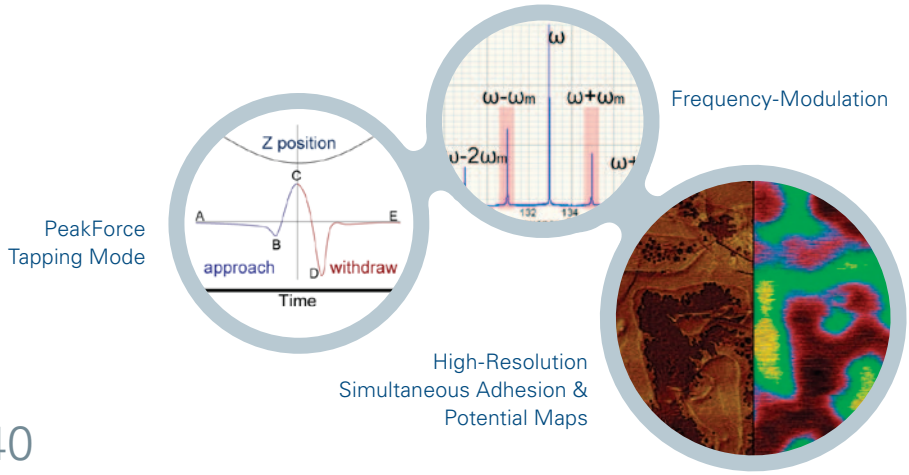


Application Note #140

PeakForce Kelvin Probe Force Microscopy

Kelvin probe force microscopy (KPFM), also called surface potential microscopy, has found broad applications, ranging from corrosion studies of alloys, photovoltaic effects on solar cells, and surface analysis. KPFM, together with conductive AFM, have been recognized as the two most used nanoscale electrical characterization tools, complementing each other.[1] However, limited spatial resolution and lack of measurement repeatability and accuracy has limited its usefulness in some critical areas, such as in the identification of donor and acceptor domains in bulk heterojunction organic solar cells, material differentiation in composite materials, and trapped charges on insulators.

The two major KPFM detection techniques are amplitude modulation KPFM (AM-KPFM) and frequency modulation KPFM (FM-KPFM).[2,3] This application note presents an intuitive, geometrically realistic probe model to illustrate their drastic differences in spatial resolution and accuracy. This modeling has led Bruker researchers to combine FM-KPFM with an innovative new AFM mode, PeakForce Tapping™, which offers ease-of-operation and simultaneous quantitative nanomechnical property mapping capability (via PeakForce QNM®).[4] Together with a novel probe design and auto-optimization software, this new approach has enabled a drastic increase in KPFM performance.

Background

Using a gold-leaf electroscope in 1898, Sir William Thomson, later known as Lord Kelvin, observed that plates of copper and zinc mounted on insulating shafts created charge when they were brought into electrical contact and then moved apart. His discovery can now be explained in terms of work function differences. The work function is the minimum energy (or work, usually measured in eV), needed to remove an electron from a solid, to a point immediately outside the solid surface (or energy needed to move an electron from the Fermi level into vacuum).

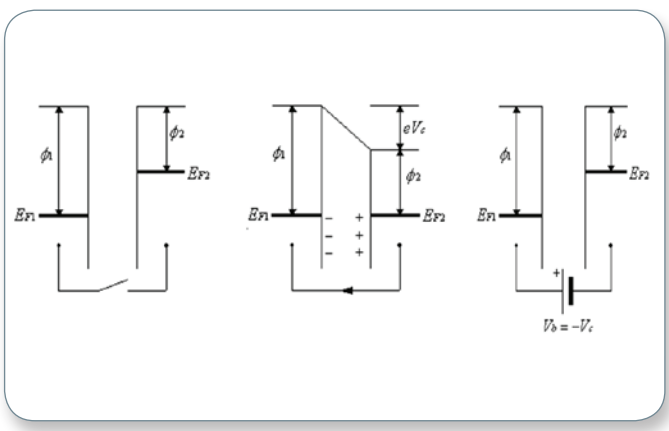


Figure 1. Energy and charge diagram illustrating Kelvin probe technique principle.

When two different conductors are brought into electrical contact, for example via an external wire contact, electrons will flow from the one with lower work function to the one with higher work function, equalizing the Fermi energies. If they are made into a parallel plate capacitor, equal and opposite charges will be induced on the surfaces. The potential established between these two surfaces is called the contact potential difference (CPD), contact potential, or surface potential, which equals the work function difference of the two materials. Measuring the CPD is thus quite simple. An external potential (also called the backing potential) is applied to the capacitor until the surface charges disappear. At this point, the external potential equals the CPD. The various Kelvin probe techniques developed thus far differ mainly only on how this charge-free state is detected.

In 1932, William Zisman of Harvard University introduced the vibrating electrode technique and the "nulling" concept.[5] Vertically vibrating the tip over a sample causes the capacitance to vary as the distance changes. This induces charge to flow, giving rise to an AC current. The backing potential, at which AC current is at a minimum or ideally 0, "nulled," is found to equal the CPD. This technique leads to development of systems that automatically track shifts in contact potential due to changes in the work function of the sample.

J.M.R. Weaver and coworkers were the first to combine Kelvin method with AFM.[6] They embraced the nulling concept in finding the charge-free point, and capitalized on AFM's unique capability to detect small forces and force gradients. The central idea is that the electric force and electric force gradient between the two plates of a capacitor will become "0," when charge disappears. It is fitting, for this reason, to call the technique Kelvin probe force microscopy (KPFM), as Nonnenmacher did in 1991.[7]

KPFM opened the door to measuring CPD, therefore work function, in the nanometer regime. AM-KPFM and FM-KPFM are based on electric force and electric force gradient detection respectively.

Electric Force and Electric Force Gradient

A conductive probe and a conductive sample form a capacitor. The electrostatic force between is:

$$F_{el} = -\frac{1}{2}\frac{\partial C}{\partial z}(\Delta V)^2$$

where F_{el} is the electric force, and ΔV is the potential difference between the probe and the sample. ΔV is the sum of the intrinsic CPD, an externally applied DC voltage V_{DC} and ac voltage V_{AC}:

$$\Delta V = V_{DC} - V_{CPD} + V_{AC}\sin(\omega t)$$

Combining the above two equations, we arrive at:

$$F_{el} = \underbrace{\frac{\partial C}{\partial z}\left((V_{DC}-V_{CPD})^2 + \frac{1}{2}V_{AC}^2\right)}_{\text{DC Term}} + \underbrace{\frac{\partial C}{\partial z}(V_{DC}-V_{CPD})V_{AC}\sin(\omega t)}_{\omega\text{ Term}} + \underbrace{\frac{1}{4}\frac{\partial C}{\partial z}V_{AC}^2\cos(2\omega t)}_{2\omega\text{ Term}}$$

The above equation states that the applied ac bias at frequency ω is causing the electric force to modulate at both ω and 2ω, which can be measured directly using cantilever deflection. Figure 2 shows the forms prescribed by the above equation. Most relevant is the fact that *oscillation amplitude* at ω (shown as amplitude 1) drops to 0 when $V_{CD}=V_{CPD}$, the very idea of "nulling" electric force to find surface potential in amplitude modulation KPFM.

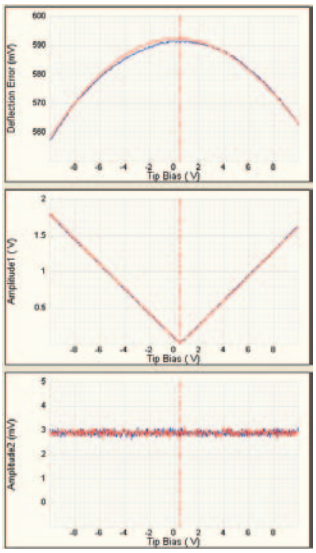


Figure 2. DC deflection (top), amplitudes at frequency ω (center) and 2ω (bottom) when the DC tip bias is swept while an ac bias with frequency ω is superimposed, corresponding to the DC term, ω term and the 2ω term described in equation 1.

The electric force gradient is associated with electric force,

$$F_{el}' = \frac{\partial F_{el}}{\partial z}$$

Therefore,

$$F_{el}' = \underbrace{\frac{\partial^2 C}{\partial z^2}\left((V_{DC}-V_{CPD})^2 + \frac{1}{2}V_{AC}^2\right)}_{\text{DC Term}} + \underbrace{\frac{\partial^2 C}{\partial z^2}(V_{DC}-V_{CPD})V_{AC}\sin(\omega t)}_{\omega\text{ Term}} + \underbrace{\frac{1}{4}\frac{\partial^2 C}{\partial z^2}V_{AC}^2\cos(2\omega t)}_{2\omega\text{ Term}}$$

Similarly, $V_{CD}=V_{CPD}$ when the modulation amplitude of the electric force gradient at ω drops to 0, the basis for "nulling" the electric force gradient to find the surface potential in frequency modulation KPFM.

AM-KPFM through Electric Force Detection

The modulated electric force, by the application of an ac bias between the tip and sample, can be conveniently measured using the oscillation of the cantilever. The ac bias frequency is typically selected to be the resonant frequency of the AFM cantilever for enhanced sensitivity afforded by cantilever's quality factor Q. The KPFM feedback, using the oscillation amplitude as input, adjusts a DC bias until the oscillation amplitude drops to 0, when V_{DC} equals CPD.

