deformation is required. For example, with some multicomponent polymers, the sub-surface structures are hidden beneath an amorphous top layer; the tip therefore needs to exert sufficient vertical force to compress this top layer. However, the high lateral forces generated by contact mode make it unsuitable for softer or fragile samples such as graphene or carbon nanotubes. These forces can also wear the tip and dislodge loosely attached objects.

Non-contact mode and tapping mode are clearly more appropriate for softer samples. However, non-contact mode is limited by its reliance on weak attractive forces between the tip and the surface. Not only do these weak forces produce a weak signal, but the thin liquid layer that forms on many hydrophilic samples in air can be too thick for the tip to detect these forces at all.

Meanwhile, tapping mode can still cause damage, especially to samples with high adhesion forces. This is because the cantilever has to oscillate with a high amplitude with these samples, to ensure the tip leaves the surface. This raises the energy in the cantilever and thus increases the force exerted upon the surface during tapping, increasing the risk of damaging the tip or sample (Figure 6).

Other issues with tapping mode include the scanner tending to drift away from the setpoint in fluids due to changes in temperature or liquid levels. In addition, because the tip-sample forces are averaged for the entire ‘tap’, the Z feedback loop is less able to respond to abrupt transitions between hard and soft parts

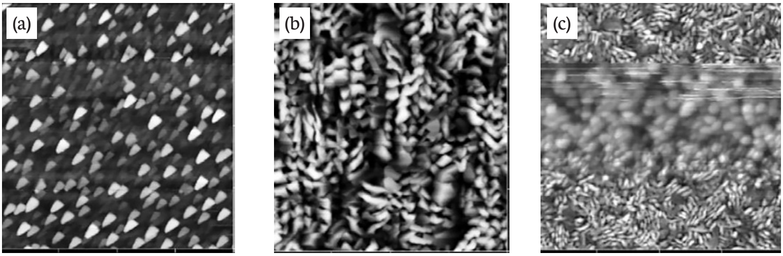


**Figure 6. Examples of tip-induced AFM errors in imaging: (a) when the tip apex of the common tetrahedral-shaped AFM probe breaks off, nano features can artificially appear as triangles and pyramids; (b) fractured tips often produce two or more asperities, which leads to a doubling up of features in an image; (c) contamination of the tip can temporarily alter the tip radius and then return to normal when the contaminant drops off. 1μm scans**

of a sample. Tapping mode can also produce artifacts when imaging surfaces that possess peaks and troughs of a similar diameter to the tip.

PeakForce Tapping solves some of these problems by directly measuring the peak force exerted during the tip–sample interaction. Also, because PeakForce Tapping uses non-resonant frequencies to oscillate the cantilever, the feedback loop is more stable than in tapping mode. The process of adjusting imaging parameters can also be automated with ScanAsyst, a proprietary method from Bruker for collecting and analyzing force–distance curves.

A wide range of cantilevers and tips are available for AFM, adapted for specific samples and modes. With samples that are harder to deform or have strong adhesive forces, either soft or stiff cantilevers can be used for imaging. Softer cantilevers, with spring constants less than 5N/m, are more easily attracted to the surface and produce better, more reproducible images. Stiffer cantilevers give better contrast when mapping surfaces with regions that differ in composition, such as magnetic recording heads or contaminant deposits.

The softer the material, the fewer AFM modes are suitable and the more constraints on the cantilever and tip. To protect soft or fragile materials from damage, AFM is often conducted using a soft cantilever with a sharp tip at a low oscillating amplitude.

Specialized cantilevers and tips are needed for many of the secondary AFM modes. For nanoindentation of very hard samples such as certain polymers or metals, for example, a very stiff cantilever and hard tip with known mechanical properties are required to leave an indentation in the surface. One such probe is the Bruker DNISP, which consists of a corner cube diamond glued

