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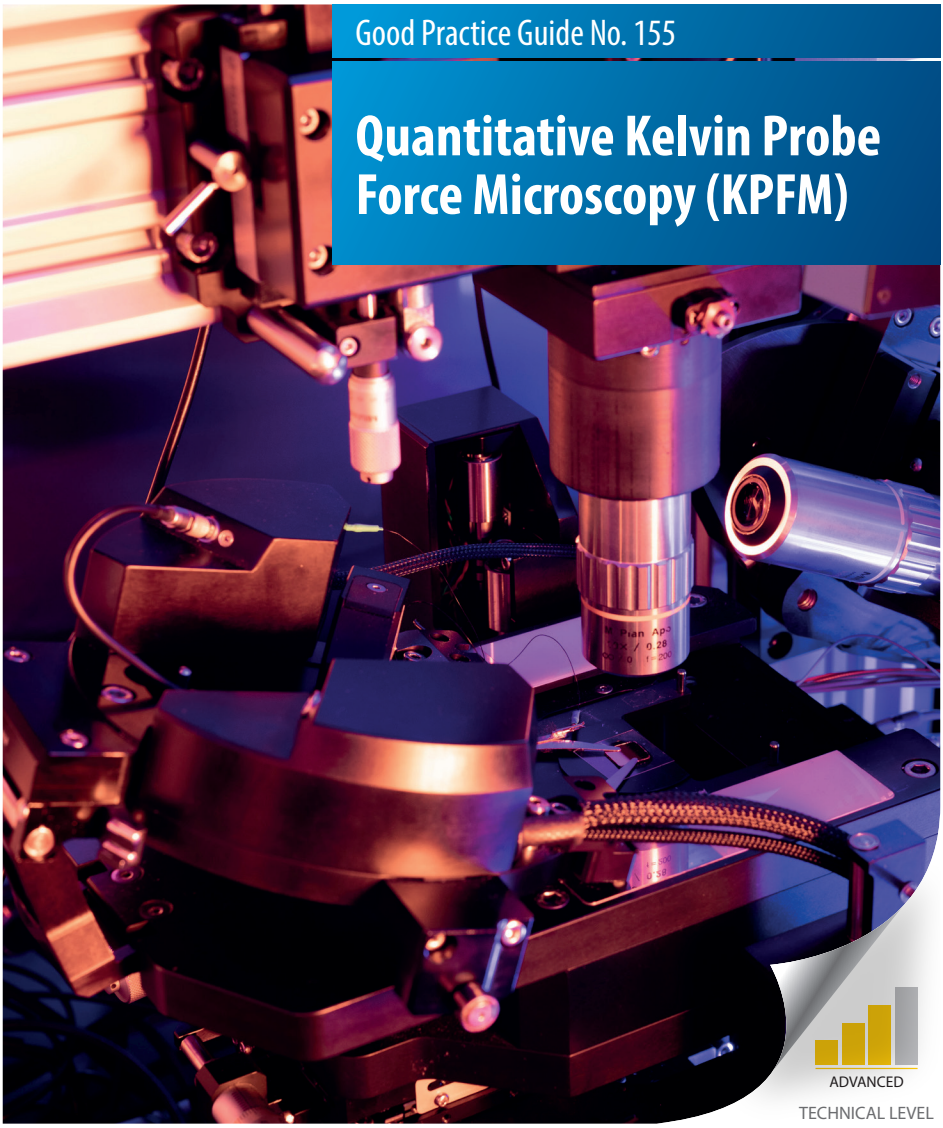
Quantitative Kelvin Probe Force Microscopy (KPFM)



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NPL Authors and Contributors

Dr Dong Kuk Kim
Dr Sebastian Wood
Dr Fernando A. Castro

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National Physical Laboratory
Hampton Road
Teddington
Middlesex
TW11 0LWdom

Telephone: +44 (0)20 8977 3222
e-mail: training@npl.co.uk
www.npl.co.uk

Abstract

Kelvin Probe Force Microscopy (KPFM) is a mode of scanning probe microscopy for measurement of surface potential (or work function) with nanometre-scale spatial resolution. Despite the widespread use of KPFM there are no existing international standards for how to perform these measurements resulting in confusion over definitions and interpretation. The community of practice requires a clear statement of the current state-of-the-art to support correct use of KPFM and further development of the technique. This Good Practice Guide is intended for KPFM users to provide a clear and consistent framework for performing, understanding and interpreting measurements. Many commercial and customised instruments can be used for KPFM measurements using different specific modalities. This guide does not address these differences in detail, nor does it replace technical training on any specific instrument, rather it relates to the basic principles common to all KPFM measurements.

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1.1 Introduction

Surface analysis is important for many fields of materials science. The electrical surface potential and work function are key parameters that relate to the functional properties of a material, structure, or device. At the nanoscale, surfaces and structures can exhibit local variation in surface potential, and therefore analysis requires a measurement technique with corresponding spatial resolution. Kelvin probe force microscopy (KPFM) is a type of scanning probe microscopy (SPM) that measures the variation in local surface potential across a sample surface using an electrically conductive scanning probe. Topographic information is also recorded and provides a means to correlate topography and surface potential with nanoscale resolution. Although KPFM is a widely used characterisation technique, there is often confusion over how to perform and interpret measurements correctly. This Good Practice Guide maintains the same principle of measurements described in peer-reviewed journals[1–3] on KPFM and is designed to provide clarity for a typical user, assuming a basic level of familiarity with the technique.

1.2 Scope

This Good Practice Guide describes the current best practice for performing KPFM measurements, where the measured quantity is the contact potential difference (V_{CPD}) between the probe tip and sample. This document includes the definitions of relevant terms, and recommended methods for verifying that the instrument is operating as expected. Particular attention is given to the polarity of the contact potential difference (*CPD*) output from the instrument and its relationship to V_{CPD} and work function. Methods for data processing and analysis are also described.