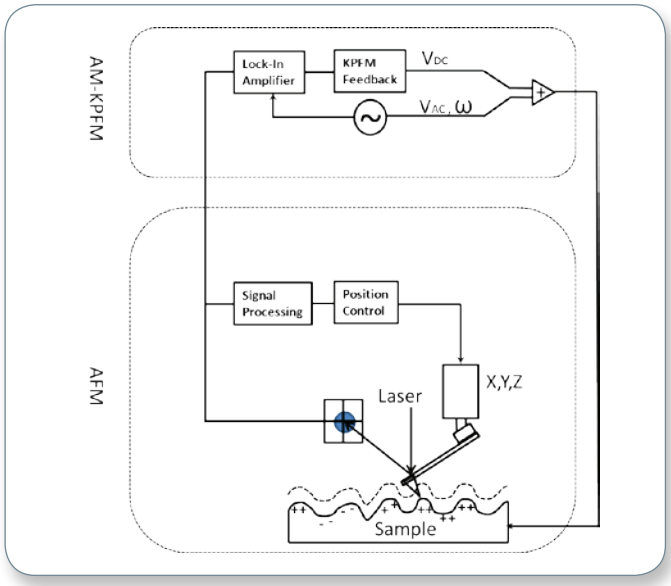


Figure 3. AM-KPFM diagram. An ac bias with a frequency ω, typically the resonant frequency of the cantilever, is applied between the probe and the sample, giving rise to an alternating electric force between the probe and sample that causes the probe to oscillate.

FM-KPFM through Electric Force Gradient Detection

The detection of electric force gradient is less straight forward. The force gradient changes the effective spring constant of the cantilever. When placing a conductive cantilever in an electric field, its effective spring constant is the sum of its natural spring constant k and the electric force gradient, the same effect of connecting two springs in parallel.

$$k_{eff} = k - \frac{\partial F_{el}}{\partial z}$$

We know the resonant frequency of a cantilever depends on the spring constant:

$$\omega = \sqrt{\frac{k}{m}}$$

Therefore the electric force gradient will cause the resonant frequency to change:

$$\Delta\omega \approx -\frac{\omega}{2k}\left(\frac{\partial F_{el}}{\partial z}\right)$$

When the electric force gradient is modulated, as caused by an ac bias, the resonant frequency of the cantilever will be modulated. As implied in the equation, resonant frequency will be modulated at both the ac bias frequency ω and its second harmonic 2ω. If one is mechanically shaking the cantilever at its resonant frequency ω, and simultaneously applying an ac bias at frequency ω_m, usually only a few kHz, the modulation of the resonant frequency gives rise to two pairs of sidebands at $\omega \pm \omega_m$, and $\omega \pm 2\omega_m$ (see Figure 4). The amplitude of the sideband measures the resonant frequency modulation amplitude; using the amplitude of the side band at $\omega \pm \omega_m$ for KPFM feedback, and adjusting the DC bias until they disappear leads to the point of $V_{CD}=V_{CPD}$.

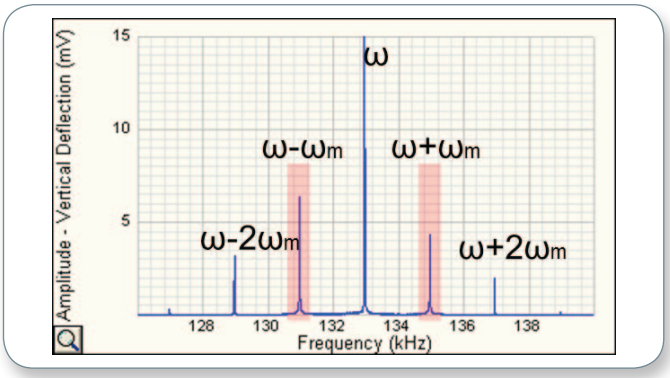


Figure 4. Amplitude vs. frequency plot of the vertical deflection signal recorded with high-speed data capture when a MESP-RC probe is shaken, near a sample surface, by the tapping piezo at its resonant frequency while an ac bias of 2kHz is applied, illustrating the emergence of sidebands due to ac bias-induced frequency modulation.

In practical implementations, side band amplitude is rarely directly measured at the sideband frequency using a single lock-in amplifier. A more common method uses two cascaded lock-in amplifiers, with the first one locking at the resonant frequency, the phase output of which is fed into the second lock-in, which locks at the ac bias frequency. The amplitude output of the second measures the amplitude sum of $\omega \pm \omega_m$, which is then used for KPFM feedback (see Figure 5).

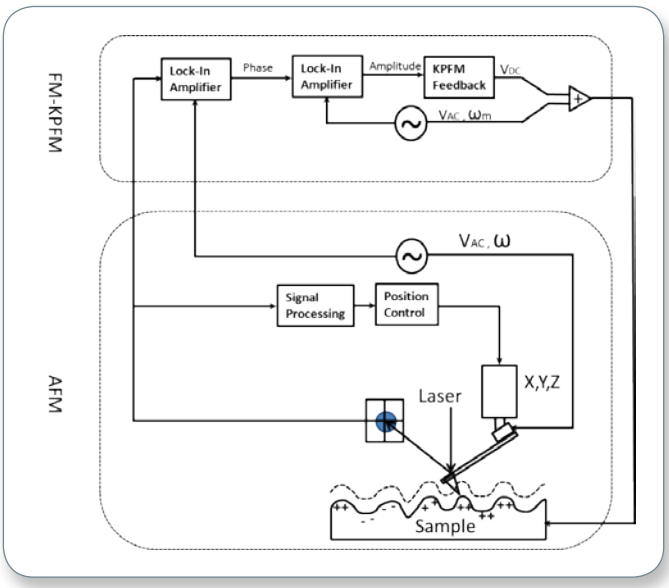


Figure 5. FM-KPFM diagram. An ac voltage is applied to the tapping piezo to oscillate the AFM cantilever at its resonant frequency ω. An ac bias at frequency ω_m, usually a few kHz, is applied between the probe and the sample, modulating the resonant frequency. Two cascaded lock-in amplifiers are used to detect the sum amplitude of sideband pair $\omega \pm \omega_m$.

Probe Modeling—Spatial Resolution and Accuracy of AM-KPFM and FM-KPFM

Probe modeling illuminated our understanding of the spatial resolution and accuracy provided by the two KPFM modes. We utilized a realistic yet straightforward approach to m odeling the probe in an attempt to understand how much

of the tip needs to be included to account for (1) half of the total electric force in AM-KPFM, or (2) half of the total electric force gradient in FM-KPFM.

We set out with the capacitor model of probe and sample, and approximated the probe as consisting of a micro-cantilever and a tip cone with a point end (see Figure 6). As a good conductor, the potential is the same all over the probe, and charges are only present on the surfaces. The integrated capacitance of the cantilever and tip cone can be analytically expressed. Electric force and electric force gradient are deduced from the first and second derivatives of capacitance. (See Appendix I for the mathematic deductions.)

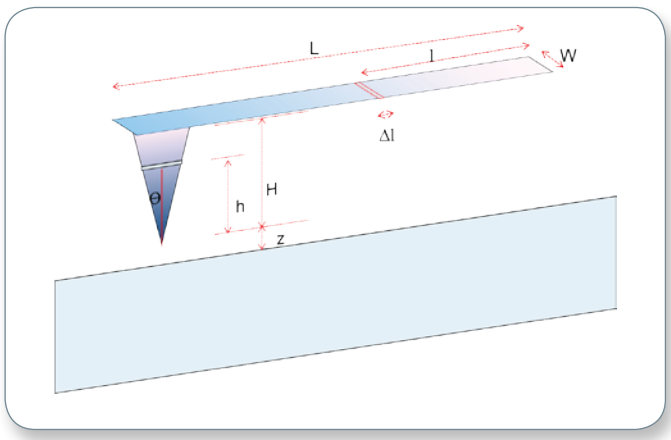


Figure 6. Model of a KPFM Probe with a rectangular cantilever. The capacitance of the cantilever is an integration of capacitance of each tiny rectangle along the cantilever. As the same force would cause different deflection depending on its distance to the base of the lever, the capacitance is normalized to recognize this.

Figure 7 shows the simulation result of the widely used SCM-PIT probe, which has the following nominal geometry: cantilever 225µm long, 30µm wide, tip 10µm tall, and cone half angle of 22.5°. The relative contribution of the tip cone, integrated to height h, versus total interaction, is plotted against tip height. To quantify the spatial resolution of KPFM, we adopted the similar definition used by Cohchero,[2] the radius of the ring at the height up to which the integral contribution of the tip cone accounts half the total electric force in case AM-KPFM; or half the total electric force gradient for FM-KPFM. For AM-KPFM, when lift height is 5nm, the contribution of the whole tip cone remains below 50%, indicating its spatial resolution is dominated by the width of the cantilever-on the micrometer scale, also implying the CPD obtained is not local, but a convolution over the large area covered by the cantilever. This calls its accuracy into question, except on large uniform samples. On the other hand, for FM-KPFM, when the tip is lifted 5nm above the surface, half of the signal is gathered from up to 15nm above the tip end, corresponding to a diameter of 12nm. This suggests a possible resolution of 10nm may be achieved with FM-KPFM. The CPD information collected is local to the area right underneath the tip affording credible accuracy. Lifting the tip higher, for instance, 50nm above the surface, the spatial resolution decays to around 200nm, which demonstrates the sharp dependence of spatial resolution on probe-sample distance.

