Quantitative 3D-KPFM imaging with simultaneous electrostatic force and force gradient detection

L Collins\textsuperscript{1,2}, M B Okatan\textsuperscript{3}, Q Li\textsuperscript{3}, I I Kravenchenko\textsuperscript{3}, N V Lavrik\textsuperscript{3}, S V Kalinin\textsuperscript{3}, B J Rodriguez\textsuperscript{1,2}\textsuperscript{1} and S Jesse\textsuperscript{3}

\textsuperscript{1}School of Physics, University College Dublin, Belfield, Dublin 4, Ireland
\textsuperscript{2}Conway Institute of Biomolecular and Biomedical Research, University College Dublin, Belfield, Dublin 4, Ireland
\textsuperscript{3}Center for Nanophase Materials Sciences, Oak Ridge National Laboratory, Oak Ridge, TN 37831, USA

E-mail: liam.collins@ucdconnect.ie and sjesse@ornl.gov

Received 22 January 2015, revised 24 February 2015
Accepted for publication 2 March 2015
Published 8 April 2015

Abstract
Kelvin probe force microscopy (KPFM) is a powerful characterization technique for imaging local electrochemical and electrostatic potential distributions and has been applied across a broad range of materials and devices. Proper interpretation of the local KPFM data can be complicated, however, by convolution of the true surface potential under the tip with additional contributions due to long range capacitive coupling between the probe (e.g. cantilever, cone, tip apex) and the sample under test. In this work, band excitation (BE)-KPFM is used to negate such effects. In contrast to traditional single frequency KPFM, multifrequency BE-KPFM is shown to afford dual sensitivity to both the electrostatic force and the force gradient detection, analogous to simultaneous amplitude modulated and frequency modulated KPFM imaging. BE-KPFM is demonstrated on a Pt/Au/SiO\textsubscript{x} test structure and electrostatic force gradient detection is found to lead to an improved lateral resolution compared to electrostatic force detection. Finally, a 3D-KPFM imaging technique is developed. Force volume (FV) BE-KPFM allows the tip–sample distance dependence of the electrostatic interactions (force and force gradient) to be recorded at each point across the sample surface. As such, FVBE-KPFM provides a much needed pathway towards complete tip–sample capacitive de-convolution in KPFM measurements and will enable quantitative surface potential measurements with nanoscale resolution.

Keywords: Kelvin probe force microscopy, surface potential, 3D imaging, scanning probe microscopy

(Some figures may appear in colour only in the online journal)

1. Introduction
Kelvin probe force microscopy (KPFM) [1] has become the gold standard for characterization of electrostatic and electrochemical properties of materials and devices on nanometer length scales. KPFM is well established as a quantitative technique, providing an accurate measurement of the local contact potential difference (CPD) between tip and sample material, which in turn can be related to a range of electrochemical properties depending on the material under test. KPFM has found applications across a broad range of material research, for measuring work function in metals [1], surface photo-voltage in photovoltaics [2–6], surface potential distribution in polymeric thin films [7] ferroelectrics [7–14] and across working devices [15]. In biology, KPFM has been
used for label free detection of biomolecules [16–18], for
detection of specific binding events [19], surface photo-vol-
tage in optically active proteins [20], as well as presenting an
interesting opportunity for non-invasive DNA sequencing
[19, 21]. Although conventional KPFM has been applied
across a broad range of disciplines, the technique is known
to suffer from systemic errors and a dependence of the measured
CPD on both operational parameters (e.g. ac drive amplitude,
tip–sample distance, feedback optimization) [8, 22–26] and
sample-topographical effects [27]. In light of such imperfec-
tions, the broad applicability of KPFM across diverse fields
of study has been remarkable in the face of the technical diffi-
culties. We note two major obstacles for readily achieving
truly quantitative high resolution KPFM which are; (i) over-
coming long range capacitive coupling between the probe
(e.g. cantilever, cone, tip apex) and sample surface and (ii)
eliminating the influence of instrumentation in the measure-
ment, in particular the feedback effect [24]. The former ori-
ginates from the long range nature of the electrostatic force,
which means that not only the tip apex, but also the cone and
the cantilever beam strongly contribute to the measured CPD
[28]. As a direct result, the CPD measured does not purely
reflect the local CPD under the tip apex but is a weighted
average over the entire probe and the sample surface, and as
such is heavily tip–sample separation dependent [24]. Con-
sidering the long range nature of the interactions probed,
combined with the known distance dependence in KPFM
measurements [24], the lack of an established 3D-KPFM
imaging approach [29] is somewhat surprising.