KPFM is sometimes referred to as scanning Kelvin probe microscopy (SKPM), and the terms are used interchangeably but KPFM is preferred here as the more common choice. There is also a related macroscopic Kelvin probe measurement, however the mode of operation is different and is not within the scope of this Good Practice Guide.

As with all measurements, an understanding of uncertainty is essential to meaningful reporting of results. The NPL Good Practice Guide No. 11 ‘A Beginner’s Guide to Uncertainty in Measurement’ offers a general introduction to uncertainty analysis. The uncertainty budget for KPFM measurements depends on the specific system, method, and sample so must be determined on a case-by-case basis. This Good Practice Guide describes the general sources of uncertainty that are commonly associated with KPFM.

1.3 Key Principles of Measurement

KPFM is an advanced measurement mode that is based on non-contact atomic force microscopy (AFM) with a mechanically oscillating probe but has the additional requirement that the probe is electrically conductive. In addition to obtaining topographic information (like conventional AFM), KPFM measures the local surface potential. The working principle of KPFM is indicated in Figure 1 with energy level diagrams considering the simple case of a metallic sample and tip with different work functions. In this case, the sample work function (WF_s) is smaller than that of the tip (WF_t). Work function is defined as the difference between the Fermi level (E_F) and vacuum level (E_{vac}) and is always a positive value with units of energy (usually electron-volts, eV). The Fermi levels of the sample and tip are defined as $E_{F,s}$ and $E_{F,t}$ respectively. Without electrical contact or applied bias, the vacuum levels for clean metal surfaces are aligned. However, when the tip and sample are electrically connected (via the external circuit in KPFM) the Fermi levels align. In this case, electrons flow from the sample to the tip resulting in a build-up of opposing charges on the surfaces and a contact potential difference, V_{CPD}. The resulting energy difference in the vacuum levels arising from Fermi level alignment is given by eV_{CPD}. The convention in energy level diagrams is to consider the energy of an electron and eV_{CPD} is negative in this example corresponding with the sample having a higher electric potential than the tip (remember that the convention for electric potential is to consider the potential energy of a unit of positive charge). The KPFM measurement itself applies an external DC bias (V_{DC}) to nullify the potential difference V_{CPD}, and V_{DC} is the magnitude of the output signal from the instrument.

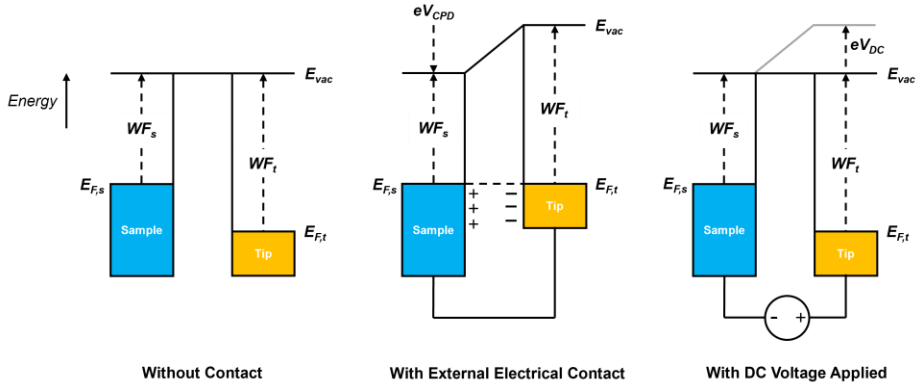

Figure 1. *Schematic diagram of a KPFM measurement for a metallic sample and tip. Energy level diagrams are shown without electrical contract, with external electrical contact, and with DC voltage applied (i.e. during the KPFM measurement). In all diagrams the arrow point upwards for positive values and downwards for negative values.*

Some sources use the symbol φ to denote the work function whereas this symbol is more commonly used for electric potential, hence we define φ_s and φ_t as the electric potential of the sample and tip, respectively. In this case the contact potential difference, V_{CPD}, is defined by:

$$V_{CPD} = \varphi_t - \varphi_s \tag{1}$$

In our example, assuming clean metallic samples, the contact potential difference arises fully from the relative work functions of the tip and sample, hence we have:

$$V_{CPD} = \frac{WF_t - WF_s}{-e} \tag{2}$$

where e is the elementary charge (which is positive and has a value of approximately 1.602×10^{-19} C). We note that alternative definitions are possible and hence different forms of this equation occur in literature but we adopt the majority convention as best practice to prevent confusion.[4] The above equation only considers the simplest scenario of metallic samples. For materials beyond simple metals – particularly semiconductors and insulators – the interpretation of the KPFM measurement requires particular care, as phenomena such as surface band bending, surface trap states, and other frequency-dependent charge processes can introduce additional contributions to the measured *CPD*. Equation 2 would need to be modified to account for these additional contributions:

$$V_{CPD} = \frac{WF_t - WF_s}{-e} + V' \tag{3}$$

where V' encompasses the additional voltage contributions.

The KPFM measurement applies an external bias V_{DC} (here indicated as a positive bias applied to the tip) to nullify the potential difference (V_{CPD}), giving:

$$V_{CPD} + V_{DC} = 0 \tag{4}$$

This relationship defines V_{DC} to have an equal magnitude to V_{CPD} but with opposite polarity. The output signal from the instrument referred to as the *CPD* may correspond to either V_{CPD} or V_{DC} as defined in Equation 4. A related instrumentation consideration is whether the bias V_{DC} is applied to the tip or to the sample, which results in an inversion of the sign, and some instruments allow both modes of operation. Therefore care must be taken to correctly understand the sign convention applied by the specific instrument being used. Determining the correct sign convention for the output signal *CPD* can be achieved either with reference to the instrument documentation or using a reference sample (as described in Chapter 2).