While the above modeling is only a first order approximation, it is useful for conceptual understanding and it does reach the same conclusion as Colchero, who used a different set of assumptions.[2] It has been recognized that the electric force from the tip cone and cantilever predominate over that from the small tip-apex, therefore, AM-KPFM is not at all a quantitative nanoscale measuring tool. Only FM-KPFM, where dominating electric force gradient signal comes from the tip apex, offers high spatial resolution and accurate local CPD information. The effect of tip geometry on spatial resolution is only secondary.

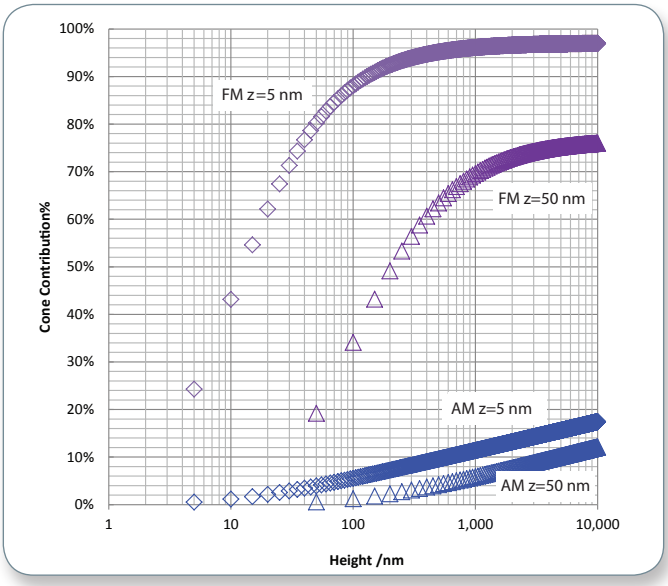


Figure 7. The contribution of the tip cone integrated up to height h over total electric force (blue) and electric force gradient (purple) are plotted versus height from tip end for a SCM-PIT probe. Geometries are: cantilever 225µm long, 30µm wide, tip 10µm tall, and cone half angle of 22.5°. The "BLUE" plots are electric force at tip-sample separation 5nm and 50nm. The "purple" plots are electric force gradient at tip-sample separation 5nm and 50nm.

Modes Overview and Comparison

KPFM, as a combination of the Kelvin probe technique and AFM, makes surface potential measurements accessible on the nanometer scale. KPFM traditionally operates in conjunction with TappingMode™, however, there are many reasons to combine it with the tried and proven PeakForce Tapping mode (see Bruker application note AN135). The four possible combinations are charted in Table 1 (the naming of each combination will be used through this application note). Some of these combinations may be done either in a single-pass fashion, where AFM imaging and KPFM measurement run simultaneously on one scan line; or in a dual-pass (or lift-mode) fashion, where AFM imaging mode is run on the first pass and KPFM on the second pass using lift-mode.

PeakForce KPFM™, the combination of PeakForce Tapping mode and FM-KPFM, integrates the benefits

KPFM \ AFM	Tapping Mode	PeakForce Tapping Mode
AM	*KPFM-AM*	PeakForce KPFM-AM
FM	KPFM-FM	PeakForce KPFM

Table 1. Chart summarizing the four major combinations between two major KPFM modes, AM-KPFM and FM-KPFM, and two major AFM modes, TappingMode and PeakForce Tapping. All modes are implemented in a dual-pass fashion (lift-mode), except KPFM-FM, which is done in single-pass.

and capabilities of PeakForce Tapping (ease of use and simultaneous PeakForce QNM capability) and the superior spatial resolution and accuracy of FM-KPFM. It is best done in a dual-pass fashion. It is possible to implement PeakForce KPFM in a single-pass fashion but not without sacrificing performance, as interference from PeakForce Tapping can sometimes be severe. KPFM-FM is done in a single-pass fashion. Though it can also be done in a dual-pass fashion, there is no benefit that is not covered by PeakForce KPFM. It is helpful to clear some confusion in the literature, where single-pass KPFM is sometimes improperly used to refer exclusively to KPFM-FM, albeit KPFM-AM can also be done in a single-pass fashion.

PeakForce KPFM and PeakForce KPFM-AM

Bruker offers a standard KPFM sample, which is patterned with Au, Si, and Al strips. Both the Al and Au films are 50nm in thickness deposited on an n-doped silicon substrate. In theory, when the tip is on any one of the three different regions, a constant potential value (CPD) should be read. A staircase potential profile is therefore expected across the three different materials. There is a noticeable slope, however, present on each of the stairs of the potential profile acquired with PeakForce KPFM-AM. This can be readily explained by the probe modeling described above. The potential data is a convolution from the tip, the tip cone, and the cantilever. Although the tip is on one single material, the relatively gigantic cantilever covers other materials and thus contributes a large portion of the total value. For instance, when the tip is on the the Al/Si interface, only half of the cantilever is over Al, and with the majority of the other half over Si (and smaller portion extending over the Au). The final measured value ends up a weighted average of the work function of the three materials. As the tip moves away from the edge, more contribution comes from the Al, and less from Si and Au, giving rise to the slope. This is true of all of the interfaces, and not only speaks of the poor lateral resolution of AM-KPFM, but also its inaccuracy as a result of convolution. In contrast, the stairs on the potential profile acquired using PeakForce KPFM are largely level, a manifestation that the dominant contribution is from the tip apex. Thus, the cantilever contribution becomes negligible. The data confirms that FM-KPFM offers much higher lateral resolution, due to the minimal contribution from the cantilever, and much better accuracy than AM-KPFM.

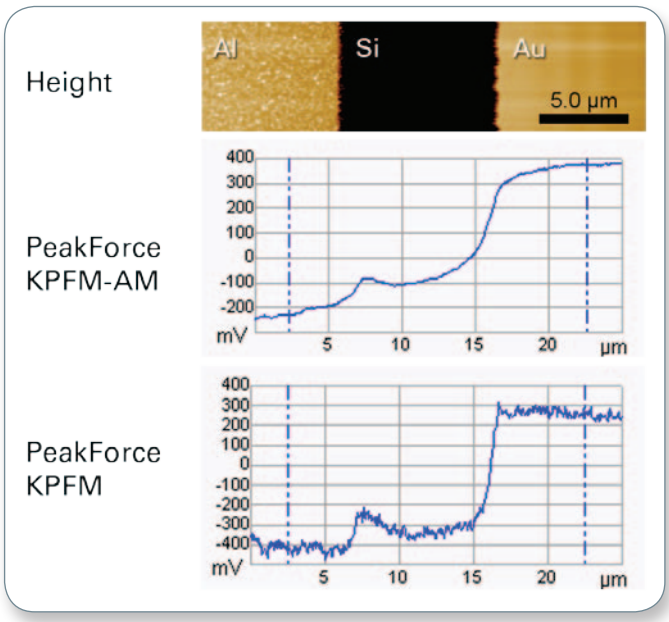


Figure 8. Height (top) and potential profiles using PeakForce KPFM-AM (middle) and PeakForce KPFM (bottom) on the Bruker KPFM standard sample, on the same location and with the same tip (PFQNE-AL).

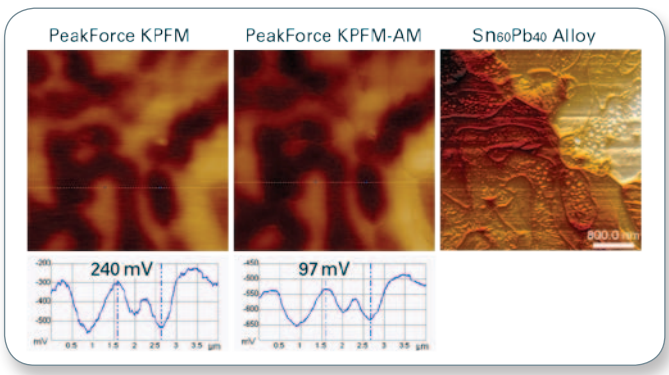


Figure 9. PeakForce KPFM and PeakForce KPFM-AM potential maps and cross section profile of a Sn-Pb alloy (60:40 by weight, at right is the topography (4µm scan).

Data on a Sn-Pb alloy further illustrates this point. The topography reveals different domains in the alloy (see Figure 9, right). They are clearly resolved on both potential maps acquired with PeakForce KPFM-AM (see Figure 9, left) and PeakForce KPFM (see Figure 9, middle) with little difference perceivable by qualitative evaluation of the potential maps. Their cross section, however, reveals a stark contrast. PeakForce KPFM gives a difference of 240mV between the two selected domains, consistent with the work function difference between Sn (4.42eV) and Pb (4.25eV), whereas KPFM-AM gives only a difference of 97mV, which is less than half of the expected theoretical difference, and half of what is seen from PeakForce KPFM. Again, this highlights the better accuracy of FM-detection

KPFM over AM-detection KPFM. The lateral resolution is thus defined as the smallest dimension on which a certain accuracy (90%) can be achieved, the distinction here being between whether you can resolve the difference and whether you can resolve the difference accurately.