The feedback effect is a less well recognized problem in
KPFM measurements, however, it has been shown to intro-
duce systematic instrumentation dependent errors
[24, 30, 31], as well as a long list of related artefacts including
a dependence of the recorded CPD on drive amplitude $V_{ac}$
[8, 23, 24], tip–sample distance [25], and topographical
crosstalk into the recorded CPD channel [26, 27]. This makes
comparison between measurements, or comparison between
measurement and theory difficult using conventional KPFM
methods. Furthermore, an inherent distance dependence in
closed loop KPFM, introduced by the feedback effect [8, 24],
complicates its applicability to 3D measurements and is likely
a large reason for the absence of such an approach to date.
Recently, however, several open loop KPFM approaches
have been demonstrated in ambient [12, 24, 32, 33], where
‘open loop’ refers to a system which does not require feed-
back control. Crucially, these approaches offer the potential to
overcome feedback related artefacts [32], at the same time
have shown success towards extending KPFM measurements
to liquid environments [34, 35].

In this work open loop variants of KPFM techniques are
developed as pathways to overcoming the existing limitations
of conventional KPFM approaches. In particular we investi-
gate the use of multifrequency open loop KPFM, using the
band excitation (BE) approach [36–38], which we show to
have several advantages over its single frequency coun-
terparts [32]. First we demonstrate the capabilities of BE-KPFM
for simultaneous measurement of electrostatic force and
electrostatic force gradient interactions. BE-KPFM is shown
to be successful in extracting information on both local (e.g.
electrostatic force gradient detection) and non-local (e.g.
electrostatic force detection) electrochemical parameters
simultaneously. In this way BE-KPFM has similarities with
combined frequency modulated (FM) and amplitude modu-
lated (AM)-KPFM, respectively, while avoiding complica-
tions associated with closed loop bias feedback. Finally, we
develop and implement force volume (FV) BE-KPFM, a
three-dimensional open loop KPFM imaging approach, which
provides the entire probe-sample interaction at each distance
and spatial location across the sample surface.

2. Background

KPFM was developed to provide quantitative measurements
of CPD between tip and sample and can be implemented in
several ways. Many variants of KPFM techniques have
evolved and are discussed in various book chapters or reviews
[25, 38, 39]. The measurement can be made in lift mode
where the topography is recorded in the first pass, and the
KPFM measurement is performed in a second pass as the
topography is retraced at a constant defined distance above
the surface. Alternatively, the experiment can be performed
simultaneously with surface topography acquisition using an
electrical excitation at a frequency far from the mechanical
excitation used for topographical feedback [40, 41]. KPFM
can be operated in AM [41] or FM-KPFM [42–46] modes,
which are sensitive to the electrostatic forces or force gra-
dients, respectively. Common to all conventional KPFM
techniques, however, is the application of a dc voltage, $V_{dc}$,
superimposed on an ac voltage, $V_{ac}$, applied to the tip such
that, $V_{tip}=[(V_{dc} − V_{cpd}) + V_{ac}\sin(\omega t)]$, where $V_{cpd}$ is the CPD
between tip and sample.

2.1. AM-KPFM

In AM-KPFM the bias dependent response, is detected via
the first harmonic electrostatic force of the cantilever,
$F_{z}(\omega)=C_z(V_{dc} − V_{cpd})V_{ac}$, where $C_z$ is the tip–sample
capacitance gradient. The periodic electrostatic force pro-
duces cantilever oscillations, where the first harmonic
amplitude response is given by: $A(\omega)=−C_z(V_{dc} − V_{cpd})V_{ac}\omega
G(\omega)$, which is proportional to the transfer function ($G(\omega)$) of
the cantilever itself. For this reason it is beneficial to perform
KPFM measurements at the cantilever resonance frequency
to achieve resonant amplification and hence improved signal
to noise ratios. The amplitude response, $A(\omega)$, is minimized
when the applied dc bias is equal to the CPD between tip and
sample (i.e., when $V_{dc} = V_{cpd}$). Traditionally, lock-in ampli-
fiers (LIAs) are employed to detect the amplitude ($A(\omega)$) and
phase ($\theta(\omega)$) response of the electrostatic force at the fre-
quency of the applied bias, and the mixed response ($A(\omega)\cos(\theta(\omega))$) is used as the input to the feedback loop. For ‘ideal’
KPFM operation [8, 24], the dc bias output of the KPFM
feedback loop can thus be used to construct a map of the CPD
as the tip is scanned across the sample surface.
FM-KPFM is sensitive to the electrostatic force gradient ($F_{el}$), as opposed to electrostatic force as in AM-KPFM. The cantilever resonance frequency ($\omega_r$) shifts as a result of conservative interactions as described by: $\Delta \omega \approx \omega_r/2k(F_{el})$, where $k$ is the cantilever spring constant. The resultant frequency shifts ($\Delta \omega$), due to changes in the gradient of the static electrostatic force between tip and sample, are governed by: $F_{el} = C_{er}[V_{dc} - V_{cpd}]^2 + \frac{1}{2}V_{dc}^2$, where $C_{er}$ is the derivative of the capacitance gradient. FM-KPFM can be operated using a phase-locked loop (PLL) to determine the bias-induced frequency shift. Alternatively sideband detection can be implemented using two cascaded LIAs and requiring a low frequency electrical excitation applied to a mechanically excited tip [47]. Both approaches however require closed loop bias feedback where, in a fashion similar to AM-KPFM, the bias feedback is used to nullify $\Delta \omega$ and hence determine the CPD.