If the desired measurement is the work function of the sample surface, then this can be obtained using Equation 2, but this requires knowledge of the tip work function. A method for this is described in Chapter 4.

This description of the KPFM measurement is generally applicable, but it is important to recognise that there are multiple possible measurement schemes for detecting the electrostatic force arising from the tip-sample potential difference. These modes are often described as amplitude-modulation (AM) and frequency-modulation (FM). Detection schemes can vary, but in both cases, an alternating bias is applied between the tip and sample. AM-KPFM is sensitive to the resulting electrostatic force, whereas FM-KPFM is sensitive to the electrostatic force gradient (with respect to tip-sample distance). In addition, KPFM can be performed in either two-pass or single-pass modes. A two-pass mode involves measuring the topography profile in the first pass, followed by retracing the profile at a constant height above the surface to measure the *CPD* in the second pass. A single-pass setup measures both the topography and *CPD* signals simultaneously and is made possible by driving the mechanical oscillation and the electrical bias on the probe at different frequencies to minimise cross-talk between the topography and *CPD* signals during the measurement. Two-pass KPFM minimises the cross-talk between topography and *CPD* signals and improves accuracy of the measurement, but at the cost of slower scanning and increased sensitivity to environmental noise. Single-pass KPFM is faster and less prone to tip-sample drift but does suffer from cross-talk between topography and *CPD* signals. Many other modes and variations of KPFM have been reported with different advantages and disadvantages that are beyond the scope of this Good Practice Guide.

1.4 Measurement and Terminology Standardisation

There are many commercial SPM systems available that provide KPFM as a capability, but the use of terminology is not universally consistent. The terms used in this Good Practice Guide are consistent with definitions given in existing ISO standards, specifically ISO 18115-2:2021.[5]

1.4.1 Abbreviations

AFM	Atomic Force Microscopy
AM	Amplitude-Modulation
FM	Frequency-Modulation
KPFM	Kelvin Probe Force Microscopy
SKPM	Scanning Kelvin Probe Microscopy
SPM	Scanning Probe Microscopy

1.4.2 Mathematical Variables

CPD	Contact Potential Difference Signal Measured by the Instrument
e	Elementary charge
V_{CPD}	Contact Potential Difference Voltage
V_{DC}	DC Voltage Bias
WF	Work Function
φ	Electric Potential

1.5 Measurement Environment

The environment in which the surface potential measurement is performed can strongly influence the result. KPFM can be performed in different environmental conditions including ambient, inert glovebox, or under vacuum. Mechanical isolation is typically required to minimise noise in the measurement. In vacuum, the lack of air damping of the tip oscillation can substantially limit the scanning speed of the measurement. In ambient conditions, a surface water-layer typically forms and would be expected to modify not only the measured surface potential but also the achievable lateral resolution of KPFM measurements, relative to measurements on a dry surface. In general, a dry inert atmosphere is preferred but is not always practical.

1.6 Choice of Probe

The probe used for KPFM measurements must be electrically conductive. Cantilever-type probe tips coated with a metallic conductive coating are commonly used. The thin coating on the probe should be chemically inert and mechanically durable to maintain a stable work function throughout the measurements. Typical coating materials include the metals Pt, Pt-Ir, and Au. Doped semiconductors can also be used (typically Si, Pt-Si, or diamond) but should be highly doped to approximate metallic conduction.

The length and sharpness of the probe (i.e. the aspect ratio and tip radius) will impact the lateral resolution of the *CPD* mapping, where longer probes minimise the parasitic capacitance from the cantilever, and sharper tips give high spatial resolution. For operation in vacuum, a low quality-factor cantilever can allow for a faster scanning speed.

1.7 Applicable Samples

KPFM results are often interpreted in terms of work function, which is a well-defined surface parameter for metallic samples. However, surface cleanliness is a ubiquitous concern since any contamination will modify the measured *CPD*.

KPFM is also commonly applied to semiconductor samples but interpretation of the *CPD* signal is complicated by the sensitivity of the surface potential to the doping level, surface dipoles, trap states and experimental conditions (such as exposure to light).

KPFM can also be used for resistive samples, but for highly insulating samples, local surface charging can prevent stable measurement and confound interpretation of the resulting signal.

An electrical connection to the sample surface is required to ensure a robust reference for the *CPD*. For a metallic sample, this can be readily achieved with a simple metal spring probe, however, for semiconducting or resistive samples there can be an additional potential difference between the point on the surface being measured and the electrical contact, which must be considered in interpreting results. For this reason, measurements on semiconductor samples tend to focus on relative differences between equivalent samples or a single sample under different conditions.

1.8 Data Analysis

SPM topography maps are typically processed with flattening, aligning rows, correcting horizontal scars, and zeroing the height scale prior to further analysis. However, *CPD* images should not be processed in this way unless there are specific measurement artefacts to be addressed. For presentation of *CPD* maps, it may be appropriate to correct 'scars'[a] or apply averaging to improve visibility of features but flattening or offsetting the *CPD* values will change the measurement result.

To extract a *CPD* value for a particular region of a map, a mask can be used to extract all the recorded *CPD* values from that region. An arithmetic mean and standard deviation of these values can be reported as a measurement of *CPD* for that region. Note that other sources of uncertainty must be considered for any further processing and analysis steps.

Linear profiles of *CPD* values can also be extracted from a map. In this case, it may be appropriate to take an average of several line profiles to reduce measurement noise. If the spatial resolution or spatial gradient of the *CPD* signal is relevant, then the line profiles must be perpendicular to the features of interest to avoid artificial broadening. Broadening of features in line profiles can also be avoided (e.g. for lateral resolution estimation) by obtaining multiple line profiles (at least three) and analysing them individually to extract the mean and standard deviation of the relevant quantity.