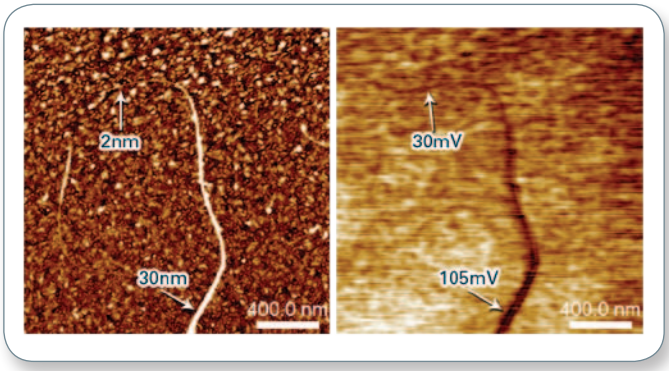


Figure 10. Height (left) and PeakForce KPFM potential (right) map of single-walled carbon nanotubes (SWCNTs) laid on a Si substrate. A single strand CNT (pointed to by the upper arrow) sticks out of a CNT bundle (pointed to by the lower arrow), which can be resolved in potential map, but no longer with accuracy as the dimension is too small to give dominant contribution in FM-KPFM.

Figure 10 is a height and PeakForce KPFM potential map of single-walled carbon nanotubes (SWCNTs) laid on a Si substrate. The 30nm part suggests a CNT bundle, with a single strand CNT (~2nm in diameter) sticking out at the top, which can be seen on the potential map. Note a 30mV difference from the substrate is obtained on the single strand CNT, which is only a third of that read on the CNT bundle (105mV). PeakForce KPFM can indeed resolve nanometer features, but is no longer accurate. The smaller dimension contributes only a non-dominant portion to the total electric force gradient, with the rest coming from the substrate, ending up with a much smaller contrast due to signal convolution. Note an even smaller value would be read when using PeakForce KPFM-AM, as the contribution from the tip-apex diminishes. This exemplifies that PeakForce KPFM has nanometer resolving power, but is only accurate on features 10nm or larger.

PeakForce KPFM and KPFM-FM

PeakForce KPFM is a combination of PeakForce Tapping mode AFM with FM-KPFM, whereas KPFM-FM is a combination of TappingMode AFM with FM-KPFM. In principle, their major difference lies solely on the AFM side. Where PeakForce Tapping affords ease of use, simultaneous quantitative and distinctive mechanical properties, TappingMode provides phase contrast and resulting in data ambiguity. Little difference is expected in KPFM performance, and this is largely true, with some exceptions. Figure 11 shows the potential maps on Sn-Pb acquired with PeakForce KPFM and KPFM-FM on the same spot with the same probe (PFQNE-AU, prototype). The contrasts between Sn (lighter) and Pb (darker) domains measured using the two modes are indeed almost identical, 240mV and 235mV respectively. Their absolute values, however, differ by about 100mV, which is not yet fully accounted for.

Mechanical Property Mapping: The adhesion channel from PeakForce KPFM shows a distinct contrast between the Sn and Pb domains and also has good correlation with potential data, rendering additional assurance in domain identification. On the other hand, little contrast is shown on the phase map by TappingMode. The simultaneous quantitative nanomechanical property mapping (PeakForce QNM) is an outstanding capability that only PeakForce Tapping can offer. This is further illustrated on a polymer film comprised of polystyrene (PS) and low-density-polyethylene (LDPE) cast on a silicon substrate. In addition to the potential map, modulus, deformation, and adhesion data were obtained.

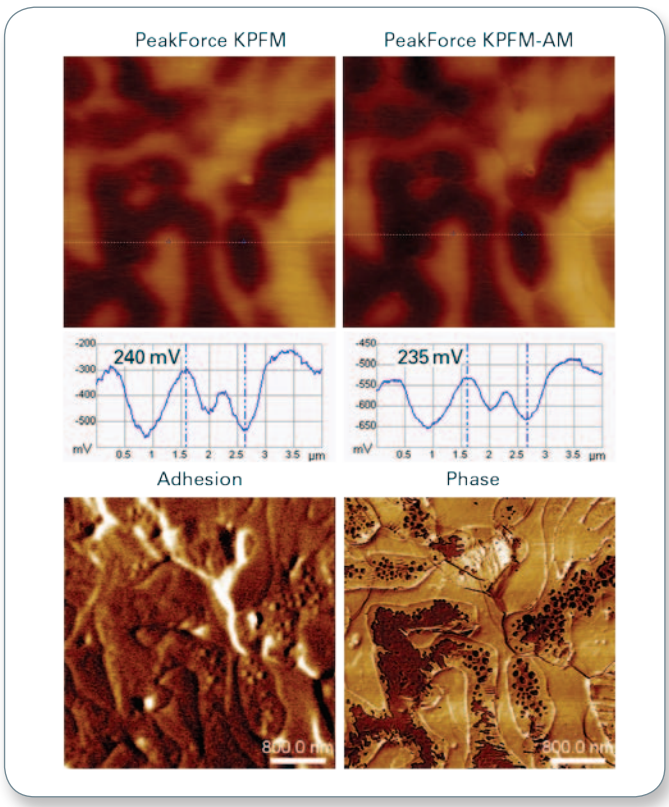


Figure 11. PeakForce KPFM and KPFM-FM Potential Maps and cross section profiles (top) of the Sn-Pb (60:40 by weight), and at bottom are the respective adhesion and phase imaging (4µm scan).

Artifacts in TappingMode KPFM-FM: Figure 11 shows that the tapping phase image from KPFM-FM does not display much contrast on the Sn-Pb alloy sample. While this can be interpreted as a shortcoming of TappingMode in revealing mechanical properties, a small phase contrast proves mandatory for faithful KPFM measurement. Frequency modulation KPFM uses phase as a means of frequency shift detection and any sharp phase change from tip-sample direct contact can be a source of error leading to artifacts in the potential map. In light of this, if there is a sharp phase contrast, care must be taken to ensure that the potential map is least affected. One measure is to use light tapping (a default setting in Bruker's implementation), that is, to

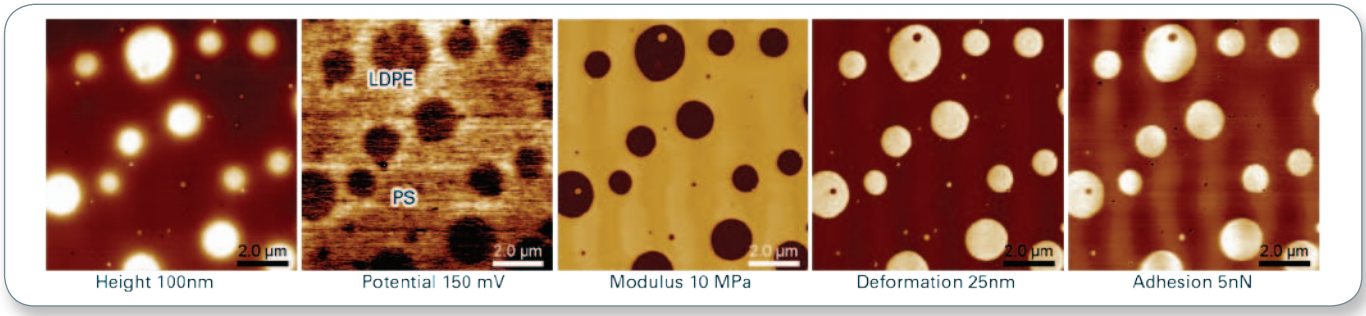


Figure 12. PeakForce KPFM data including height, potential and quantitative mechanical property maps such as Young's modulus, deformation and adhesion on a polymer blend consisting of polystyrene (PS) and low-density-polyethylene (LDPE) (10µm scan).

use the maximum possible tapping amplitude setpoint. Our experience suggests light tapping is beneficial in most cases. It may not, however, be sufficient to eliminate possible artifacts for certain samples when running single-pass-based KPFM-FM. Phase contrast sometimes can be so strong that single-pass KPFM-FM simply cannot remove phase cross-talk (e.g., on polymers with strong dipoles). In this case, one has to turn to dual-pass based techniques, where sufficient lift-height can be used for the tip to clear the sample surface to eliminate phase shift due to direct tip-sample contact.

PeakForce KPFM proves advantageous on this regard, and can also be used to identify possible artifacts. By incrementally changing the lift height, if potential contrast shows an abrupt change in response to a small change in lift height, one can determine beyond doubt that the potential contrast obtained below a certain lift-height contains artifacts. This is exemplified in the imaging of a brush polymer sample on mica where, when the lift height is changed from 25nm to 27nm (a relatively small change compared to the polymer chain width of 5nm), instead of a possible blurring of the potential contrast on the chains as the tip goes up, the chain structure disappeared altogether (see Figure 13). The chain pattern seen at smaller lift heights can therefore be attributed to artifacts. PeakForce KPFM provides a means to identify and eliminate possible artifacts from tip-sample direct contact.