2.3. AM-KPFM versus FM-KPFM

There are several advantages and disadvantages of both AM and FM modes of KPFM detection [47, 48] as summarized in Table 1. A major drawback of AM-KPFM measurements originates from the long range nature of the electrostatic force, meaning not only the tip apex, but also the cone and the cantilever beam strongly contribute to the KPFM imaging mechanism [28]. FM-KPFM does obviate unspcific interactions to a large extent by virtue of the fact that it is sensitive to electrostatic force gradients. The electrostatic force gradient decays at much shorter distance than the electrostatic force, and hence shows much less influence from cone and cantilever to the overall CPD image. As a consequence higher lateral resolution is routinely achieved using FM-KPFM [47, 49, 50]. FM-KPFM, however, is known to demonstrate reduced bias sensitivity as compared to AM detection requiring excitation with relatively high ac bias (>2 V [47]) which is not suitable for some voltage sensitive materials [51]. In general FM-KPFM is less straightforward to implement than the AM-KPFM as it requires additional electronics and most commonly operated in single pass mode during non-contact imaging, which can be problematic for rough samples. Although possible, FM-KPFM is not as well suited to lift mode operation in comparison with AM-KPFM [50].

3. Methods

3.1. Experiment and sample details

All measurements were performed using Pt/Ir-coated cantilevers (MicroMasch, DPE18) with nominal resonant frequencies and stiffnesses of 75 kHz and 2.8 nN. Experiments were performed using a Cypher AFM (Asylum Research). BE-KPFM and FVBE-KPFM was implemented using NI 5122 and 5412 cards (National Instruments) run by custom Matlab software (MathWorks). Excitation amplitude of 0.5 V with a center frequency at the resonance frequency (65–80 kHz) and bandwidth of 8–20 kHz having between 38–96 bins per band was applied to the tip. Test structures were fabricated by evaporating Au (100 nm) and Pt (20 nm) electrodes deposited on a SiO2 surface, forming a cross pattern of 20 × 20 μm dimensions (figures 2 and 3). The test structure in figure 5 was formed by evaporation of a circular Au (100 nm) electrode on a SiO2 coated Si surface. Conductive silver paint (Agar Scientific Ltd) was used to attach the samples to metal discs, which were used to ground the sample surface.

3.2. Open loop BE-KPFM

In this work we use open loop BE-KPFM [32], referred to here as simply BE-KPFM, in which the first harmonic frequency-dependent response is probed using a train of BE pulses with varying dc voltage offset, as shown in figure 1(a). Contrary to single frequency techniques, in BE an excitation waveform with amplitude, $V_{ac}$, is applied in a frequency band with a central frequency at a cantilever resonant frequency, $\omega_0$. The full cantilever response (versus bias) can then be detected using high speed data acquisition methods. In BE-KPFM the full amplitude and phase response as a function of frequency and bias is acquired at each XY spatial location. Figures 1(b) and (c) show the amplitude response versus frequency and bias for a single point measurement collected 10 nm above a freshly cleaved high ordered pyrolytic graphite (HOPG) surface. This 2D response contains information both
3.3. FVBE-KPFM

In FVBE-KPFM rather than raster scanning in the plane of the surface as with conventional scanning probe techniques, a fine grid of points is specified on the surface and the tip is gently approached toward the surface at each point. Tip positioning is controlled by custom software written in Igor Pro (Wavemetrics), where, at each pixel on the grid, the tip is brought into contact with the sample, afterwards the tip is retracted to the largest user defined tip–sample distance and stepped linearly towards the surface in a closed loop manner while electrically excited with a waveform comprised of a train of BE waveforms superimposed on a linear voltage ramp. In this manner a 5D data set comprising amplitude (and phase) response versus frequency, bias, and position (X, Y, Z) is acquired.

