HIGH RESOLUTION KELVIN FORCE MICROSCOPY ON SEMICONDUCTOR MATERIALS AND ORGANIC MONOLAYERS

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INTRODUCTION

In addition to high-resolution visualization of surface morphology and nanoscale structures, atomic force microscopy (AFM) 1 has been broadly applied for examination of mechanical, electromagnetic, optical and other properties. The core of this technology is the measurement and control of force interactions between a minute probe (the AFM tip) and a sample surface. These measurements can be either performed at a single location, or can be applied for surface imaging with contact or oscillatory techniques. The techniques complement each other yet studies of soft matter are mostly carried out with oscillatory amplitude modulation (AM) mode 2-3. Despite an expanding penetration of AFM and the related scanning probe microscopy methods into academic and industrial research, a critical analysis of the existing capabilities of this method reveals a number of undeveloped areas that are essential for further progress of the field. We will mention only a few of them. The current efforts towards imaging with true molecular and atomic resolution in different environments benefit from an extension of frequency modulation (FM) mode 4 to measurements in air and under liquid 5. The improvement of noise characteristics of AFM electronics and the minimization of thermal drift of the microscopes will undoubtedly assist researchers using extremely sharp probes in achieving superior imaging resolution.

In the probing of local mechanical and electric properties increasing attention is paid to multi-frequency measurements that offer new capabilities for quantitative analysis. Studies employing multifrequency measurements in the broad frequency range help avoid cross-talk of topography with mechanical and electric tip-sample force effects and have other advantages. A successful realization of these possibilities simultaneously with improved resolution of imaging and mapping of materials’ properties will open new horizons for AFM characterization especially if these applications can be performed in the properly-controlled environments. In the commercial scanning probe microscopes made by Agilent Technologies the first steps towards advanced AFM measurements were undertaken with the introduction of the MACIII accessory especially useful for multi-frequency measurements. The MACIII has three dual phase lock-in amplifiers (LIA) converting the AC inputs to amplitude and phase. These digitally-controlled analog LIA have a broad bandwidth (up to 6MHz) that covers the operation bandwidth of the photodetector employed in the microscope. The auxiliary inputs and drive outputs are accessible through the MACIII signal access box. The software, which is flexible in routing signals back to the microscope controller, supports two servo systems related to these LIA. One LIA is used for AM tracking of sample topography with the probe peak-to-peak amplitude or its X-, Y- vector components used for feedback. The other servo can be applied to electric or mechanical measurements. The third LIA can be used for tuning the operational parameters or for recording
various signals (lateral response, torsional signal, harmonics, etc) during measurements. Voltages up to 20V in DC or in different pulse regimes can be applied to the probe-sample junction as an external stimulus for lithography or other applications.

1.1 Background on Electric Force Microscopy (EFM) and Kelvin Force Microscopy (KFM)

The use of AFM for examination of local electric properties of surfaces was suggested since the advent of this technique. A typical scheme of detection of electrostatic forces includes a conducting probe which is biased with respect to a back electrode or substrate carrying a sample on top. In a simplified form the contribution of electrostatic force is proportional to $\Psi^2$ and $\partial c/\partial z$, where $\Psi$ – potential difference, $C$ – capacitance and $Z$ – the probe-sample separation.

1. $F_{elec}(Z) = \frac{1}{2} \partial c/\partial z \Psi^2$

When DC ($U_{DC}$) voltage and AC ($U_{AC}$) voltage at frequency $\omega$, are applied to the probe then the electrostatic force can be expressed as

2. $F_{elec}(Z) = \frac{1}{2} \partial c/\partial z \left[ (\phi - U_{DC} - U_{AC} \sin(\omega t)) \right]^2$,

where $\phi$ is the surface potential or contact potential difference (CPD) between the probe and the sample.