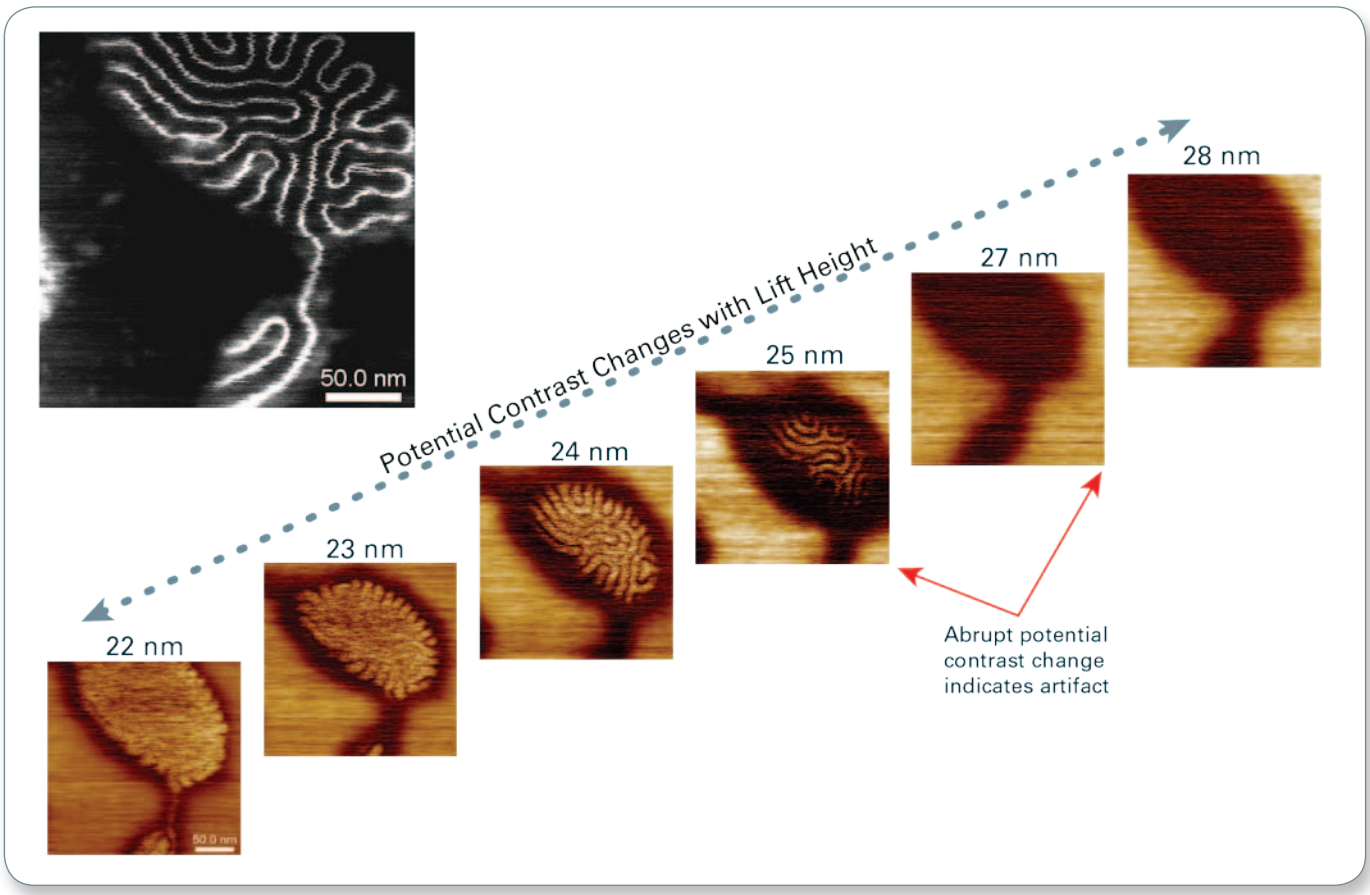
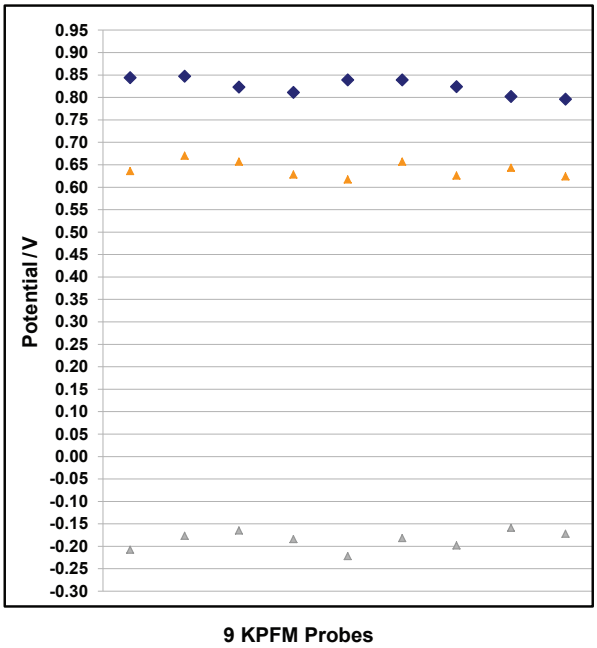


Figure 13. Sequential PeakForce KPFM maps of a brush polymer sample on mica substrate versus lift height. An abrupt change in potential contrast is observed when lift height increases from 25nm to 27nm, suggesting that the potential contrast of the polymer chains seen at a lift height of 25 nm or below are artifacts, caused by phase shift from direct tip-sample contact. Scan size is 250nm. The inset at the upper-left corner is the height image.



	Average (V)	Std Dev (V)	Maximum (V)	Minimum (V)
Au-Al	0.825	**0.019**	0.847	0.796
Au	0.639	**0.018**	0.617	0.670
Al	-0.185	**0.020**	-0.159	-0.222

Figure 14. PeakForce KPFM data obtained using nine different PFQNE-AL (Bruker) probes on the Bruker KPFM standard sample. The value on Al (grey triangle), Au (gold triangle) and their differences (blue diamond) are plotted. Standard deviation of each is listed at right, which is on the order of 5x improvement over traditional KPFM measurements.

It is worth noting that KPFM-FM does have some perceived advantage when imaging features smaller than a few nanometers, as the average tip-sample separation can be maintained smaller than can be practically achieved with lift-mode-based PeakForce KPFM. This, however, does not offset the substantial advantages that PeakForce KPFM offers.

Interpreting KPFM Phase: In addition to KPFM potential data, KPFM phase data is simultaneously obtained and can prove useful. It reflects the dielectric constant contrast of the sample. Referring to equation 2 above, one finds the second derivative of capacitance, which has dependence on dielectric constant of the material between the tip and the conductive portion of the sample, can be obtained from the 2ω term. It can also be obtained from the DC term, especially when $V_{CD}=V_{CPD}$, which is the case when KPFM is actively running. This is equivalent to electrostatic force microscopy (EFM) phase imaging, with the advantage that work function and dielectric information are separated, while the standard EFM phase imaging is a mix of work function and dielectric information

Repeatability

While repeatability of relative contrast within one KPFM image has been reasonably good, even with the same type of probe, absolute values can vary hundreds of mV from experiment to experiment. Improving measurement consistency is a crucial step toward quantitative work function measurement. With a new probe design and optimized instrumentation, we have found ways to reduce probe-to-probe measurement scatter to below a standard deviation of 50mV. This represents a major advance for quantifying KPFM, which in turn expands KPFM's utility in ever more demanding applications.

Table 2 lists some of the major sources responsible for measurement inconsistency. Even with a sound electronic design that has little electronic cross-talk, operating parameters and probe variation can cause data fluctuation. These include (1) whether ac drive is right on, and always on, the resonant frequency of the cantilever; (2) whether tip-sample separation is kept the same from run to run; (3) whether the work function of the tip, which is essentially the reference point, remains unchanged; and (4) whether the sample is undergoing oxidation, adsorption of molecules, or alteration due to possible electrochemical reactions (as current may flow between the tip and sample).

Source of Uncertainty	Bruker Solution
Operating Frequency	Tight parameter control (ScanAsyst-KPFM): ▪ Thermal tune for resonance frequency ▪ Fixed oscillation amplitude ▪ Optimal phase setting
Tip-Sample Seperation	
Tip Work Function Change Due to Tip Wear	Probe Design: ▪ Single tip material ▪ Proprietary way to limit DC currrent flow
Electrochemical Reaction Under Bias	

Table 2. Possible sources for KPFM measurement inconsistency.

To overcome these uncertainties, a ScanAsyst® KPFM operation mode was implemented, which resembles ScanAsyst in that it provides automated imaging optimization, but differs in its technical implementation.

In ScanAsyst KPFM, the algorithm seeks the resonant frequency of the cantilever using thermal tune to ensure the accuracy and consistency of the operating frequency. The cantilever is always driven to a free-air oscillation amplitude of 20nm when performing either PeakForce KPFM or KPFM-FM, and the drive phase is always accurately and automatically set. A proprietary probe design eliminates possible DC current flow between the tip and sample, and the uncoated silicon tip ensures no significant work function change will occur from tip wear (as often happens with metal coated probes). These enhanced capabilities have greatly improved KPFM repeatability; Figure 15 showcases the repeatability obtained with nine different PFQNE-AL probes on the Bruker KPFM standard sample. A standard deviation of less than 20mV has been achieved in the potentials measured on an Al strip, an Au strip, and in their potential difference. When the tip work function is properly calibrated, an accurate work function of the sample can be deduced. In addition, the ScanAsyst KPFM mode brings ease-of-use to the operation.