3.4. Quantitative data analysis of BE-KPFM measurements

The raw BE-KPFM data, figures 1(b) and (c), can be well approximated by a simple harmonic oscillator (SHO) model [36, 37]. For extracting quantitative properties from BE-KPFM measurements, the response at each bias is fitted to the SHO model used to describe a resonance frequency spectrum, which has amplitude/phase forms as:

\[
A(\omega) = \frac{\omega_0^2 A_{\text{drive}}}{\sqrt{(\omega_0^2 - \omega^2)^2 + (\omega_0 \omega / Q)^2}},
\]

\[
\varphi(\omega) = \tan^{-1}\left(\frac{\omega_0 \omega}{Q (\omega_0^2 - \omega^2)}\right) + \varphi_{\text{drive}},
\]

where \(\omega_0\) is the resonance frequency and \(Q\) is the quality factor; \(A_{\text{drive}}\) and \(\varphi_{\text{drive}}\) are the amplitude and phase, respectively, of the driving force. The BE approach allows accurate decoupling of these SHO parameters since the cantilever response spectra is recorded across a band of frequencies. The SHO fitting step reduces the 4D BE-KPFM (5D FVBE-KPFM) array to a vector 3D (4D) dataset of \(\{A, \omega_0, Q, \varphi, x, y, z, V_{dc}\}\) yielding the amplitude and phase of response at the resonance, \(\omega_0\) and \(Q\) as a function of bias. The electronic properties of the sample can be determined at each spatial location from the bias dependence of the SHO fit parameters corresponding to the electrostatic force (i.e. amplitude response) and force gradient (i.e. frequency

Figure 1. Operating principle of BE-KPFM. (a) A train of band excitation waveforms superimposed on a linear voltage ramp is applied to the tip. (b) Cantilever response amplitude versus bias and frequency is acquired at each location. (c) Cantilever response amplitude versus frequency for negative bias values. (d) Bias dependence of cantilever mixed amplitude response (left: y axis) and resonant frequency (right: y axis).
response) interactions. Figure 1(d) shows the corresponding bias dependence of mixed response, and \( \omega_0 \) obtained from SHO fitting. For the electrostatic force equations, for purely capacitive interactions, the tip–surface capacitance gradient and CPD can be determined from the bias dependence of the mixed response. The CPD is found from the nulling potential (or zero amplitude crossing) and the \( C_z \) is proportional to the slope of the linear fitting. Hence, if the experimentally measured bias dependence is linear, as is the case for figure 1(d), the tip–surface capacitance gradient and CPD can be determined. This linear fit thus reduces the 4D (5D FBV-E-KPFM) BE-KPFM dataset into two 2D (3D) maps containing information on tip–surface capacitance and CPD, respectively. In terms of the electrostatic force gradient the frequency shift is parabolic as a function of bias for a purely capacitive system. In this case, parabolic fitting of the bias dependence of the frequency shift can be used to find the CPD from the point of inflection of the parabola (i.e. \( F_{dc} = 0; V_{dc} = V_{gap} \)) and the derivative of the capacitance gradient \( (C_z') \) can be inferred from the parabolic fitting parameters. In this way, BE-KPFM allows simultaneous measurement of local (i.e. force gradient, FM-KPFM) and non-local (i.e. force, AM-KPFM) response. Importantly, the ability to determine the validity of the bias dependence of the (electrostatic force and force gradient) response in BE-KPFM represents a significant advantage over its closed loop counterpart, while also providing valuable information on the dielectric properties of the sample under test which can be used for surface [54, 55] or subsurface [56, 57] mapping of dielectric properties. Noteworthy, at values close to the nulling bias (i.e. when the bias value approaches the CPD between tip and sample) the frequency shift can deviate from a parabolic trend as a direct result of difficulty in accurately SHO fitting small response amplitudes. For this reason, points close to the CPD values were not used in parabolic fitting to avoid influencing the quality of fit. In future, this complication can be avoided by adopting excitation mechanisms which are insensitive to the surface bias but still provide clean response, such as has recently been demonstrated using photothermal excitation [58, 59].

### 4. Simultaneous force and force gradient KPFM

In this section we implement BE-KPFM [32] on a model sample, shown in figure 2(a), formed by Au (100 nm) and Pt (20 nm) electrodes deposited on a SiO\(_2\) surface. Such test structures are useful for examining KPFM operation as they contain topographic (cross edge), work function (Au versus Pt), and dielectric constant variation. Figure 2(a) is a 3D representation of the surface topography, where the red star indicates the location of the point spectroscopy measurement and, in figures 2(b) and (c), we make comparison between the bias dependence of the electrostatic force and force gradient detection collected 10 nm above the gold electrode. From figure 2(b) it can be seen that the electrostatic force results in a linear bias dependence of the amplitude response with a minima at \( V_{dc} \) corresponding the CPD. A phase inversion of 180° is observed when the response passes through the CPD indicating a reversal of the charge polarity between tip and sample (not shown). From this data, the CPD can be determined as the bias value that nullifies the amplitude response, in this case, found by performing a linear fit to the mixed response as shown.