1.9 General Sources of Uncertainty in KPFM

There are several general sources of uncertainty that can significantly influence KPFM measurements and the subsequent quantitative data interpretation. A primary source of

[a] 'Scars' in KPFM measurements are artefacts that do not correspond to real variation of the sample. They are typically present as transient noise signals affecting a small number of adjacent pixels within a scan line.

uncertainty is the conductive probe itself. The tip work function can vary due to oxidation, contamination, coating degradation or wear introduced from the interactions between the tip and sample. This variation in the tip work function would subsequently introduce offsets in the *CPD* signal measured. The electrostatic interactions that underline the KPFM measurements is not strictly confined to the apex of the tip but can also include contributions from the tip cone and the cantilever. The inclusion of all contributions result in a weighted average of the *CPD* signal and also can reduce lateral resolution. Independent of the feedback setup used for the KPFM measurements, crosstalk between the different channels can introduce surface potential contrast originating from either mechanical, electronic or topographical coupling. The feedback electronics used for neutralising the tip-sample potential difference also contribute uncertainty. This may include systemic bias in addition to random noise.

Environmental and sample-related effects can also contribute to measurement uncertainty. Ambient humidity and airborne adsorbates can form a nanoscale water meniscus between the tip and sample. This results in the screening or re-distribution of the surface potential between the tip and sample and can reduce measurement accuracy and mask true work function differences. For quantitative KPFM measurements, the work function of reference materials used (i.e. highly oriented pyrolytic graphite, HOPG) can carry its own uncertainty arising from variations in surface cleanliness and ambient exposure, both of which can shift the effective work function and limit the absolute accuracy of the quantitative KPFM measurement. Care should be taken during all measurements to reduce the contributions of the as-described sources of uncertainty. All sources of uncertainty identifiable should be taken into consideration in uncertainty budgets generated for KPFM measurements.

Chapter 2

CPD Signal Verification

- CPD Signal Polarity
- CPD Signal Magnitude

2.1 CPD Signal Polarity

As noted above, the *CPD* signal output from the KPFM instrument does not have a universally-followed sign convention and may correspond to either V_{CPD} or V_{DC}. If this is unclear from the instrument documentation, it can be experimentally determined using reference samples with well-known work functions. Here we describe a method based on the contrast between *CPD* measurements on dissimilar metals.

Various reference samples may be used in this method, but it requires *CPD* measurements to be performed on two surfaces with different work functions whilst keeping all other experimental variables fixed. The precise work functions of the reference materials are not required but it is essential to know which one has the higher work function. An ideal sample would have closely spaced regions of contrasting metals, both of which have macroscopic electrical contact pads or wire bonding for connection to the measurement circuit. A pair of metals with strongly contrasting work functions and good chemical stability is the best choice e.g. Al (there is a thin oxide layer of Al_2O_3 which is the surface that is measured) and Au. Surface cleanliness is important, but a large work function difference means that this method can accommodate some level of oxidation and organic contamination.

2.1.1 Measurement Protocol – CPD Signal Polarity Verification

- Select a reference sample with contrasting metal regions.
- Place the reference sample on the sample stage according to the local standard operating procedure. Depending on the system used, the sample will be held in place either on a sample disc on a magnetic sample stage or by spring probes on the sample stage.
- Electrically connect the reference sample to the instrument (typically this will be an electrical ground). Ensure that both metals are electrically connected together. Contact may be made via wire bonds or with a simple metal spring probe on the metal surfaces.
- Select a conductive probe suitable for the KPFM measurement and install on the microscope probe holder according to the local standard operating procedure. Bear in mind that probe tips can be damaged or contaminated with use, so it is best to use a fresh probe.
- Configure the instrument for the KPFM measurement according to the local standard operating procedure. Consider that even for a particular instrument, changing the KPFM mode or other aspects of the configuration may apply a signal inversion to the *CPD* signal, so the outcome of this test applies only to the precise measurement configuration considered.
- Position the reference sample under the KPFM probe so that the measurement field of view encompasses both metal surfaces. This is most easily achieved using a coupled

optical microscope, if available. Take care to ensure that the contrasting metals are identifiable, so you know which is which in the KPFM measurement.

- Perform the KPFM measurement on the reference sample according to the local standard operating procedure to optimise the feedback and scanning parameters. The scan area must be large enough (minimum scan size of 30 µm) to clearly capture regions of both metal surfaces where the *CPD* signal is spatially uniform (i.e. not just the interfacial gradient region). Refer to Figure 2b for an example *CPD* map covering two metal regions with varying *CPD* distribution.
- There are multiple channels that can be selected for KPFM, but most importantly, at least the topography and *CPD* channels must be recorded. The amplitude and phase signals are also useful for monitoring scanning instabilities.
- Obtain a *CPD* map showing the contrast between the two metal regions. Ensure that the measurement does not exhibit unexpected discontinuities that would indicate scanning instability.

2.1.2 Analysis – CPD Signal Polarity Verification

- Ensure that the measured *CPD* map corresponds with the topography map and expected layout of the reference sample features. It is anticipated that the metal surfaces will exhibit uniform *CPD* across their respective areas, one having a high average value and the other having a low average value. Between the different metals there will be an interfacial region which is disregarded in this measurement.
- Identify which of the reference regions exhibits the higher and lower *CPD* values and compare this with the prior knowledge of which regions correspond with the higher and lower work function surfaces. Note that the *CPD* values can be positive or negative (depending on the work function of the tip), so 'higher' is understood in the conventional sense of 'more positive'.
- If the higher measured *CPD* value corresponds with the higher work function reference surface, then $CPD = V_{CPD}$. If the higher measured *CPD* value corresponds with the lower work function reference surface, then $CPD = V_{DC}$.