Sensitivity

Frequency modulation KPFM was first realized under ultrahigh vacuum (UHV) in 1998,[8] and was not introduced into ambient AFM until about ten years later. In addition to the environment change that can affect KPFM measurement fidelity, there is also a dramatic difference in detection sensitivity. This is immediately noticeable when you compare AM-KPFM and FM-KPFM data in an ambient setting. The latter is usually much noisier, an evidence of lack of sensitivity. It is therefore helpful to understand what governs FM-KPFM detection sensitivity. Mathematical deduction is not included in this application note, but as previously mentioned, the electric force gradient can be viewed as an addition to the natural spring constant of the cantilever. For a smaller spring constant, the same electric force gradient would mean a larger relative change, causing a larger frequency shift and thus a stronger signal. The Q simply makes the phase versus frequency plot steeper, further enhancing the signal:

$$KPFM\ Sensitivity \propto \frac{Q}{k}$$

It is noteworthy that under UHV (i.e., without air damping) the Q of standard EFM probe can be hundreds of times larger than in air, thereby affording ample signal amplification of the FM-KPFM signal. Measurement sensitivity has rarely been an issue and high quality data is regularly attained. Sensitivity is neither an issue for AM-KPFM in ambient conditions, as the signal itself, convoluted from the tip apex, tip cone and the cantilever, is often large enough with conventional EFM probes. The low Q in air, however, imposes a practical challenge for FM-KPFM detection, where the signal is often weak as the majority of the signal is only from the tip apex and the lower part of the tip cone (the same reason FM-KPFM has better spatial resolution). A large Q/k ratio, meaning smaller spring constant and larger Q, is demanded of the probe.

PeakForce KPFM opens up room for improvement, as opposed to KPFM-FM based on TappingMode. TappingMode requires the cantilever to have a sufficiently large spring constant to overcome capillary forces from water layers that are often present on sample surfaces. It also requires the Q to be not so large as to limit TappingMode bandwidth. PeakForce Tapping removes these limitations, allowing the use of cantilevers with a much smaller spring constant and larger Q, enabling room for probe optimization. Currently, PFQNE-AU probes are twice as sensitive as the commonly used SCM-PIT probes. Probes with higher Q/k ratio can be designed to further improve PeakForce KPFM sensitivity.

Platforms and Accessories

All KPFM modes are available on Bruker Dimension Icon® and MultiMode® 8 AFMs, and can be used in conjunction with a variety of accessories.

Figure 15. Turnkey glove-box enabling all AFM functions to be performed in a 1ppm level oxygen and water environment. Shown inside is a Dimension Icon AFM, a version of glove-box for the MultiMode 8 is also available.

Environmental Control: Most notably, for samples that require stringent environmental control (e.g., lithium battery anode or cathode materials, organic photovoltaic or light emitting devices), a turn-key 1ppm-level of oxygen and water capable glove box (customized for best performance) can be used. The glove box solution proves beneficial to measurement repeatability of samples subject to change when exposed to ambient air, including most semiconductor materials and metals.

Backside Illumination: The Photoconductive AFM module, offered on the Dimension Icon system, is compatible with industry-standard Newport solar simulators to enable even, backside sample illumination across the scan area. This allows KPFM potential mapping while illuminating with achievable intensities equivalent to 300 suns, enabling study of static and dynamic photovoltaic responses to illumination of organic solar cells/materials. Figure 16 shows PeakForce KPFM data on a MDMO (poly[2-methoxy-5-(3',7'-dimethyloctyloxyl)]-1,4-phenylene

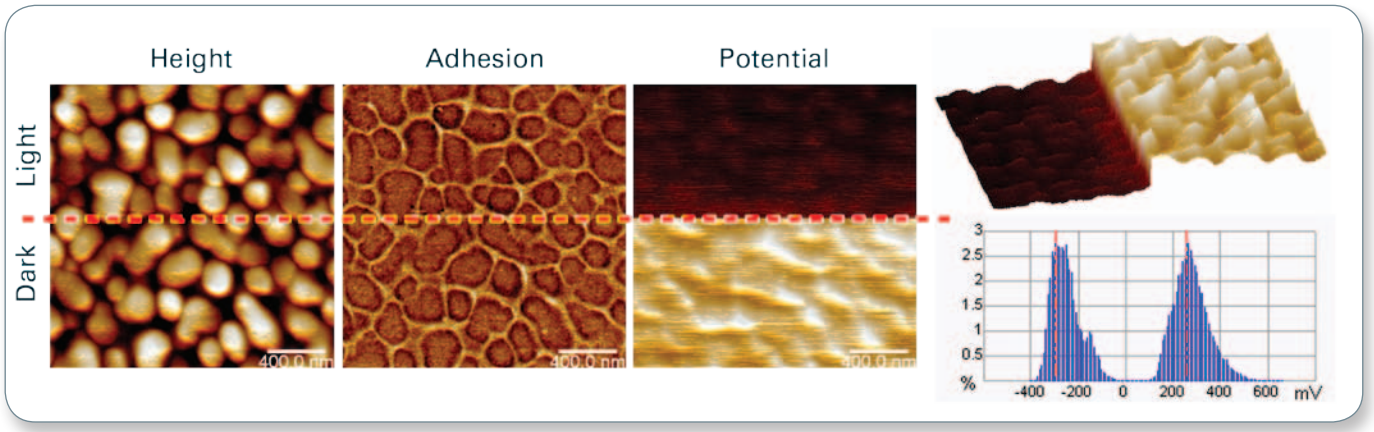


Figure 16. PeakForce KPFM Potential map (third from left) of MDMO-PCBM bulk heterojunction solar cell on an ITO substrate in dark (bottom half) and under illumination with an intensity equivalent to 300 suns (top half). A 535mV downshift of work function is seen under illumination, a 3D rendering and histogram of potential data is at the right. Sample courtesy of Dr. Philippe Leclere, University of Mons.

vinylene)-PCBM ([6,6]-phenyl C61-butyric acid methyl ester) bulk heterojunction solar cell. Work function down-shifts 535mV under illumination simulating 300 suns intensity.

KPFM-HV Mode

KPFM-HV stands for High-Voltage KPFM mode, which measures electrostatic potential beyond ±10V. KPFM-HV is a dual-pass technique, with PeakForce Tapping as the base AFM mode. Question arises as why one would need to measure high voltage. KPFM, as we have learned, measures the work function difference between the sample and tip. When we look through the work function table of the elements,[9] the highest work function is 5.93eV (Osmium) and lowest 2.14eV (Cesium), so the maximum possible work function difference will never exceed 3.79V. All the KPFM techniques described above cover the range up to ±10V, and therefore suffice for any work function measurement task. Demand arises when it comes to measuring trapped (immobilized) charges in insulators. For instance, when one walks on a carpet on a dry day, static charge can accumulate up to tens, hundreds, or even thousands of volts. The KPFM-HV mode meets the need for measuring high voltage electrostatic potentials. This technique is no longer using a KPFM feedback loop, nor a high voltage source as one may logically think. It deviates from the force or force-gradient-nulling concept central to the aforementioned KPFM techniques. It is done with existing hardware common to an AFM, and through calculation.

We adopt the concept that the sample and tip form a capacitor. We further assume the electric force follows the same expression:

$$F_{el} = \underbrace{\frac{\partial C}{\partial z}\left(\Delta\phi^2 + \frac{1}{2}{V_{AC}}^2\right)}_{\text{DC Term}} + \underbrace{\frac{\partial C}{\partial z}\Delta\phi V_{AC}\sin(\omega t)}_{\omega\text{ Term}} + \underbrace{\frac{1}{4}\frac{\partial C}{\partial z}{V_{AC}}^2\cos(2\omega t)}_{2\omega\text{ Term}}$$

where Δφ is the electrostatic potential difference at the tip in reference to the sample.

Therefore, the amplitude at ac bias driving frequency ω and the second harmonic 2ω are:

$$A_\omega = \frac{\partial C}{\partial z}\Delta\phi V_{AC}$$

$$A_{2\omega} = \frac{1}{4}\frac{\partial C}{\partial z}{V_{AC}}^2$$

We obtain the electrostatic potential difference:

$$\Delta\phi = \frac{1}{4}V_{ac}\frac{A_\omega}{A_{2\omega}}$$

and

$$\frac{\partial C}{\partial z} = \frac{4A_{2\omega}}{{V_{AC}}^2}$$

dC/dz reflects the dielectric constant variations across the sample.