Furthermore, the BE-KPFM approach affords the bias dependence of the electrostatic force gradient which results in a parabolic bias dependence of the resonance frequency, having a maximum close to the nulling bias of the amplitude response. The bias at which the maximum of the parabola is located yields the local CPD and the derivative of the capacitance gradient can be determined from the derivative of the slope. From figures 2(b) and (c) it was found that the CPD measured by force detection was 196±9 mV compared to 661±14 mV by force gradient detection. Since both measurements are made simultaneously, using the same instrumentation and the same signal pathways, we can conclude that the difference of ~465 mV corresponds to the stray capacitance effect and non-local electrostatic interactions.

In figure 3, BE-KPFM imaging is illustrated where linear and parabolic fitting of the electrostatic force and force gradient at each point reduces the BE-KPFM dataset into four 2D maps containing information on tip–surface capacitance and CPD, determined independently using force (figures 3(a) and (b)) and force gradient (figures 3(c) and (d)) detection. The average CPD between Pt and Au electrodes was determined to be 306±56 mV using force gradient detection and 136±32 mV using force detection. This large difference can be explained by lateral averaging of the CPD in force detection due to the long range interaction between the AFM cone and cantilever with the sample test structure [49, 53]. This effect is less pronounced in the force gradient response since the interaction decays faster than the force, hence why FM-KPFM shows no influence from the cone and the cantilever [53]. The frequency shift can additionally be used to map the second derivative of the capacitance, figure 3(d), which results in a high resolution material contrast of dielectric sample properties [59]. Figure 3(e) shows cross sections of the CPD in both force and force gradient detection. As a consequence of the short decay length of electrostatic force gradient, a higher lateral resolution can be achieved and the local CPD can be measured directly without the need of de-convolution techniques [59, 60].

### 5. Distance dependence in BE-KPFM

In figure 4 we compare the distance dependence in a single point BE-KPFM with a standard AM-KPFM measurement over a freshly cleaved HOPG sample. For a metal tip–sample configuration with a uniform sample work function one would not expect variation in the measured CPD with changing tip–sample distance. BE-KPFM SHO fit parameters are shown as a function of bias, figures 4(a) and (b), and distance, figures 4(c) and (d). The electrostatic force, figures 4(a) and (c), demonstrate a linear bias dependence for all tip–sample distances investigated, with slight deviations from linearity.
evident at small distances and large applied bias due to static deflections of the tip. It is clear that the slope of the bias dependence, figure 4(a), changes as a function of distance providing a measure of the increase in the capacitance gradient with decreasing tip–sample distance. The capacitance gradient can also be determined from the distance profile of the BE-KPFM for a single bias value other than the nulling potential, see figure 4(c). On the contrary, the electrostatic force gradient, figures 4(b) and (d), the response shows a strong parabolic bias dependence for small tip–sample distances (<50 nm), which becomes much less pronounced with increasing tip–sample distance. Furthermore, the distance profile of the electrostatic force gradient, see figure 4(d), is much shorter range than figure 4(c), as it is sensitive to the derivative of the capacitance gradient.

In figure 4(e) we compare CPD measurements determined using BE-KPFM (electrostatic force and force gradient detection) and standard AM-KPFM as a function of distance at the same location on a freshly cleaved HOPG sample, demonstrating uniform work function over at least 20 μm area (confirmed by AM-KPFM, not shown). The BE-KPFM data in figure 4(e) again demonstrates a large deviation in CPD between measurements determined by electrostatic force and force gradient detection. The CPD values determined from the bias dependence of the electrostatic force gradient demonstrates a large spread in CPD values (~200 mV) at large tip–sample distance (>50 nm) due to the lower bias sensitivity of the approach. Note this result explains the difficulties in implementing FM-KPFM in lift mode due to the requirement for very small tip–sample separation [50], and hence why FM-KPFM is more usually operated during non-contact FM-AFM imaging. On the other hand, CPD values determined from the bias dependence of the electrostatic force demonstrate a small spread in CPD values, however, a decreasing CPD with tip–sample distance (~65 mV) is observed, which is not expected for a uniform metal sample. This can potentially be related to contamination/damage of the metal coating of the tip which have not been fully characterized. Finally, we overlaid data collected using conventional closed loop AM-KPFM at the same location. The deviation in the CPD with decreasing tip–sample distance was found to be approximately double (~110 mV) that observed using BE-KPFM electrostatic force detection. For non-ideal KPFM feedback (i.e. when the feedback is incorrectly optimized or when parasitic signals reach the input to the bias feedback loop), the tip response is not completely nullified and will have a finite amplitude (δ), hence the applied $V_{dc} \neq V_{cpd}$ but governed by:

$$V_{dc} = V_{cpd} + \frac{\delta}{k(V_cC_d^2)}.$$  \hspace{1cm} (2)