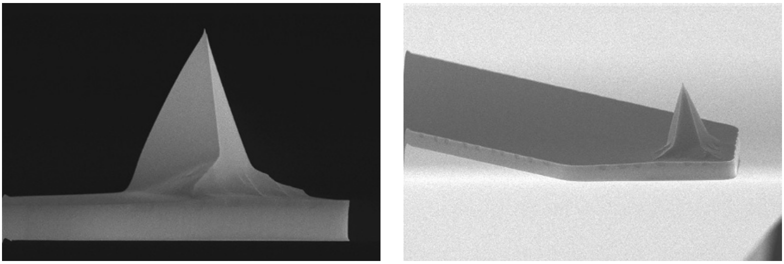


**Figure 7. Scanning electron microscopy images of a platinum-iridium coated SCM-PIT-V2 probe**

to a stainless-steel cantilever. Probes for nanoelectrical or magnetic studies are often solid metal, doped diamond or have a metal coating that is electrically conductive or magnetic. An example is the Bruker SCM-PIT-V2 probe, which has a platinum-iridium coating on the tip (Figure 7).

The shape of the tip is also important for imaging, especially the radius of curvature of the tip and the angle of the sidewalls. A sharper tip will be able to resolve smaller lateral features than a dull tip with a larger radius of curvature, while only a tip with steep sidewalls will be able to image features with steep sides, such as the troughs in semiconductors. The choice of tip will thus depend on the type of sample being studied. For samples comprising lots of spherical particles, for example, an etched tetrahedral pyramid-shaped tip will make the spheres look like pyramids. A spike-shaped tip will give a truer representation of spherical surfaces.

# WHAT'S NEXT?

Traditionally, AFM was regarded as slow and somewhat difficult to use. Samples could take five to ten minutes to scan, while preparing the sample and setting up the microscope could take up to an hour. In addition, rougher or more complex surfaces could even take longer to scan. With an older atomic force microscope, this limited the analysis rate to maybe six samples a day.

Over the past decade, instrument manufacturers have delivered major increases in scan speeds by improving the electronics and probes. Modern atomic force microscopes have ultra-small cantilevers to reduce mass and increase cantilever response times, and more sensitive optics and photodetectors to detect deflection of these smaller cantilevers. The Z feedback loop is faster, allowing faster movement of the scanner, and this is accompanied by high-speed electronics. These faster systems not only accelerate existing studies, and make analyzing hundreds of datasets feasible for the first time, but also allow AFM observations of dynamic material processes such as melting and crystal growth.

Setting up, calibrating and optimizing an atomic force microscope was also a time-consuming process. The Z feedback loop needed to be constantly optimized during the scan and this required an experienced user, especially if the feedback loop was non-linear. In tapping mode, for example, changes in cantilever amplitude at a sharp edge can be an order of magnitude greater than the tip-sample forces. Failure to adjust the feedback loop correctly can cause the tip to become damaged by the surface.

Newer AFM systems have image optimization software that can automate the adjustment of scan rates, feedback gains and setpoints. Software such as Bruker's ScanAsyst utilizes advanced algorithms to analyze the force-distance curves during the tip-sample interaction. With these new AFM systems, inexperienced users can limit their input to setting the scan area and size. The software can deliver results on a wide range of samples, including soft hydrogels, sticky polymers and powders with steep edges, at the atomic scale.

The range of material applications of AFM is also increasing as manufacturers combine the technology with other analytical techniques, such as near-field scanning optical microscopy (NSOM) and Raman spectroscopy. NSOM is basically an optical version of AFM, employing AFM technology to overcome the resolution limits of traditional light microscopy by focusing infrared light through a narrow optical fiber onto a sample and collecting the scattered light as the beam is scanned across. Because the interaction between the light and the sample surface is extremely localized, NSOM can have a spatial resolution of as little as 10nm. Combining these two scanning techniques allows optical and topographical images of a sample to be obtained simultaneously.

Raman spectroscopy can identify specific molecules from the characteristic way they scatter laser light, and can be combined with AFM secondary modes such as PeakForce QNM or PeakForce TUNA. This can allow information about the composition of material in a layer, and its adhesion and elastic modulus to be obtained simultaneously.

As with many microscopy techniques, AFM images use visual contrast to show differences in surface properties. This visual contrast is relative across different areas of the sample, which means it's not always clear what these measurements represent.

In tapping mode, for example, the cantilever amplitude does not provide a direct measurement of the tip-sample forces.