Implementation: KPFM-HV is implemented in a dual-pass fashion. On the first pass, PeakForce Tapping is used to obtain topography and mechanical properties. On the second pass (lift-mode), PeakForce Tapping drive is stopped, and an ac bias with a frequency lower than half of the cantilever resonant frequency is applied between the tip and sample. The vertical deflection signal is simultaneously fed to two synchronized but separate lock-in amplifiers; one to detect the amplitude and phase at the drive frequency, and the other the amplitude at the second harmonic. Calculation is carried out in the background to obtain electrostatic potential difference Δϕ, and dC/dz. This technique allows one to measure voltage in the range of ±200V with an error less than 15%. Higher voltage (up to ±1000V) can be measured with accuracy only limited by nonlinearity of photodetectors in the AFM. This technique is available on MultiMode 8 AFMs (no additional hardware required) and Dimension Icon AFMs (a PeakForce HV module is required to minimize measurement distortion from electronic interference).

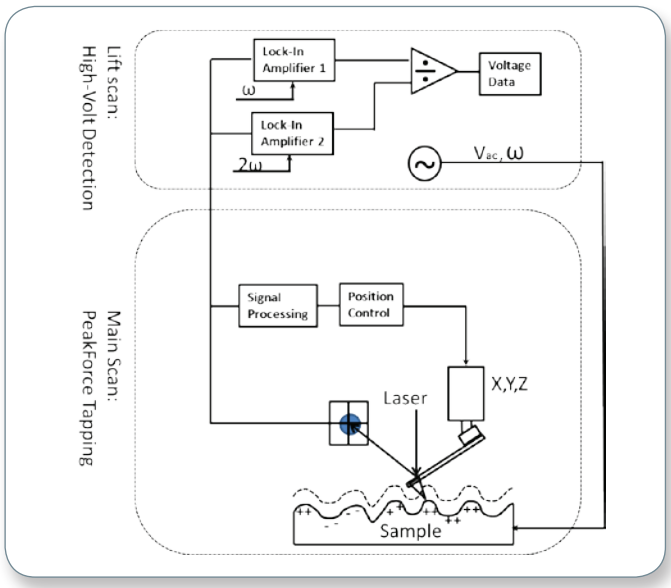


Figure 17. KPFM-HV diagram, in the first pass, surface topography and mechanical properties are obtained in PeakForce Tapping; in the second pass, an ac bias at a frequency lower than half of the cantilever resonant frequency is applied between the probe and the sample, which causes the probe to oscillate at frequency ω and its second harmonic 2ω. The electric potential between the tip and sample is calculated based on the oscillation amplitude at frequency ω and 2ω. Note that no KPFM feedback is involved.

Examples: Some polymers can be charged through contact electrification. Simply contacting and then separating two similar or dissimilar polymer pieces, or contacting it to and then separating it from a conducting surface, induces charge on surfaces being contacted. Figure 19 shows the potential map (left), phase (middle), and a 3D rendering of the potential map of a PDMS (polydimethylsiloxane) film. The sample is prepared by casting a PDMS film about 0.5mm in thickness on a silicon wafer. A piece is peeled off the silicon substrate and then its underside is imaged. The potential map shows the electrostatic potential, reflecting electrostatic charge density (absolute value), and sign, which is learned from the phase data. The 3D rendering shows a minimum of -99V at the center of a negatively charged area, with positive charges having an electrostatic potential as high as 156V.

PDMS samples can be easily obtained, in fact, a PDMS gel-pad is often found in AFM probe packaging. Simply cut off a piece of gel-pad from the bottom of an AFM probe box, and use the contact electrification technique to have it charged. Charge can also be introduced through triboelectric charging (one type of contact electrification, through rubbing), for instance, by repeatedly scanning the same area for some extended period of time. Figure 19

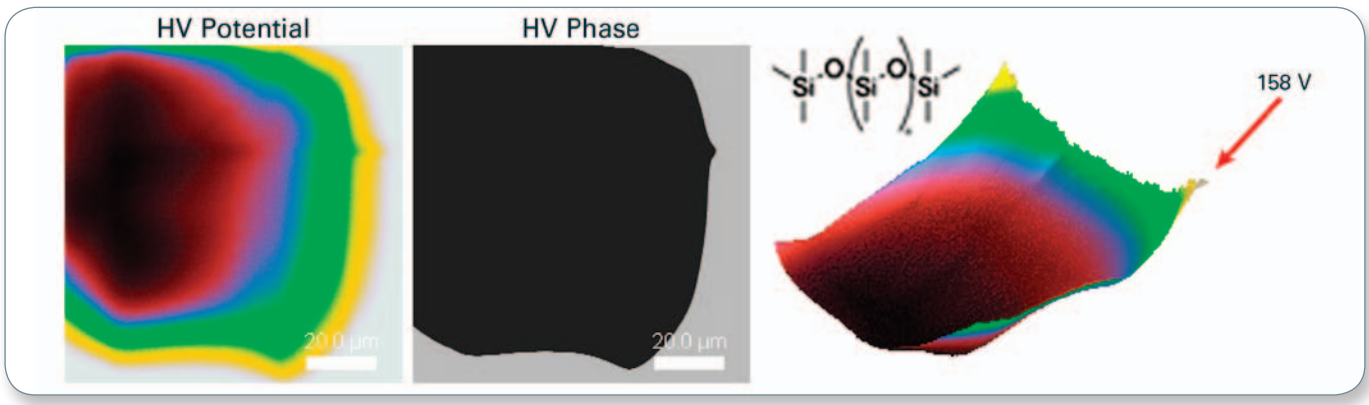


Figure 18. KPFM-HV images of PDMS (polydimethylsiloxane) films after being charged by peeling off from the silicon substrate upon which it was cast. The HV Potential data (left) shows the electrostatic potential and the sign of charge; HV Phase data (middle) denotes negative charge with negative phase, and positive charge with positive phase. At the right is a 3D rendering of the potential map, the negative charge gives rise to an electrostatic potential of -99V at its center, and some of the adjacent positive charges go as high as 158V.

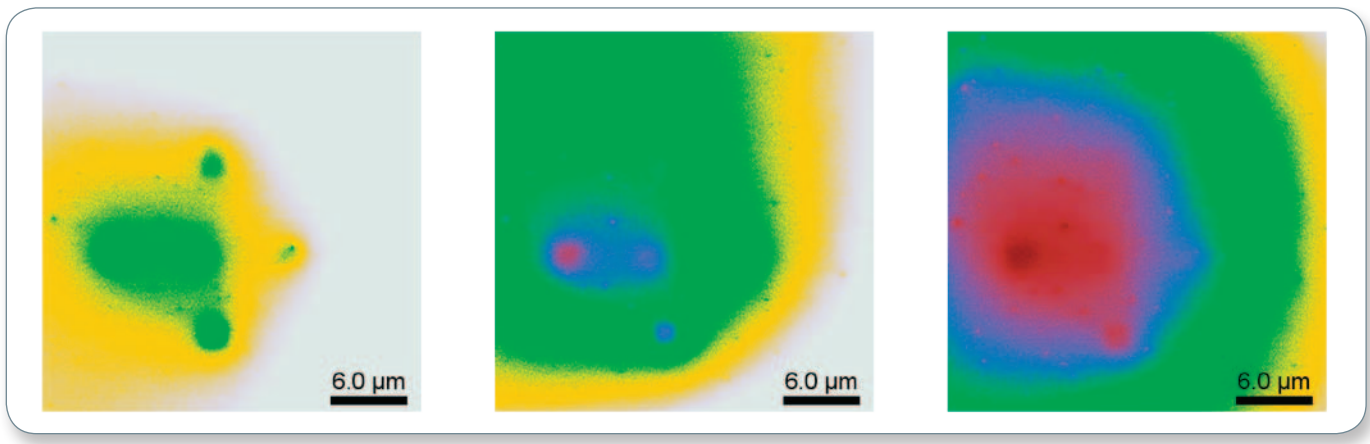


Figure 19. KPFM-HV potential map on PDMS, encasing five previously scanned sites in a square-center arrangement. Sequential images from left to right reveal that the negative charges are accumulating, spreading out and merging with each other as scanning goes on.

Probe Choices	KPFM Modes				
	PeakForce KPFM	PeakForce KPFM-AM	KPFM-FM	KPFM-AM	KPFM-HV
1st	PFQNE-AL	PFQNE-AL	PFQNE-AL	PFQNE-AL	TAP150A
2nd	SCM-PIT	ScanAsyst-Air HR	SCM-PIT	SCM-PIT	SCM-PIT
3rd	None	SCM-PIT	None	None	MESP-RC

Table 3. Probe Selection Guide for Each KPFM Mode.

(left) shows five previously scanned sites with negative charges. Sequential imaging indicates the negatively charged areas spreading out and merging with each other as scanning continues.

KPFM-HV mode provides a simple means to measure electrostatic potential of immobilized charges as high as ±200V.

Probe Selection Guide

Table 3 is a probe selection guide for each mode, as of the date this note is published. For up-to-date information, please follow the guidance provided in the NanoScope® software. Other probes not in the list may also work, but their performance in relation to KPFM measurement sensitivity, accuracy, and/or repeatability may not be guaranteed.

Conclusion

Bruker offers a suite of new KPFM modes, three of which are based on the breakthrough PeakForce Tapping technology with a dual-pass implementation:

- PeakForce KPFM, using Frequency Modulation detection;
- PeakForce KPFM-AM, using Amplitude Modulation detection;
- PeakForce KPFM-HV, using Amplitude Modulation and extending the accessible potential range by more than a factor of ten.