This equation can be separated into three components defining the DC and frequency responses:

3. $F_{DC}(Z) = \frac{1}{2} \partial c/\partial z (\phi - U_{DC})^2 + \frac{1}{2} U_{AC}^2$

4. $F_{\omega}(Z) = - \partial c/\partial z \left[ (\phi - U_{DC}) \right] U_{AC} \sin(\omega t)$

5. $F_{2\omega}(Z) = - \frac{1}{4} \partial c/\partial z U_{AC}^2 \cos(2\omega t)$

This set of equations describes the electrostatic force measurements in the capacitor-like set-up. The idea of using two frequencies for simultaneous and independent measurements of surface topography and electrostatic forces was implemented in one of the first AFM applications. In these non-contact experiments, AC voltage was applied to a conducting probe at $\omega_{elec}$ and the changes of the probe amplitude at this frequency were detected at different probe-sample separations, which were adjusted by changing $A_{sp}$ at the frequency of mechanical resonance, $\omega_{mech}(>\omega_{elec})$. These measurements showed high sensitivity of the applied detection scheme. In the next step, maps of electric properties of a photoresist on a Si substrate and of a working p-n junction in a transistor were obtained by recording the amplitude changes at $\omega_{elec}$ and $2\omega_{elec}$.

These pioneering measurements of the AFM probe response to electrostatic forces and mapping it over a scanned area defined electric force microscopy (EFM). The extraction of quantitative electric properties from surface maps of amplitude changes at $\omega_{elec}$ is a challenging task. The quantitative detection of surface potential was simplified with a null-force method. In this procedure, a combination of DC and AC (at $\omega_{elec}$) voltages was applied to the probe and the DC level is changed until the AC vibration of the probe (at $\omega_{elec}$) is nullified, see equation (4). In first demonstration of the null-force method a voltage map of the precision
operational amplifier in a functioning state was made. Later, the null-force method was applied to detection of local contact potential difference (CPD)\(^8\) and this set-up was named Kelvin probe force microscopy (KFM). In addition to EFM and KFM, probing of local electrostatic properties in non-contact mode has been diversified by using the \(2 \omega_{\text{elec}}\) response [see equation (5)] for the feedback mechanism. In such a way one can get information regarding the local dielectric constant and its high-frequency dispersion. Simultaneous measurements of sample topography (\(\omega_{\text{mech}} = 70\text{kHz}\)), surface potential (\(\omega_{\text{elec}}\)) and dielectric or polarization response (\(2\omega_{\text{elec}}\)) were performed while the probe was scanning \(~30\text{nm}~\) above the sample surface. The use of EFM and KFM has increased as they become available in commercial scanning probe microscopes. This happened with the introduction of the lift mode\(^9\), that makes possible 2-pass EFM and KFM measurements at the single frequency (\(\omega_{\text{mech}}\)). The 2-pass method is a simple separation of the mechanical and electrostatic interactions by switching between the intermittent contact and the non-contact operations. In principle, this switching can be realized by changing \(A_{\text{sp}}\). Yet due to thermal drift and other instrumental imperfections the imaging in the non-contact regime where the probe feels only long-range forces is not stable. The problem is solved when in each scan line the probe is raised above the surface only a small height to the non-contact position where the electrostatic response is measured separately from the topography. The tradeoff is the extra time needed for such operation and the remote position of the probe sensing electrostatic forces.

![Image](image_url)

Fig 1: Topography (A) and surface potential (B) images of an SRAM chip (30\(\mu\text{m}~\)xy scan size).

2 PRACTICAL KFM MEASUREMENTS

The first two examples are taken from KFM studies of semiconductor samples: SRAM and a SiGe structure. The topography and surface potential images of the same sample regions show dissimilar patterns, Figures 1 and 2. The locations of different doping types and levels as well as few local defects visualized in surface potential images are clearly different from topographic features. This is confirmed by the cross-section profiles taken in the images along the directions marked with white arrows. Therefore, we conclude that the cross-talk between the topography and the probe response to the electrostatic forces is negligible. In the control experiments we obtained surface potential images of SRAM with different combinations of \(\omega_{\text{mech}}\) and \(\omega_{\text{elec}}\) (first flexural resonance/\(10\text{kHz}\), first flexural resonance/second flexural resonance; second flexural resonance/first flexural resonance). The comparison of the quantitative values in the surface potential profiles showed that the variations did not exceed 10\%. As regarding the sensitivity of this approach, the variations as small as 10mV are distinguished in the surface potential profiles (not shown). It is also noticeable that the surface potential is substantially negative in the SRAM locations, and is around 0 in the SiGe structure. In KFM of semiconductors a correlation between the surface potential as the probe location and surface Fermi level is established by a following equation:

\[
(6) \quad E_{Fs} - E_{vac} - V_{\text{probe}} - \varphi_{p},
\]
where $E_{Fs}$ - the surface Fermi level, $E_{vac}$ – vacuum level, $V_{probe}$ – surface potential measured by the probe, and $\phi_p$ – work function of the probe material.

Fig 2: Topography (A) and surface potential (B) images of an SiGe structure (30µm xy scan size).

Figure 3: Topography (A) and surface potential (B) images of PMMA layers on Si around the locations subjected to tip-voltage pulses. The insert in the (B) shows the cross-section profiles along the directions indicated with white arrows. (C) - (D) The topography and surface potential images of normal alkane $C_{60}H_{122}$ adsorbate on graphite around the location subjected to a tip-voltage pulse.

Therefore, evaluation of local surface Fermi level is a feasible task in KFM of semiconductor samples\(^1\), after a proper calibration of the probe, an appropriate sample preparation and thoroughly performed the experiments. These applications are beyond the scope of this paper. In further evaluation of KFM operation we conducted experiments similar to those described in 11, which are often used for surface lithography\(^1\). In these experiments, surface charges were deposited by a tip-sample voltage discharge on surface of PMMA and normal alkane $C_{60}H_{122}$ layers on Si and graphite, respectively. The charges were deposited above the voltage threshold, which is around 5-10V (depending on a layer thickness and annealing state), and a 2ms pulse was used. The first pair of images in Figures 3A-B shows the PMMA topography and a circular surface charge pattern with maximum around 1.5V. In this case, there is no discernible cross-talk between the charge and topography. The situation is different when a higher voltage impulse was applied (not shown). The topography image exhibits a pattern of complex shape with negative and positive levels, thus
demonstrating a strong involvement of the electrostatic forces in the tracking feedback when the local charge is large. In other words, the large spatial dimensions and high intensity of the generated charge makes its compensation by the probe voltage inefficient. AFM studies of ultrathin adsorbates of normal alkanes on graphite revealed that the alkanes form lamellar domains in which the chains are aligned parallel to the surface. The voltage pulse applied to the C_{60}H_{122} layer on graphite induced a circular damage pattern in the adsorbate and even in graphite substrate visible as a hole in the center. The surface potential shows a bright-contrast at the circular pattern, which can be assigned to the surface potential of the substrate. In addition, dark patterns surrounding the disk-like region represent the generated negative charges on the elevated alkane domains. The negative charges on the alkane domains have persisted for several days. Further high-resolution AFM images (not shown here) demonstrated that the lamellar order of the domains was destroyed and the material of the domains displays a granular morphology. Most likely, the discharge caused a variety of different chemical processes. Therefore, this approach can be applied not only for lithography but also for local initiation and monitoring of chemical reactions.

Self-assembly of F_{14}H_{20} adsorbates results in nanoscale structures of different morphologies (toroids, ribbons, spirals and their intermediates) and various packing motifs\(^{13}\) that make them attractive for a demonstration of KFM resolution. A region of F_{14}H_{20} adsorbate on graphite, which is densely populated with deformed toroids and short ribbons, is shown in the topography image in Figure 4A. The surface potential contrast of this area is not very pronounced, except for the bright spot seen at the location, which is closer to the substrate than the rest of the surface, Figure 4B. This is apparently a void in the packing of surface structures. The crosssection profile in the insert of the image indicates that the width of the void is less than 10nm. This allows us to claim that the spatial resolution of KFM operating in the intermittent contact mode is better than 10nm. The variations of the contrast between the different self-assembled structures (up to 0.2V) are much smaller as compared to the 0.8V average contrast between the void's location and the rest of the image. The fact that the void contrast is approximately that of the substrate is confirmed by the images and cross-section profiles shown in Figures 5A-C. The topography image in Figure 5A presents a larger area of the F_{14}H_{20} adsorbate after its central part was removed from the substrate by mechanical abrasion (scanning of this location in the contact mode).

