A simple KPFM-based approach for electrostatic-free topographic measurements: the case of MoS$_2$ on SiO$_2$

Aloïs Arrighi$^{1,2}$, Nathan Ullberg$^3$, Vincent Derycke$^3$ and Benjamin Grévin$^1$

$^1$Univ. Grenoble Alpes, CNRS, CEA, IRIG-SyMMES, F-38000 Grenoble, France
$^2$Institut Néel, CNRS, Univ. Grenoble-Alpes, F-38042 Grenoble Cedex 09, France
$^3$Université Paris-Saclay, CEA, CNRS, NIMBE, LICSEN, F-91191 Gif-sur-Yvette, France

E-mail: benjamin.grevin@cea.fr

Received 14 September 2022, revised 10 January 2023
Accepted for publication 22 February 2023
Published 13 March 2023

Abstract

A simple implementation of Kelvin probe force microscopy (KPFM) is reported that enables recording topographic images in the absence of any component of the electrostatic force (including the static term). Our approach is based on a close loop z-spectroscopy operated in data cube mode. Curves of the tip-sample distance as a function of time are recorded onto a 2D grid. A dedicated circuit holds the KPFM compensation bias and subsequently cut off the modulation voltage during well-defined time-windows within the spectroscopic acquisition. Topographic images are recalculated from the matrix of spectroscopic curves. This approach is applied to the case of transition metal dichalcogenides (TMD) monolayers grown by chemical vapour deposition on silicon oxide substrates. In addition, we check to what extent a proper stacking height estimation can also be performed by recording series of images for decreasing values of the bias modulation amplitude. The outputs of both approaches are shown to be fully consistent. The results exemplify how in the operating conditions of non-contact AFM under ultra-high vacuum (nc-AFM), the stacking height values can dramatically be overestimated due to variations in the tip-surface capacitive gradient, even though the KPFM controller nullifies the potential difference. We show that the number of atomic layers of a TMD can be safely assessed, only if the KPFM measurement is performed with a modulated bias amplitude reduced at its strict minimum or, even better, without any modulated bias. Last, the spectroscopic data reveal that certain kind of defects can have a counterintuitive impact on the electrostatic landscape, resulting in an apparent decrease of the measured stacking height by conventional nc-AFM/KPFM compared to other sample areas. Hence, electrostatic free z-imaging proves to be a promising tool to assess the existence of defects in atomically thin TMD layers grown on oxides.

Supplementary material for this article is available online

Keywords: nc-AFM, KPFM, z-spectroscopy, transition metal dichalcogenides

(Some figures may appear in colour only in the online journal)
Very early on, it became also evident that better height measurements would be performed by combining dynamic AFM modes with KPFM. In the case of heterogeneous materials, or samples nanostructured on purpose, local variations in the effective work function affect the electrostatic force (and its gradient), and hence the tip-sample distance regulation. In KPFM, these electrostatic-related topographic artefacts are mitigated by the active compensation of the tip-surface potential difference. This has been nicely illustrated in the pioneering work of Sadewasser and Lux-Steiner [2], who demonstrated that noncontact-AFM combined with KPFM allowed performing correct estimations of C60 sub-monolayers stacking height on highly oriented pyrolytic graphite. Almost twenty years after, there is no doubt about the relevance of this approach, which continues to contribute to the improvement of AFM-based techniques. For instance, electrostatic artefact compensation by KPFM has recently been applied to improve the performances of scattering scanning near-field optical microscopy [3].

It would however be a dangerous illusion to think that performing topographic measurements with an active KPFM loop provides an absolute guarantee against electrostatic-induced topographic artefacts. A well-known fact [4], unfortunately too often overlooked, is that the application of the modulated bias (used for the electrostatic force detection via a lock-in scheme) generates a static force component proportional to the tip-sample capacitive gradient. Consequently, topographic artefacts may exist if this last parameter displays spatial variations.

In some cases, it is reasonable to assume that this effect will not impact significantly the topographic profiles recorded by an nc-AFM. This should hold true, for instance, for the abovementioned C60/graphite benchmark: there is here no reason to expect significant variations of the tip-surface capacitive gradient, regardless of the material under the tip. By contrast, artefacts should be an unavoidable consequence of the capacitance variations for conducting layers deposited on insulating thin films. For instance, in the case of graphene flakes deposited on doped-silicon covered by silicon oxide (SiO2), the capacitance is either the one between the AFM tip and the backside doped silicon, or a serial concatenation of two capacitances [5] (between the tip and the flake, and between the flake and the doped silicon).