2.1.3 Worked Example – CPD Signal Polarity Verification

As an example of the above method we consider a reference sample with closely spaced Al and Au films deposited on a SiO_2 surface with wire bonding to both the Al and Au regions. Al and Au are used to give strong contrast in *CPD*, with Au having a higher work function than Al. This sample was measured using two-pass AM-KPFM and the bias being applied to the tip and the results are shown below:

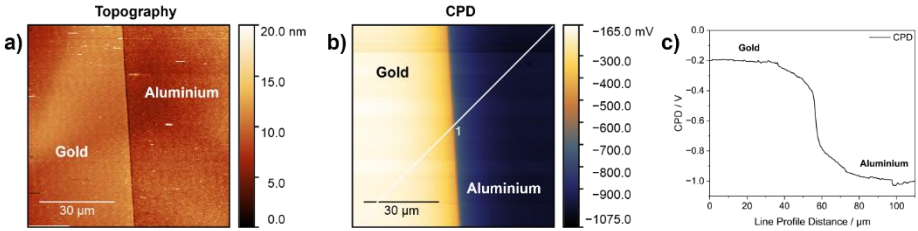

Figure 2. *a) Topography scan of the Au/Al sample with the Au and Al pads clearly labelled. b) The corresponding CPD scan of the same area with the Au and Al pads labelled. c) The line profile extracted from the CPD scan to present the change in CPD across the two metals.*

An 80 µm × 80 µm scan was measured to include areas of both the Au and Al pads. The Au and Al pads were clearly identified prior to the scan and are labelled. From the *CPD* scan, the Au pad clearly exhibits the higher average *CPD* value in comparison to the Al pad. This is further demonstrated by extracting a line profile across the two metal pads in the *CPD* scan (Figure 2c). Hence, for our SPM system, $CPD = V_{CPD}$. The difference is approximately 0.8 V, which is smaller than the typically quoted values (approximately 1 V) for the difference in work function between atomically clean Au and Al. This can be attributed to the measurements being performed in ambient conditions which has been reported to record smaller work functions for Au.[6,7]

2.2 CPD Signal Magnitude

In an ideal KPFM measurement the magnitude of the *CPD* signal directly reflects the difference in surface potential between the apex of the probe tip and the area of the sample immediately under the tip. However, in real measurements there are multiple factors such as non-ideal feedback conditions, interactions between the sample and the probe shanks, or parasitic capacitance between the sample and cantilever, that can introduce deviations from the ideal behaviour.

It is therefore important to experimentally verify the performance of the KPFM measurement in terms of the *CPD* signal magnitude. A simple approach is to directly apply a known electrical bias to a metallic sample and measure the corresponding *CPD* signal. As mentioned above, in ideal conditions, the applied bias should be directly reflected in the measured *CPD* and this is showcased in the worked example below. Any deviation from this relationship provides a practical means of identifying and quantifying non-idealities in real measurements, although they do not necessarily isolate the specific underlying source or contribution.

2.2.1 Measurement Protocol – CPD Signal Magnitude Verification

- Select a reference sample with a clean metal surface.
- Place the reference sample on the sample stage according to the local standard operating procedure. Depending on the system used, the sample will be held in place

either on a sample disc on a magnetic sample stage or by spring probes on the sample stage.

- Electrically connect the reference sample to the instrument (typically this will be an electrical ground) via an external power supply. Contact may be made via wire bonds or with simple metal spring probes on the metal surface. The power supply should ideally be operated as a floating voltage source, such that the applied bias is only defined between the sample and the KPFM ground. Care should be taken to minimise electrical noise and ensure stable operation, as poorly grounded supplies may introduce measurement artefacts.
- Select a conductive probe suitable for the KPFM measurement and install on the microscope probe holder according to the local standard operating procedure. Bear in mind that probe tips can be damaged or contaminated with use, so it is best to use a fresh probe.
- Configure the instrument for the KPFM measurement according to the local standard operating procedure.
- Perform the KPFM measurement on the reference sample according to the local standard operating procedure to optimise the feedback and scanning parameters. During the KPFM measurement, a known electrical bias (e.g. +0.5 V) should be applied to the sample for a fixed duration using the external power supply. Measure the bias with a calibrated volt-meter for an accurate value.
- There are multiple channels/images that can be selected, but most importantly, at least the topography and *CPD* maps must be recorded. The amplitude and phase signals can be recorded as well and can provide additional information.
- Obtain a *CPD* map showing the contrast between the no bias and known electrical bias regions. Ensure that the measurement does not exhibit unexpected discontinuities associated with scanning instability.

2.2.2 Analysis – CPD Signal Magnitude Verification

- Ensure that the measured *CPD* map corresponds with the topography map and expected layout of the reference sample features. It is anticipated that the metal surface will exhibit uniform but distinct *CPD* values across the areas measured with no bias and the applied electrical bias.
- Both regions with and without applied electrical bias in the *CPD* map should be masked and extracted. The masked areas should be used to obtain the arithmetic mean and standard deviation of *CPD*.
- The difference in the average *CPD* value with and without electrical bias should equal the magnitude of the electrical bias applied. An ‘acceptance criterion’ should be implemented to the user’s preference, but as a guideline a difference of less than 5 % would be consistent with the typical uncertainty that can be expected to be introduced

by instrumental noise, tip-sample drift and cross-talk artifacts inherent to KPFM measurements.[8,9]

- If the calculated difference in average *CPD* with and without electrical bias is greater than the acceptance criterion (e.g. 5 %), the instrument set-up and scanning parameters should be reviewed. Careful tuning of the scanning parameters can improve the stability of the feedback loop and reduce measurement noise. Otherwise review the electrical connection between the sample, power supply and instrument. Installing a fresh probe or cleaning the sample following local standard operating procedures may also help by reducing the influence of surface contamination.