In figure 4(f) the CPD determined using AM-KPFM is overlaid with the inverse capacitance gradient term in equation (2). The measured CPD demonstrates the expected trend described for non-ideal feedback and is proportional to the inverse capacitance gradient. This complication of closed loop KPFM limits its application to 3D-KPFM imaging modes without the adoption of additional correction procedures [61, 62]. Note that open loop KPFM modes, and all electrical AFM measurements in general, can suffer from crosstalk if electronic offsets are not calibrated correctly or signal pathways are not sufficiently shielded from each other [31]. However, since BE-KPFM detects the entire bias dependence, any parasitic contributions can be more easily detected and calibrated for than in closed loop operation.

6. FVBE-KPFM

The distance dependence of the tip–sample electrostatic interactions has motivated the development of a 3D open loop KPFM technique to capture not only the spatial variation in the X–Y plane, but also as a function of tip–sample distance. Figure 5 shows the result of a FVBE-KPFM measurement of a simple gold electrode test structure deposited on SiO₂. Figure 5(a) shows a simple schematic of the FVBE-KPFM measurement and sample topography, where rather than raster
scanning in the plane of the surface, as with conventional scanning probe techniques, the electrostatic interactions are recorded as function of tip–sample distance across a fine grid (X, Y, Z; 30×30×50) of points on the surface. The fitting parameters can be used to determine the 3D CPD and capacitance gradient determined using the electrostatic force and force gradient respectively, providing a wealth of information on the tip–sample interactions. Figures 5(b) and (c) show CPD measurements collected using standard AM-KPFM and FVBE-KPFM both at 50 nm from the sample surface. Again, a significant deviation from the CPD values determined from open and closed loop operation even at the same tip–sample distance is observed, as was previously been reported [24]. A significant advantage of FVBE-KPFM, is that unlike standard KPFM, information on the capacitance gradient can also be determined (see figure 5(e)), as well as the distance

Figure 3. Combined electrostatic force and force gradient detection using BE-KPFM. (a) and (b) CPD and capacitance gradient determined by electrostatic force detection (scale bar = 5 μm). (c) and (d) CPD and second derivative of the capacitance gradient determined electrostatic force gradient detection. Averaged cross section of the CPD in both (a) and (c) determined from the region indicated with the black lines (force detection-red) (force gradient detection-blue). Data collected at a lift height of 10 nm. Image size 128 × 128 pixels.
dependence of the CPD and capacitance gradient for each spatial location or across a section of the sample surface as shown in figures 5(d) and (f). The data acquisition for the FVBE-KPFM image shown in figure 5 took approximately 8 times longer to collect than a standard conventional 2D KPFM image (≈25 mins), however we note that this technique affords a significant increase in the channels of information obtainable over conventional KPFM. Furthermore, in most instances, a single 2D BE-KPFM image combined with a high density 3D FVBE-KPFM line scan will be sufficient to deconvolute the long range tip-sample interactions across the entire image. In this case we only show the results determined from the electrostatic force, however, similar information can be obtained from the electrostatic force gradient.

7. Summary

We have developed a quantitative 3D-KPFM imaging approach based on the BE method. It was shown that CPD and capacitance gradient information can be obtained from the bias dependence of the electrostatic force and force gradient, respectively. Comparative measurements were performed at fixed height above the surface to demonstrate the force gradient detection provided higher spatial resolution than the electrostatic force detection when operated close to the sample surface (<50 nm). KPFM measurements performed using BE-KPFM are shown to be less distant dependent than conventional AM-KPFM measurements, likely a result of eliminating the requirement for bias feedback.
which was shown to introduce artefacts into the measured CPD. FVBE-KPFM is expected to offer a useful bridge between KPFM experiment and modeling ultimately leading to a complete de-convolution of the effect of the probe geometry in KPFM measurements.

Acknowledgments

This publication has emanated from research conducted at the Center for Nanophase Materials Sciences, which is sponsored at Oak Ridge National Laboratory by the Scientific User Facilities Division, Office of Basic Energy Sciences, US Department of Energy (CNMS2012-036). LC gratefully acknowledges financial support from UCD Research.

Figure 5. 3D CPD mapping with force volume band excitation-KPFM. (a) Schematic of the FVBE-KPFM measurement. (b) AM-KPFM image and (c) electrostatic force detection FVBE-KPFM collected at 50 nm from tip–sample separation. (d) FVBE-KPFM cross sectional CPD data from region indicated with black dashed line in (c). (e) Spatial map \((x, y, \text{height} = 50 \text{ nm})\) of capacitance gradient and (f) capacitance gradient as function of distance from location indicated with dashed black line in (c).