Transition metal dichalcogenides (TMDs) are another class of two-dimensional materials, which are very often processed on silicon oxide substrates as the active parts of opto-electronic devices such as field effect transistors and photodetectors [6]. Their optoelectronic properties are strongly dependent on the material thickness. In particular, many TMDs (such as MoS2, WS2, MoSe2, WSe2) exhibit an indirect to direct band gap transition when thinned down to the 2D monolayer. For a wide community of researchers, assessing correctly the stacking height (and consequently the number of atomic layers) of TMDs on oxide surfaces is an essential prerequisite to any basic or applied research.

Numerous studies use optical methods and spectroscopies [7, 8] to determine the number of layers in TMD samples. The AFM has become a widespread basic laboratory tool, and complementary investigations by AFM profiling are often performed. The amplitude modulation mode (AM-AFM), often referred to as ‘intermittent-contact’ or ‘tapping’ AFM, has frequently been used to perform these characterizations. However, as highlighted in many reports (see for instance the work by Ottaviano et al [7]), there exist a significant disparity between the results of published AM-AFM studies on exfoliated TMD flakes on SiO2. The inadequacy of AFM to yield consistent stacking height values of 2D layers on oxide surfaces has also been noted in the case of graphene [9, 10]. A number of reasons have been put forward to explain these observations. For instance, anomalously large stacking distances deduced from AM-AFM profiling between the substrate and 2D monolayers (or the first layer of a multilayered 2D stack) have been attributed to the presence of water molecules and/or other contaminants trapped between the oxide surface and the flake [7]. Early on, it became also evident that due to variations in the nature of the tip-surface interaction (when moving from the bare substrate to the 2D stack), the effective stacking heights probed by AM-AFM can critically depend on the experimental parameters, such as the cantilever vibration amplitude and its reduction set-point. Particularly, Nemes-Inceze and co-workers have shown [9] that contrary to a common expectation, minimizing the tip-sample interaction (by using a small set-point to keep the vibration amplitude as close as possible to the ‘free’ oscillation regime) may result in an overestimation of the stacking height. More precisely, they concluded that the operating parameters (i.e. the free amplitude and/or the reduction set-point) should be set in order to maximize the contribution of the repulsive part of the force field to the tip-surface interaction.

Following this work, others have eventually come to conclude that contact-mode AFM (C-AFM) should provide a better accuracy than AM-AFM when one aims at assessing the stacking height of a 2D material on an oxide substrate [11]. By mean of a comparative approach, Nemes-Inceze et al had indeed observed that the stacking height values deduced from C-AFM were close to the ones obtained with AM-AFM in the ‘repulsive regime’. Nevertheless, they had also concluded that in C-AFM, shear forces induce significant deviations between the topographic profiles acquired in the forward and backward scan directions [9]. This effect has more recently been observed and thoroughly discussed in the case of single-layer graphene deposited on mica [12]. Besides this scan-directional dependency of the topographic profiles, other artefacts can also occur in C-AFM imaging. In particular, it has been shown that the combination of compressive stress and shear forces can result in the existence of a negative compressibility effect, which results in an overestimation of the stacking height of multilayer samples. This effect, which scales with the applied load, has been observed in few-layer graphene, hexagonal boron nitride, and MoS2 [13]. On the contrary, Shearer et al have provided compelling evidence that enough load shall be applied to achieve a correct estimation of the stacking height of graphene monolayers on SiO2 [10].
These few examples from the literature show that, regardless of the chosen AFM mode, performing an accurate measurement of a 2D sample stacking height on an oxide is not straightforward. In all cases, changing the experimental parameters is likely to modify the characterization outputs. Performing accurate thickness measurements cannot be divorced from following suited protocols, and even doing so significant errors can remain. To name just one example, in the case of graphene monolayers on SiO₂, Shearer et al conclude [10] that with an optimal force set point, the error related to inaccuracy of the first layer can be on the order of 0.1–0.3 nm (the upper limit being close to one graphene layer).