2.2.3 Worked Example – CPD Signal Magnitude Verification

As an example of the above method we consider a reference sample with closely spaced Al and Au films deposited on a SiO_2 surface with wire bonding to both the Al and Au regions (the same sample used in Chapter 2.1.3). For simplicity, only the Au region was measured with the electrical bias. An Au region with no surrounding Al surface was chosen to minimise any contributions from the interface between the metals. The sample was measured using two-pass AM-KPFM with a nominal +0.5 V electrical bias applied during the KPFM measurement. The results are shown below:

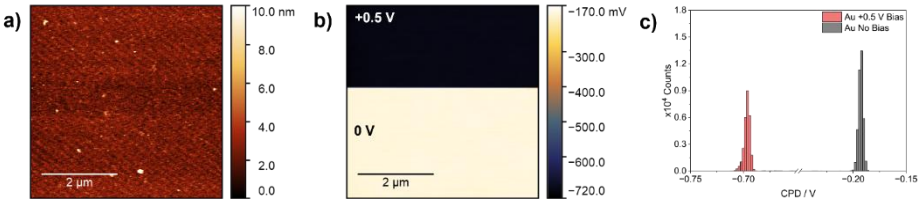

Figure 3. *a) Topography scan of the Au region. b) Corresponding CPD scan of the same area with the +0.505 V electrical bias applied halfway through the measurement. c) Extracted CPD histograms of regions of Au with both no bias and the +0.505 V electrical bias.*

The measured electrical bias applied to the sample during the KPFM measurement was actually +0.505 V ± 0.003 V. The *CPD* values from regions with and without the +0.505 V electrical bias were extracted using masks. The extracted *CPD* values were averaged and returned *CPD* values of -0.192 V ± 0.002 V and -0.697 V ± 0.007 V for the regions with and without electrical bias, respectively. This gives a difference of -0.505 V ± 0.015 V, in good agreement with the magnitude of the applied bias. Here the measured difference in *CPD* is the inverse of the applied bias due to the instrument convention discussed above. The close agreement between the applied external voltage and the CPD-derived voltage difference shows that our SPM system is accurately capturing the tip-sample potential variations and performing as expected. Whilst this gives confidence in the instrument set-up, it does not guarantee that the measurement will exhibit the same performance once the reference sample is replaced with a sample of interest.

Chapter 3

CPD Lateral Resolution

- Measurement Protocol – CPD Lateral Resolution
- Analysis – CPD Lateral Resolution Evaluation
- Worked Example – CPD Lateral Resolution Evaluation

The nanometre-scale spatial resolution of KPFM is a key feature of the method and therefore it is often necessary to estimate what resolution is achieved. The typical spatial resolution of KPFM has been quoted to range from 30 nm – 100 nm depending on the mode used.[10] Robust measurement of lateral resolution is a complex activity and depends on the specific sample and measurement parameters as well as the instrument hardware. However, a simple test can be performed to estimate the spatial resolution using the Straight Edge Method. This method involves scanning across a sharply-defined edge of a feature that exhibits strong contrast in surface potential. Further details on the Straight Edge Method are referred to in the ISO standard, ISO 18516:2019.[11]

The Straight Edge method can be performed on any sample that exhibits sharply defined surface potential features, where the potential changes abruptly over a lateral distance significantly smaller than the resolution being assessed. The spatial resolution measurement should ideally be performed on a reference sample with features exhibiting strong contrast in surface potential, but which is atomically smooth and flat to avoid cross-talk between the topography and *CPD* measurement signals. This can be approximated using surface monolayers or 2D materials, but a thin deposited metal layer can also be used as a more readily available sample. A protocol is outlined below describing this method to estimate the spatial resolution of a KPFM measurement.

3.1 Measurement Protocol – CPD Lateral Resolution

- Prior to performing this measurement protocol, ensure that the AFM system is dimensionally calibrated, as accurate spatial scaling is essential for quantifying CPD lateral resolution. Further detail on dimensional calibration of AFM systems is referred to in the ISO Standard, ISO 11952:2019.[12]
- Place the sample on the sample stage according to the local standard operating procedure. Depending on the system used, the sample will be held in place either on a sample disc on a magnetic sample stage or by spring probes on the sample stage.
- Electrically connect the sample to the instrument (typically this will be an electrical ground). Contact may be made via wire bonds or with a simple metal spring probe on the sample surface.
- Select a conductive probe suitable for the KPFM measurement and install on the microscope probe holder according to local practices. Bear in mind that probe tips can be damaged or contaminated with use, so it is best to use a fresh probe.
- Configure the instrument for the KPFM measurement according to the local standard operating procedure.
- Find an area of interest on the sample surface that contains a sharp edge/ feature in surface potential.
- Perform the KPFM measurement on the sample according to the local standard operating procedure to optimise the feedback and scanning parameters. The scan area must be large enough to clearly capture the area of interest.
- Extract a minimum of five line profiles across the sharp edge of the feature and ensure that there is also a minimum of five data points within the 'gradient region' of each line profile extracted. If a large gradient in *CPD* is present across the chosen sharp feature in the *CPD* scan, a partial mean plane correction may be applied to one side of the feature (i.e. one of the metal surfaces) to remove the gradient.

3.2 Analysis – CPD Lateral Resolution Evaluation

- The lateral resolution is calculated by determining the distance along a line profile perpendicular to the sharp edge that corresponds to a change in surface potential from x % to (100-x) %. Common choices for the value of x are 12, 16, 20 and 25. The upper (100 %) and lower (0 %) levels are determined as the mean values of the flat regioins in selectively chosen line profiles that consist of only uniform regions on either side of the sharp gradient region. This helps eliminate contributions from noise within the measurement. The recommended guidance is to select a lower threshold (12 % or 16 %) as these thresholds correspond to the steepest portion of the surface potential transition and minimises the influence of artifacts arising from long-range electrostatic interactions and tip convolution effects.