**Fig 4:** Topography (A) and surface potential (B) images of F_{14}H_{20} adsorbate on graphite (0.5µm xy scan).

**Fig 5:** Topography (A) and surface potential (B) images of F_{14}H_{20} adsorbate on graphite in the area around the “window” made by the AFM tip scanning in the contact mode.

This procedure, which is often applied for the
evaluation of thickness of adsorbates on different substrates, is also useful in KFM analysis because it provides access to the substrate. The surface potential image in Figure 5B clearly demonstrates that the “window” is ~0.7V higher in potential than the rest of the area. The images and the cross-section profiles (not shown), which were taken along the directions marked with white arrows, show that the adsorbate is ~8nm thick and that mechanical interference of the probe induced the formation of large micelles at the “window” edges and several ribbons inside the “window”. Both the micelles and the ribbons are discernible in the surface potential image, where they are seen respectively darker and brighter than their immediate surroundings.

Up to this point, we have shown that KFM in the intermittent contact mode is not subject to noticeable cross-talk artifacts and provides sensitive imaging of surface potential with a spatial resolution of 10nm or better. In studies of semifluorinated alkane F$_{14}$H$_{20}$, KFM distinctively differentiates material’s features and ordered self-assemblies with the latter exhibiting negative surface potential. These applications were performed using the probe amplitude at $\Delta$elec as a measure of electrostaticallyinduced tip-sample force interactions. Following the classification given in 14 we will use AM-AM abbreviation for this mode. This abbreviation indicates that AM is used in both feedback loops employed for topography tracking and electrostatic measurements. Another approach to KFM measurements and its use in the intermittent contact regime are introduced below.

2.1 KFM in AM-FM operation

The problem of sensitivity and spatial resolution in the AFM-based electrostatic measurements attracted increasing attention for several years. A thorough consideration of the imaging procedures, optimization of probe and data interpretation was given in 15. The authors estimated the cantilever, tip cone and tip apex contributions to the electrostatic probe-sample force and force gradient and came to the conclusion that high spatial resolution can only be achieved when the tip-apex contribution is dominant. This condition can be realized by using probes with a special geometry (the probes with long and sharp tips) or by employment of force gradient detection. The other possibility – imaging at tip-sample distances smaller than 2nm was expected to be difficult in practice. Higher spatial resolution and higher sensitivity in the force-gradient based KFM was shown in 16 – the paper, in which electrostatic force measurements in AM and FM detection schemes were critically analyzed. Particularly, the surface potential data obtained on a KCl submonolayer on Au (111) in FM nicely agree with results of ultraviolet photoelectron spectroscopy. Also in contrast to AM detection, the surface potential measured with FM did not vary with probe-sample separations in the 30nm range. The state-of-the-art EFM and KFM were presented in 14 where the AM-AM, FM-AM and FM-FM combinations used for such measurements were mentioned and briefly described. Surprising is the absence of the AM-FM combination despite the above considerations suggesting the high value of FM detection of electrostatic forces. We have implemented this capability in the Agilent 5500 microscope and critically evaluate this mode in studies of a variety of samples in the intermittent contact regime.

The block scheme of the AM-FM mode is presented in Figure 6. The principal difference of this set-up with the one used for the AM-AM approach is that the input of LIA-2 is connected to LIA-1 for
measuring the phase data at $\omega_{\text{mech}}$. The phase changes are directly related to changes in the force gradient that defines AM-FM type studies. Practically, the AC voltage is applied to the probe at $\omega_{\text{mech}}$, which should be within the bandwidth of the LIA-1. The probe response, at the mixed frequency, $\omega_{\text{mech}}$ and $\omega_{\text{elec}}$, is detected by LIA-2 and used for KFM feedback. The electrostatic forces between the cantilever and sample cause the cantilever to deflect at $\omega_{\text{elec}}$, and at twice that frequency. The voltage modulation also causes a modulation of the force gradient which is greatest between the tip and the sample.