Increasingly, however, researchers require quantitative AFM data. Newer AFM modes like PeakForce Tapping can generate quantitative data about the tip-sample forces exerted during each tip-surface interaction. By using algorithms to analyze these force-distance curves, secondary modes like PeakForce QNM can then extract nanomechanical information on properties such as adhesion, elastic modulus and deformation. This quantitative capability is admittedly limited at the moment, because AFM is still developing as a technique and the behavior of many probes, materials and modes remains poorly understood, but it will continue to evolve over the coming years.

AFM has been instrumental in the development of nanotechnology as a discipline, and is still regularly used to study nanomaterials such as carbon nanotubes and graphene. Graphene is ultra-light and flexible, a superb conductor and around 200 times stronger than steel, but it can be easily contaminated by its surroundings. AFM secondary modes such as Kelvin Force Probe Microscopy (KFPM) can examine how the surface potential of graphene changes when water sticks to the surface. This can help researchers understand how graphene-based devices will perform when exposed to varying temperatures, levels of humidity and ambient gases.

One challenge of imaging nanomaterials with AFM is their atomic-scale thickness. The measured thickness of graphene, for example, varies depending on its contact with a substrate. If the force exerted by the tip is too low, the AFM instrument will measure the gap between the graphene and the underlying substrate. If it is too high, the tip will punch through the graphene layer. Newer AFM imaging modes, such as PeakForce Tapping, allow more precise control over the contact between the tip and the graphene.

## CASE STUDY 3. Two-dimensional materials

*The exciting new field of two-dimensional (2D) materials is the focus of AFM research by Colin Woods from the School of Physics and Astronomy at the University of Manchester. 'This field has taken off since graphene was discovered in 2004,' he says. 'Since then, researchers have looked for what other 2D materials they could make and how they can combine them.'*

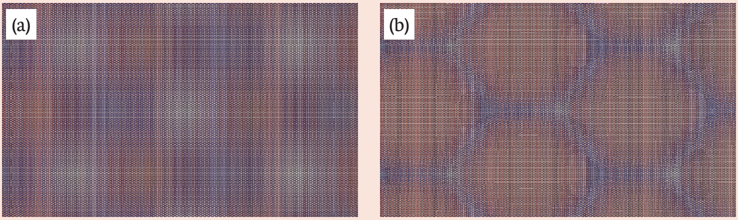
*Among those new 2D materials is hexagonal boron nitride (hBN), an insulator, whereas graphene is a semi-metal. This raises the possibility of creating new electronic devices by combining these 2D materials with very different properties. In a recent study, a scientific team led by Nobel laureate Sir Konstantin Novoselov used Bruker's Dimension FastScan atomic force microscope to examine how the properties of these materials were affected by combining them into layered stacks.*

*Woods, at that time a PhD student, did the majority of the AFM experiments on layered stacks of graphene placed upon hBN. He used conductive AFM to interrogate the local electrical properties of the graphene, and PeakForce QNM to investigate the nanomechanical properties. He observed what are known as moiré interference patterns between the materials, which had maximum periodicity when their crystal structure was most closely aligned.*

*'We noticed immediately that the moiré pattern changes when the two crystals are perfectly aligned. What is happening is that the graphene is undergoing a transition caused by the mismatch in their size; hBN is 1.8% bigger,' Woods explains. 'The graphene wants to stretch to sit perfectly on the hBN and, as they move closer to perfect alignment, the areas of graphene that can stretch become larger.'*

*At maximum alignment, the graphene stretches in the middle of each moiré unit-cell and buckles at the edges, creating coherent dark regions (stretched regions) with sharp white borders on a PeakForce QNM image. 'The real benefit of PeakForce QNM is it eliminates cross-talk between channels,' Woods says. 'In contact mode, tapping mode or scanning tunneling experiments you can never be sure what you're looking at – these light regions could simply be stick-and-slip motion due to changes in adhesion or variation in the local density of states.'*

*Although the graphene–hBN moiré pattern is still observable with these scanning modes, Woods explains, it is affected by the topography of the surface and other variables. In contrast, PeakForce QNM derives the Young's modulus, a measure of surface stiffness, from a fit to the entire force curve at each point and so shouldn't be affected by topographic changes.*



**Computational simulations show the graphene (black dots) on hBN (blue and red dots) without any stretching (simulation a), and a commensurate state when the graphene lattice is allowed to stretch to fit with hBN (simulation b). The two crystals are aligned with each other in both images (open-access images from Dr Woods' PhD thesis)**

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