References

[1] Nonnenmacher M, O’Boyle M P and Wickramasinghe H K 1991 Kelvin probe force microscopy Appl. Phys. Lett. 58 2921–3
[2] Sengupta E, Domanski A L, Weber S A L, Unch M B, Butt H J, Sauermann T, Egelhaaf H J and Berger R 2011 Photoinduced degradation studies of organic solar cell materials using Kelvin probe force and conductive scanning force microscopy J. Phys. Chem. C 115 19994–20001
[3] Weber S A, Butt H-J and Berger R 2013 Scanning Probe Microscopy in Nanoscience and Nanotechnology vol 3 (Berlin: Springer) pp 551–73
[4] Liscio A, De Luca G, Nolde F, Palermo V, Müllen K and Samori P 2008 Photovoltaic charge generation visualized at the nanoscale: a proof of principle J. Am. Chem. Soc. 130 780–1
[5] Hoppe H, Glatzel T, Niggemann M, Hinsch A, Lux-Steiner M C and Sariciftci N S 2005 Kelvin probe force microscopy study on conjugated polymer/fullerene bulk heterojunction organic solar cells Nano Lett. 5 269–74

[6] Matsuura K, Kemerink M, Wienk M M, Charrier D S H and Janssen R A J 2009 Scanning Kelvin probe microscopy of bulk heterojunction polymer blends Adv. Funct. Mater. 19 1379–86

[7] Palermo V, Palma M and Samori P 2006 Electronic characterization of organic thin films by Kelvin probe force microscopy Adv. Mater. 18 145–64

[8] Saurenbach F and Terris B D 1990 Imaging of ferroelectric domain-walls by force microscopy Appl. Phys. Lett. 56 1703–5

[9] Kalinin S V and Bonnell D A 2001 Local potential and polarization screening on ferroelectric surfaces Phys. Rev. B 63 125411

[10] Shvebelman M M, Agronin A G, Urenski R P, Saurenbach F and Terris B D 1990 Imaging of ferroelectric domain walls by Kelvin probe force microscopy J. Appl. Phys. 68 653–9

[11] Kalinin S V, Johnson C and Bonnell D A 1999 Practical aspects of Kelvin probe force microscopy for characterization of semiconductor devices and processes J. Vac. Sci. Technol. B 17 942–51

[12] Leung C, Kinns H, Hoogenboom B W, Howorka S and Samorì P 2008 Imaging of ferroelectric domain structure in BaTiO3 (100) surface Adv. Mater. 20 464006

[13] Jesse S and Kalinin S V 2014 Band excitation in scanning probe microscopy: sines of change Surf. Sci. Anal. 33 108–12

[14] Richards D N et al 2010 DNA immobilization on GaP(100) investigated by Kelvin probe force microscopy J. Phys. Chem. C 114 15486–90

[15] Jacobs H, Knapp H and Stemmer A 1999 Practical aspects of Kelvin probe force microscopy Rev. Sci. Instrum. 70 1756

[16] Wu Y and Shannon M A 2006 Ac driving amplitude dependent systematic error in scanning Kelvin probe microscopy measurements: detection and correction Rev. Sci. Instrum. 77 043711

[17] Collins L, Kilpatrick J, Weber S A, Kumar A, Balke N and Kalinin S V 2014 Probing charge screening dynamics and electrochemical processes at the solid–liquid interface with electrochemical force microscopy Nat. Commun. 5 3871

[18] Jesse S, Kalinin S V, Proksch R, Baddorf A and Rodriguez B 2007 The band excitation method in scanning probe microscopy for rapid mapping of energy dissipation on the nanoscale Nano Lett. 8 435503

[19] Jesse S and Kalinin S V 2011 Band excitation in scanning probe microscopy: sines of change J. Phys. D: Appl. Phys. 44 464006

[20] Jesse S, Vasudevan R V, Collins L, Strelcov E, Okatan M B, Bellainov A, Baddorf A P, Proksch R and Kalinin S V 2014 Band excitation in scanning probe microscopy: recognition and functional imaging Nano. Rev. Phys. Chem. 65 519–36

[21] Glatzel T, Lux-Steiner M C, Strassburg E, Boag A and Rosenwaks Y 2007 Scanning Probe Microscopy (Berlin: Springer) pp 113–31

[22] Leung C, Maradan D, Kramer A, Howorka S, Mesquida P and Hoogenboom B W 2010 Improved Kelvin probe force microscopy for imaging individual DNA molecules on insulating surfaces Appl. Phys. Lett. 97 203703

[23] Ziegler D, Rychen J, Naujoks N and Stemmer A 2007 Compensating electrostatic forces by single-scan Kelvin probe force microscopy Nano Lett. 12 525505