**Fig 6:** A block-diagram of the implementation of KFM in the Agilent 5500 scanning probe microscope using the MAC III accessory in AM-FM mode.

These changing force gradient causes the resonant frequency of the cantilever to shift, giving rise to side bands on the mechanical resonance of the cantilever. After demodulation by LIA-1, the output shows modulation at $\omega_{\text{elec}}$ and at twice that frequency. The two forms of KFM are similar in that the DC bias has a servo to minimize the $\omega_{\text{elec}}$ component from the input of LIA-2. The main differences between operation of AM-AM and AM-FM modes are related with choice of $\omega_{\text{elec}}$, which in case of AM-FM is limited to a low frequency (say 5kHz), low feedback gains of the electric servo loop and to lower AC voltages (usually much less than 1V). The use of lower voltages is very positive remembering the possible voltage influence on sample surface electric properties.

### 2.2 KFM with AM-FM operation in intermittent contact: Practical results

After implementation of AM-FM approach in KFM we have checked the value of the phase- and, additionally, Y-component-based operations by comparing these modes and AM-AM approach in the intermittent contact imaging of $\text{F}_{14}\text{H}_{20}$ adsorbate, Figures 7A-D. The chosen sample of $\text{F}_{14}\text{H}_{20}$ adsorbate has many of heterogeneities due to partial selfassembly of the material into individual micelles and their aggregates. As expected from our AM-AM studies the self-assemblies exhibits strong surface potential contrast what indeed is noticed in the images obtained with all three modes, Figures 7B-D. The comparison of the images and also the surface potential profiles (not shown) demonstrates the favorability of AM-FM approaches in studies of semifluorinated alkanes. The images in Figures 7C-D exhibit higher contrast, and therefore resolution than the image in Figure 7B. Particularly, a visualization of the patches in the top right parts of the images is the best illustration.

**Fig 7:** Topography (A) and surface potential (B) images of $\text{F}_{14}\text{H}_{20}$ adsorbate on graphite obtained in the AM-AM operation. (C)-(D) Surface potential images of the same location as in (A) and (B) obtained in AM-FM
Cross-section profiles (not shown) also indicate that the values of the surface potential are higher in AM-FM modes compared to the AM-AM. As expected the surface potential signal obtained with the phase-based and Y-component-based operations are quantitatively the same but the signal-tonoise ratio is definitely improved in the Y-component-based operation. Most likely the values of the surface potential in the 0-1.0V range obtained in the AM-FM studies are defining surface charges more precisely than the potential data obtained in the AM-AM operation similar to the findings in 16.

In an attempt to determine the spatial resolution of KFM in the AM-FM operation we further examined \( \text{F}_{14}\text{H}_{20} \) adsorbates at scales of 1 micron and smaller, and the results, which were obtained in the phase-based AM-FM operation, are collected in Figures 8 and 9. The images in Figures 8A-D show an aggregate of self-assembled structures and a single toroid less than 50 nm in diameter. As expected the aggregate, which consists of a number of toroids and other elementary self-assemblies exhibits strong negative contrast (~-1.0V) even larger than that of the toroid (~-0.8V). Remarkably, the other adsorbate patches being of comparable size and height to the self-assembled aggregate do not exhibit any noticeable variations of surface potential. The toroid, which is presented in the images in Figures 8C-D, has a height of ~3.2nm and surface potential of ~0.8V. The latter is consistent with surface potential of a Langmuir-Blodgett layer of similar compound determined with a macroscopic Kelvin probe$. The toroid is most likely formed of extended molecules (contour length 4.6nm) with fluorinated groups pointed away from the surface. At the toroid edges, the hydrocarbon segments are bending towards the surface to compensate the mismatch of electron density in the hydrocarbon and fluorinated structures.