- After deciding on the value of *x*, interpolate the lateral distance values corresponding to surface potential values of *x* % and (100-*x*) %. The difference in the distance values will provide the lateral resolution. If the extracted line profile is noisy, appropriate smoothing processes can be applied ensuring a compromise between removing noise and blurring the edges. In the example provided here, an adjacent averaging across a three point window has been applied to reduce the signal noise.
- Calculate the lateral resolution for all line profiles extracted and subsequently calculate the arithmetic mean and standard deviation.

3.3 Worked Example – CPD Lateral Resolution Evaluation

As an example of the above method we consider a reference sample with Al deposited on a SiO_2 surface with wire bonding to the Al (the same sample used in Chapter 2.1.3). This sample was measured using two-pass AM-KPFM across the SiO_2/Al edge. The results are shown below:

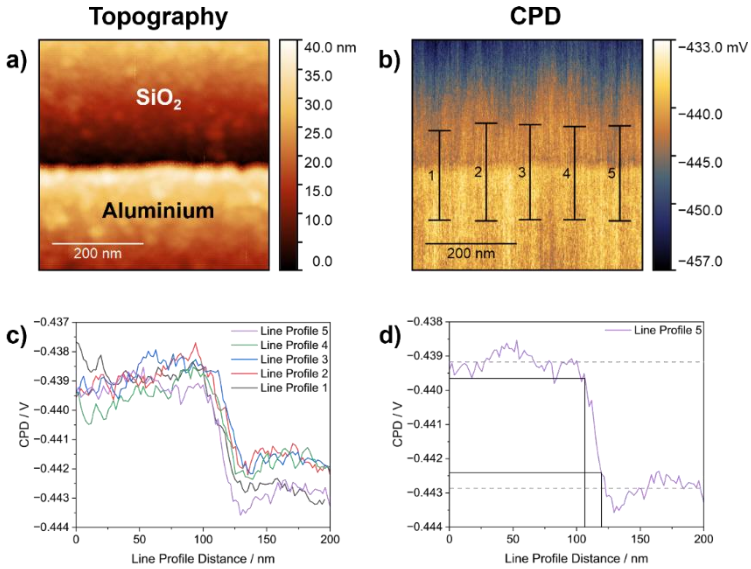

Figure 4. *a) Topography scan of the reference sample with Al on SiO_2 with the Al pad and SiO_2 clearly labelled. b) Corresponding CPD scan of the same area with the five line profiles taken across the sharp edge in CPD. c) The extracted line profiles of the SiO_2/Al film edge. d) The calculation of the lateral resolution with x = 12. The dashed grey lines mark the upper and lower limits of CPD, and the solid black lines mark the CPD values at 12 % and 88 % of the total difference.*

The *CPD* map of the SiO_2/Al edge of the sample exhibited a large *CPD* gradient due to the electric field around the metallic feature under bias. As a result, a partial mean plane correction was

applied to the Al region of the *CPD* map to remove the gradient (Figure 4b). Five line profiles were extracted across SiO_2/Al edge in *CPD*. For these measurements, the *x* value was set to 12 % and the lateral resolution was calculated for each line profile. The *CPD* value at 12 % and 88 % of the total difference between the upper and lower limits of the line profile were calculated and used to evaluate the corresponding lateral distance, which is an estimate of lateral resolution. The average lateral resolution for the measurement was estimated as 18 nm ± 2 nm. The result demonstrates that the SPM system achieves high spatial resolution in resolving surface potential variations along sample surfaces. As above, be aware that the same resolution may not be achieved once the reference sample is replaced with the sample of interest.

Chapter 4

Quantitative Surface Potential Measurement

- Measurement Protocol – Quantitative Surface Potential Measurement
- Analysis – Quantitative Surface Potential Measurement
- Worked Example – Quantitative Surface Potential Measurement

KPFM measures a relative difference in surface potential between the tip and the sample (given by the *CPD* signal), but in principle the absolute potential of the sample surface can be evaluated if the work function of the tip is known. The work function of a metallised tip can be approximated using literature values but in reality, is affected by the crystallinity of the coating, contamination, or damage. Therefore it is better to rely on a sample surface with a well-known work function in order to measure the tip work function experimentally. The most commonly accepted samples are atomically clean Au or freshly-exfoliated highly oriented pyrolytic graphene (HOPG, 4.60 eV ± 0.03 eV).[13] HOPG is the most practical choice for systems operated in ambient conditions and samples are commercially available within a range of mosaic spread angles (0.4° to 3.5°). The lower mosaic spread angles indicate higher crystallinity and better alignment of the graphite plates.

It is important to recognise that the probe tip can become contaminated or damaged at any point during measurements so the tip work function can change. Therefore the recommended practice is to perform the KPFM measurement of the HOPG reference sample before and after measuring the sample of interest to verify that it is unchanged.

4.1 Measurement Protocol – Quantitative Surface Potential Measurement

4.1.1 HOPG Sample Preparation and Measurement

- The HOPG sample should first be exfoliated before the KPFM measurement. The conventional approach to cleave HOPG is to use a piece of adhesive tape, press it on the HOPG surface and pull the tape off. This will remove the topmost layer of HOPG and prepare a freshly exfoliated HOPG surface ready for measurements. This exfoliation procedure should be performed before every measurement on HOPG.
- Place the exfoliated HOPG sample on the sample stage according to the local standard operating procedure.
- Electrically connect the HOPG sample to the instrument (typically this will be an electrical ground). This can be done with a simple metal probe on the HOPG surface.
- Select a conductive probe suitable for the KPFM measurement and install on the microscope probe holder according to the local standard operating procedure. Bear in mind that probe tips can be damaged or contaminated with use, so it is best to use a fresh probe.
- Configure the instrument for the KPFM measurement according to the local standard operating procedure. This must be maintained consistent across all measurements.
- Perform the KPFM measurement on the HOPG sample according to the local standard operating procedure to optimise the feedback and scanning parameters.

- The same measurement should be performed on the HOPG sample after the sample of interest has been measured. This will verify that the tip is undamaged and can quantify the change in the work function of the probe.