PeakForce KPFM, achieved by combining PeakForce Tapping with frequency-modulation KPFM exhibits the most outstanding performance:

- It retains the high spatial resolution and accuracy of FM-KPFM (probe modeling reveals that FM-KPFM offers a resolution down to 10nm without compromising measurement accuracy, in stark contrast to the micrometer-scale resolution offered by AM-KPFM).
- It achieves high repeatability through tight parameter control using the ScanAsyst KPFM operation algorithm and novel probe design.
- It leverages PeakForce QNM to produce simultaneous mechanical and electrical information, enhancing its material identification power.
- It promises further enhancement to FM-KPFM sensitivity (PeakForce Tapping lifts the restrictions on probe selection imposed by TappingMode, and cantilevers with lower spring constant and higher Q can be employed for improved sensitivity).

Ultimately, PeakForce KPFM has brought us a major step forward toward high-resolution, quantitative work function measurements. It is poised to meet the challenges in application areas that demand ever higher spatial resolution and better accuracy and repeatability. With proven applications on metal, semiconductor, organic materials, the superior capabilities of PeakForce KPFM also promise benefits for bio-materials, and other advanced application areas.

Appendix I: Mathematics about Frequency Modulation

The modulation of the resonant frequency, corresponding to the electric force gradient modulation at the driving frequency of the ac bias is therefore:

$$\tilde{\omega} \approx -\frac{\omega}{2k}\frac{\partial^2 C}{\partial z^2}(V_{DC}-V_{CPD})V_{AC}\sin(\omega_m t) \xrightarrow{definetion} F_m \sin(\omega_m t)$$

Where $\tilde{\omega}$ is the modulated frequency component, Fm denotes the frequency modulation amplitude. For the cantilever mechanically driven to oscillate at its resonant frequency, applied with an ac bias with frequency ω_m, the cantilever motion can be written:

$$x(t) = A\sin\left(\int_0^t(\omega + F_m\sin(\omega_m\tau))dt\right) = A\sin\left(\omega t - \frac{F_m}{\omega_m}\cos(\omega_m t)\right)$$

$$\xrightarrow{\frac{F_m}{\omega_m}<0.2(narrow-band-FM)} A\sin(\omega t) - A\frac{F_m}{\omega_m}\sin(\omega_m t)\cos(\omega t)$$

$$= A\sin(\omega t) + \frac{A}{2}\frac{F_m}{\omega_m}\sin((\omega-\omega_m)t) - \frac{A}{2}\frac{F_m}{\omega_m}\sin((\omega+\omega_m)t)$$

$$= \underbrace{A\sin(\omega t)}_{\substack{\text{Carrier}\\ \text{Resonant frequency}}} + \underbrace{\frac{m_\omega}{2}A\sin((\omega-\omega_m)t)}_{\substack{\text{Side Band}\\ \text{Differential frequency}}} - \underbrace{\frac{m_\omega}{2}A\sin((\omega+\omega_m)t)}_{\substack{\text{Side Band}\\ \text{Sum frequency}}}$$

This equation states that, in addition to the oscillation at the resonant frequency, a pair of sidebands will appear at $\omega \pm \omega_m$. This is very useful for understanding the oscillation spectrum. Figure 4 is the spectrum when an MESP-RC probe is mechanically driven at 133kHz, while an ac bias of 2kHz is applied. The amplitude of the sideband reflects the amplitude of the frequency modulation. The ratio of the sum of first side-peak pair versus the center peak height gives the frequency modulation index F_m/ω_m. For example, 0.1 would mean the frequency modulation amplitude is 200Hz (0.1 x 2kHz). The FM-KPFM feedback is to adjust DC bias so the first sideband pair disappears, at which point V_{CPD} is found.

In practical implementation, sideband amplitude is rarely directly measured at the sideband frequency using a single lock-in amplifier. A more common method uses two cascade lock-in amplifiers, with the first one locking at the resonance frequency, the phase output of which is fed to the second lock-in, which locks at the ac bias frequency. The following equation provides insight in this approach:

$$x(t) \xrightarrow{\frac{F_m}{\omega_m}<0.2(narrow-band-FM)} A\sin(\omega t) - A\frac{F_m}{\omega_m}\sin(\omega_m t)\cos(\omega t)$$

The phase is:

$$\tan(\phi) = -\frac{F_m}{\omega_m}\sin(\omega_m t)$$

For $F_m/\omega_m < 0.5$

$$\phi\ (in\ rad) \approx -\frac{F_m}{\omega_m}\sin(\omega_m t)$$

So, feeding the phase output of the first lock-in amplifier to a second lock-in amplifier locking at frequency ω_m, the amplitude output of the second lock-in will be F_m/ω_m, exactly the frequency modulation index (some scaling factor may exist).

Appendix II: Mathematics on Probe Modeling

Probe modeling starts with the capacitor model for the probe and sample, and approximates the probe as consisting of a micro-cantilever and a tip cone with a point end (see Figure 7). As a good conductor, the potential is the same all over the probe, and charges are only present on the surfaces. The integrated capacitances of the cantilever and tip cone can be analytically expressed. Electric force and electric force gradient can be deduced from the first and second derivatives of the capacitance.

Lever Contribution to Electric Force and Force Gradient

For simplicity, we assume the cantilever is parallel to the sample, ignoring the tilt of the cantilever. Recognizing that the electric force at the end of the lever causes more deflection than the same force at the base of the cantilever, the capacitance is normalized in proportion to its length from the base:

$$C_{Lever} = \int_0^L \varepsilon\frac{W}{H+z}\frac{l}{L}dl = \frac{1}{2}\varepsilon\frac{WL}{H+z}$$

where, W is the width and L is the length of the cantilever, H is the height of the tip cone, z is the distance from the tip end to the sample, and ε is the dielectric constant.

The electric force from the lever is therefore:

$$F_{Lever} = -\frac{V^2}{4}\varepsilon\frac{WL}{(H+z)^2}$$

and the electric force gradient is:

$$F'_{Lever} = \frac{V^2}{2}\varepsilon\frac{WL}{(H+z)^3}$$

Tip-Cone Contribution to Electric Force and Force Gradient

The surface of the tip cone is treated as a stack of rings. The total capacitance is the sum of the capacitance of each ring, which is approximated by the projected area of the ring and its vertical distance from the sample surface:

$$C_h = \int_0^h \varepsilon \frac{2\pi h \tan^2(\theta)}{h+z} dl = 2\pi\varepsilon z \tan^2(\theta)\left(\frac{h}{z} - \ln\frac{h+z}{z}\right)$$

Therefore, the electric force from the cone up to height h is:

$$F_h = \pi\varepsilon \tan^2(\theta)(\ln\frac{h+z}{z} - \frac{h}{h+z})$$

and the electric force gradient from the cone up to height h is:

$$F'_h = \pi\varepsilon \tan^2(\theta)\frac{1}{z}(\frac{h}{h+z})^2$$

References

1. C. Li, S. Minne, B. Pittenger, A. Mednick, M. Guide, and T-Q. Nguyen, "Simultaneous Electrical and Mechanical Property Mapping at the Nanoscale with PeakForce TUNA," Bruker application note AN132 Rev. A0 (2011).
2. J. Colchero, A. Gil, and A.M. Baro, "Resolution Enhancement and Improved Data Interpretation in Electrostatic Force Microscopy," *Phys. Rev.* B 64(24), 245403 (2001).
3. U. Zerweck, C. Loppacher, T. Otto, S. Grafström, and L.M. Eng, "Accuracy and Resolution Limits of Kelvin Probe Force Microscopy," *Phys. Rev.* B 71, 125424 (2005).
4. B. Pittenger, N. Erina, and C Su, "Quantitative Mechanical Property Mapping at the Nanoscale with PeakForce QNM," Bruker application note AN128, Rev. A0 (2010).
5. W.A. Zisman, "A New Method of Measuring Contact Potential Differences in Metals", *Rev. Sci. Instrum.* 3, 367 (1932).
6. J.M.R. Weaver and D.W. Abraham, "High Resolution Atomic Force Microscopy Potentiometry", *J. Vac. Sci. Technol.* B 9(3), 1559-61 (1991).
7. M. Nonnenmacher, M.P. O'Boyle, and H.K. Wickramasinghe, "Kelvin Probe Force Microscopy," *Appl. Phys. Lett.* 58, 2921-23 (1991).
8. S.Kitamura and M. Iwatsuki, "High-resolution imaging of contact potential difference with ultrahigh vacuum noncontact atomic force microscope," *Appl. Phys. Lett.* 72(24), 3154-56 (1998).
9. D.R. Lide, "Table of Work Functions of Elements," *CRC Handbook of Chemistry and Physics, 89th edition.* Boca Raton, Fla. London: 12-114 (2008).

Authors

Chunzeng Li, Stephen Minne, Yan Hu, Ji Ma, Jianli He, Henry Mittel, Vinson Kelly, Natalia Erina, Senli Guo, Thomas Mueller
(Bruker Nano Surfaces)

Bruker Nano Surfaces Divison
Santa Barbara, CA · USA
+1.805.967.1400/800.873.9750
productinfo@bruker-nano.com

www.bruker.com