Therefore, the \(-\text{CF}_2\text{CH}_2-\) dipole orientation towards the substrate is primarily responsible for the surface charges observed in KFM. Self-assemblies of \( \text{F}_{14}\text{H}_{20} \) and other semifluorinated alkanes \( \text{F}_n\text{H}_m \) have been under examination for some time. Despite the fact that a number of techniques (X-ray reflectivity, AFM, surface IR techniques and a macroscopic Kelvin probe)
were applied to examination of molecular arrangements in these nanostructures their molecular architecture is still not clarified\textsuperscript{18-20}. In the ongoing KFM studies of $\text{F}_{14}\text{H}_{20}$ and related compounds we examined their self-assemblies on different substrates and in different environments in pursuit of a better understanding of their structures and behavior\textsuperscript{21}. As regarding the KFM resolution we point out fine features in the sub-10nm range, which were observed in the topography and surface potential images of the $\text{F}_{14}\text{H}_{20}$ adsorbate, Figures 9A-C. This area is filled by the toroids and self-assembled ribbons. The surface potential of the ribbons is only slightly different from that of the toroids, similar to the observations in AM-AM operation (not shown). Nevertheless, there are few locations with very pronounced contrast: the voids between the toroids and the slits between the ribbons. At these locations the probe “feels” the substrate better than elsewhere. The high-resolution surface potential images of the area outlined with a red dotted square is given in Figure 9C. The insert shows the profile across one of the slits in the location pointed with a white arrow. The width of the 0.1V peak seen in this profile is around 2nm that can be used as a measure of spatial resolution of KFM AM-FM operation in the intermittent contact mode. This result suggests that the sensing apex area of the AFM probe, which is much smaller than the tip diameter (~20nm), dominates in the electrostatic measurements. The achieved high-resolution is in line with the expectation of 15 where the forcegradient detection combined with a small tip-sample distance was advocated as a way to enhance resolution. The use of sharper conducting probes might help to increase the resolution further.

### 3 CONCLUSIONS

This paper describes KFM operations using an Agilent 5500 scanning probe microscope enhanced with a MACIII accessory that allows multi-frequency AFM measurements with three dual phase lock-in amplifiers. Instrumental set-ups allowing force- and force-gradient-based KFM studies (AM-AM and AM-FM) are described and the value of these approaches is verified in studies of the doped areas of semiconductor samples, surface charges created on organic layers by voltage discharge, the contamination traces on graphite and self-assemblies of semifluorinated alkanes $\text{F}_{14}\text{H}_{20}$ on graphite and Si substrates in dry and humid air. The novelty of these applications is that they were performed in the intermittent contact regime and the AM-FM combination was introduced. The simultaneous and independent measurements of sample topography and surface potential (as small as 10mV) were successfully demonstrated in these single-pass KFM studies. The comparative studies of $\text{F}_{14}\text{H}_{20}$ selfassemblies with AM-AM and AM-FM demonstrated that the AM-FM operation provide higher and, likely more accurate values of surface potential of these nanostructures. Remarkably, the AM-FM approach in the intermittent contact mode led to high-resolution surface potential measurements where the 2-nm wide features were clearly resolved. We undertook only the first steps in the practical evaluation of new capabilities offered by KFM studies and there are several opened questions to clarify. They include finding of ways of reproducible and precise measurements of surface local work functions, development of better probes that are fully conducting with 1nm apex size, expanding KFM measurements to different environments and various temperatures and others. Furthermore, the discussed results were obtained in the intermittent contact mode at relatively small tip-sample interactions when phase images do not exhibit the pronounced contrast related to variations of local mechanical properties. It might
be quite informative to perform KFM imaging at elevated tip-sample force, i.e. in the repulsive force regime to get simultaneously topography and maps of local electric and mechanical properties as was recently suggested\(^{22}\). The newly developed scanning microwave microscopy (SMM) module by Agilent Technologies will push the limits of electrical measurements further, being able to probe also structures underneath the sample surface via changes in impedance and capacitance of a scanning AFM tip injecting a microwave (and modulated AC) field into the surface.

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