[24] Kitamura S F and Itawaki M 1998 High-resolution imaging of contact potential difference with ultrahigh vacuum noncontact atomic force microscope Appl. Phys. Lett. 72 3154–6
[43] Kitamura S, Suzuki K and Iwatsuki M 1999 High resolution imaging of contact potential difference using a novel ultrahigh vacuum non-contact atomic force microscope technique Appl. Surf. Sci. 140 265–70
[44] Kikukawa A, Hosaka S and Imura R 1995 Silicon pn junction imaging and characterizations using sensitivity enhanced Kelvin probe force microscopy Appl. Phys. Lett. 66 3510–2
[45] Kikukawa A, Hosaka S and Imura R 1996 Vacuum compatible high-sensitive Kelvin probe force microscopy Rev. Sci. Instrum. 67 1463–7
[46] Sommerhalter C, Matthes T W, Glatzel T, Jäger-Waldau A and Lux-Steiner M C 1999 High-sensitivity quantitative Kelvin probe microscopy by noncontact ultra-high-vacuum atomic force microscopy Appl. Phys. Lett. 75 286–8
[47] Glatzel T, Sadewasser S and Lux-Steiner M C 2003 Amplitude or frequency modulation-detection in Kelvin probe force microscopy Appl. Surf. Sci. 210 84–9
[48] Sadewasser S and Glatzel T 2012 Kelvin Probe Force Microscopy (Berlin: Springer)
[49] Gil A, Colchero J, Gómez-Herrero J and Baró A 2003 Electrostatic force gradient signal: resolution enhancement in electrostatic force microscopy and improved Kelvin probe microscopy Nanotechnology 14 332
[50] Ziegler D and Stemmer A 2011 Force gradient sensitive detection in lift-mode Kelvin probe force microscopy Nanotechnology 22 075501
[51] Ishii H, Hayashi N, Ito E, Washizu Y, Sugi K, Kimura Y, Niwano M, Ouchi Y and Seki K 2004 Kelvin probe study of band bending at organic semiconductor/metal interfaces: examination of fermi level alignment Phys. Status Solidi A 201 1075–94
[52] Ma Z-M, Mu J-L, Tang J, Xue H, Zhang H, Xue C-Y, Liu J and Li Y-J 2013 Potential sensitivities in frequency modulation and heterodyne amplitude modulation Kelvin probe force microscopes Nanoscale Res. Lett. 8 1–6
[53] Ma Z M, Kou L, Naitoh Y, Li Y J and Sugawara Y 2013 The stray capacitance effect in Kelvin probe force microscopy using FM, AM and heterodyne AM modes Nanotechnology 24 225701
[54] Gramse G, Casuso I, Toset J, Fumagalli L and Gomila G 2009 Quantitative dielectric constant measurement of thin films by dc electrostatic force microscopy Nanotechnology 20 395702
[55] Fumagalli L, Esteban-Ferrer D, Cuervo A, Carrascosa J L and Gomila G 2012 Label-free identification of single dielectric nanoparticles and viruses with ultraweak polarization forces Nat. Mater. 11 808–16
[56] Cadena M J, Misiego R, Smith K C, Avila A, Pipes B, Reifenberger R and Raman A 2013 Sub-surface imaging of carbon nanotube–polymer composites using dynamic AFM methods Nanotechnology 24 135706
[57] Riedel C, Alegria A, Schwartz G, Arinero R, Colmenero J and Sáenz J 2011 On the use of electrostatic force microscopy as a quantitative subsurface characterization technique: a numerical study Appl. Phys. Lett. 99 023101
[58] Li Q, Jesse S, Tselev A, Collins L, Yu P, Kravchenko I, Kalinin S V and Balke N 2015 Probing local bias-induced transitions using photothermal excitation contact resonance atomic force microscopy and voltage spectroscopy ACS Nano 9 1848–57
[59] Collins L, Jesse S, Balke N, Rodriguez B J, Kalinin S and Li Q 2015 Band excitation Kelvin probe force microscopy utilizing photothermal excitation Appl. Phys. Lett. 106 104102
[60] Ziegler D, Gava P, Güttinger J, Molitor F, Wirtz L, Lazzeri M, Saitta A, Stemmer A, Mauri F and Stamper C 2011 Variations in the work function of doped single- and few-layer graphene assessed by Kelvin probe force microscopy and density functional theory Phys. Rev. B 83 235434
[61] Machleidt T, Sprent E, Kapusi D and Franke K 2009 Deconvolution of Kelvin probe force microscopy measurements—methodology and application Meas. Sci. Technol. 20 084017
[62] Diesinger H, Deresmes D and Mélin T 2012 Kelvin Probe Force Microscopy (Berlin: Springer) pp 25–44
[63] Lee M, Lee W and Prinz F B 2006 Geometric artefact suppressed surface potential measurements Nanotechnology 17 3728