4.1.2 Sample Measurement

- Place the sample of interest on the sample stage according to the local standard operating procedure. Depending on the system used, the sample will be held in place either on a sample disc on a magnetic sample stage or by spring probes on the sample stage.
- Electrically connect the sample to the instrument (typically this will be an electrical ground). Contact may be made via wire bonds or with a simple metal spring probe on the sample surface.
- The same KPFM probe used to measure the HOPG reference sample should be used for the sample measurement. The mechanical resonance frequency of the probe oscillation should be found again by tuning prior to the measurement.
- Position the sample under the KPFM probe so that the measurement field of view encompasses the area of interest on the sample. This is most easily achieved using a coupled optical microscope, if available.
- Perform the KPFM measurement on the sample according to the local standard operating procedure to optimise the feedback and scanning parameters.
- There are multiple channels that can be selected for KPFM, but most importantly, at least the topography and CPD channels must be recorded. The amplitude and phase signals are also useful for monitoring scanning instabilities.
- After completing all measurements on the sample, the HOPG reference sample should be measured again to obtain a before- and after- measurement to validate the work function of the probe.

4.2 Analysis – Quantitative Surface Potential Measurement

- Obtain the arithmetic mean and standard deviation of the *CPD* from the *CPD* maps of the before- and after- HOPG sample measurements. The obtained before- and after-*CPD* arithmetic means should then be averaged.
- Using Equation 2 and the findings from Section 2.1.3, calculate the work function of the probe. The uncertainties associated with the KPFM measurement will be dependent on the measurement conditions. Typical uncertainties will originate from the measurement of the samples and reference value for the HOPG as well as the calibration uncertainty in the voltage source.

- Obtain the arithmetic mean and standard deviation of the *CPD* from the *CPD* maps of all sample measurements.
- Using the calculated work function of the probe and Equation 2, the work function of the sample can be calculated.

4.3 Worked Example – Quantitative Surface Potential Measurement

As an example of the above method we consider a reference sample with closely spaced Au and Al films deposited on a SiO_2 surface with wire bonding to both the Al and Au regions. This sample was measured using two-pass AM-KPFM and the work function of the probe was validated using a HOPG reference sample. The results are shown below:

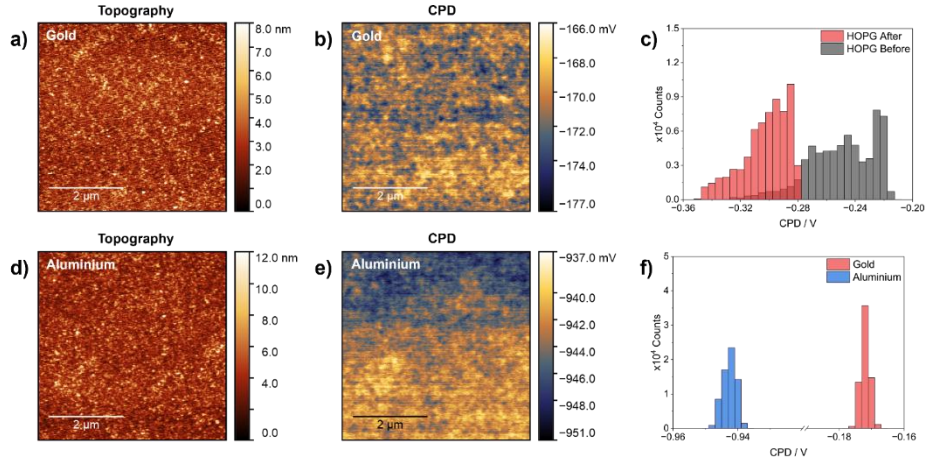

Figure 5. *a) Topography scan of the Au region on the Au/Al sample. b) Corresponding CPD scan of the same area. c) Extracted CPD histograms of the HOPG reference sample before- and after- the KPFM measurement of the Au/Al sample. d) Topography scan of the Al region on the Au/Al sample. e) Corresponding CPD scan of the same area. f) Extracted CPD histograms of the Au and Al regions.*

In Chapter 2, using the Au/Al sample, we determined the *CPD* signal recorded in our system to be V_{CPD}. The KPFM measurements were performed in regions of Au and Al where the other metal (Au or Al respectively) was not in the vicinity to prevent the influence of the interfacial gradient between the two metals. The obtained *CPD* histograms of the HOPG sample measured before and after the sample measurement were used to calculate the arithmetic mean and standard deviation of the *CPD*. Using these values and Equation 2, the work function of the probe was calculated to be 4.88 eV ± 0.09 eV. The before and after measurements of HOPG capture the tip work function changes which also contribute to the uncertainty estimate. With the calculated work function of the probe, the work functions of atomically clean Au and Al were calculated to

be 4.71 eV ± 0.09 eV and 3.93 eV ± 0.09 eV respectively. The reported expanded uncertainties are calculated to a confidence level of 95 %. The literature work function values of atomically clean Au and Al are 5.0 eV[14] and 4.0 eV[15] respectively. However, under ambient conditions, surface contamination of Au and oxidation of Al cannot be fully mitigated and often the reported work function of Au thin films has been previously reported to decrease below 5 eV, consistent with the measured value.[6,7] This method demonstrates the general suitability of KPFM for measurements of absolute work function using simple reference materials but applicability to samples of interest must be considered on a case-by-case basis.

Chapter 5

Conclusions and Acknowledgements

- Conclusions
- Acknowledgements

5.1 Conclusions

Using this guide, users with previous KPFM characterisation expertise within both academia and industry can achieve more reliable, quantitative and comparable measurements using KPFM. It is anticipated that by facilitating a more robust approach to method development and enabling intercomparisons between laboratories, this guide will contribute to ongoing efforts towards internationally agreed standards for these measurements.

5.2 Acknowledgements

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