From what precedes, it is also clear that the question of electrostatic-related artefacts in dynamic AFM has long been overlooked by the AFM community. Only very recently, a few teams have rightly pointed out that electrostatic forces can misleadingly influence the stacking height measurement of 2D materials by AFM [14, 15]. To address this problem, one may be tempted to apply an active KPFM loop to compensate the tip-surface potential difference. Unfortunately, due to capacitive-related artefacts, the cure could reveal itself worse than the disease. This is especially likely if one uses large modulated bias (V_ac), since the static electrostatic force component scales with the product of the capacitance gradient by the square of the modulated bias amplitude [4].

In a recent work [15], Ritz and co-workers have developed a Kalman-filter based methodology that allows estimating the electrostatic influence due to the applied voltage modulation on the cantilever frequency shift. The imaging can then be performed on the basis of the sole topography-induced part of the frequency shift. Doing so, they nicely confirmed that the capacitive artefacts noticeably affect the AFM/KPFM topographic measurements performed on graphene flakes on silicon oxide.

In this work, we follow an alternative strategy, which consists in tackling the root of the problem. The idea is to suppress completely the electrostatic force during the topographic measurement. This strategy is applied to the case of MoS₂ monolayers grown on silicon oxide by chemical vapour deposition. Prior to this, we show that the stacking height of a MoS₂ monolayer on SiO₂ can be accurately estimated by recording a series of AFM/KPFM images for decreasing values of the modulated bias. In a second step, we demonstrate how ‘electrostatic free’ height measurements can be performed. Our approach is based on the implementation of a new distance-spectroscopy protocol operated in data cube mode. In each pixel, curves of the tip-sample distance (z) as a function of time are synchronously recorded with trigger events that (i) drive a hold circuit which maintains the KPFM compensation potential to a constant value, and (ii) drive a second circuit that cut off the modulated bias. Artefact-free topographic images are obtained by mapping the z-values recorded when V_ac is switched off. Moreover, by comparing the data acquired on two different samples, we show that certain kind of defects can counterintuitively impact the effective stacking height measured by conventional nc-AFM/KPFM. Beyond the possibility of performing correct topographic measurements, we thus show that our approach can be very useful to avoid misinterpretations, and investigate the local electronic properties of 2D TMD samples from a new perspective.

1. KPFM background

In KPFM, the tip and sample form a capacitive junction, and the attractive electrostatic force can be expressed as:

\[ F_{el} = \frac{1}{2} C'_e (\Delta V)^2, \]

where \( C'_e \) and \( \Delta V \) are the tip-sample capacitive gradient and the electrostatic potential difference, respectively. Apart from external bias voltages that can be applied to the tip and sample, the potential difference term originates from the tip-sample work function difference, and/or from the existence of electric charges and/or dipoles in the system under consideration.

The basic principle of KPFM (figure 1) consists in minimizing the electrostatic potential difference by providing a proper dc compensation bias (V_bias). If one considers a simple junction formed by a metallic tip and a metallic sample, the electrostatic force becomes:

\[ F_{el} = \frac{1}{2} C'_e (V_{bias} \pm V_{CPD})^2 \]

where \( \Phi_S, \Phi_T, \phi \) and \( \epsilon \) stand for the sample work function, the tip work function and the electron charge, respectively. \( V_{CPD} \) designs the so-called contact potential difference. The plus or minus sign applies if the compensation bias is applied to the tip (plus sign) or to the sample (minus sign), respectively. In our setup, the sample is grounded and the bias is applied to the tip. The KPFM data will be hereafter presented as images of the compensation bias (V_{tip} = V_{dc} = -V_{CPD}), also referred to as ‘KPFM potential’ or ‘surface potential’ images, like in our previous reports. The surface potential terminology is justified by the fact that, with our convention, any additional bias that would be applied to the sample would be compensated by applying the same bias on the tip. We also note that, in our case, the CPD concept should be considered with caution, since the substrate is not metallic and consists in a thin (insulating) silicon-oxide layer grown on doped silicon.

Probing the electrostatic interaction by KPFM relies on a lock-in detection scheme, in which a modulated bias \( V_{mod} \) of amplitude \( V_{ac} \) and angular frequency \( \omega_{mod} \) is added to the static dc voltage (equation S1 in the supplementary information). The total electrostatic force becomes the sum of three components, including a static term, and modulated components at the excitation frequency \( \omega_{mod} \) and at \( 2\omega_{mod} \) referred herein to as first harmonic and second harmonic components:

\[ F_{dc} = \frac{1}{2} C'_e \left[ (V_{dc} + V_{CPD})^2 + \frac{V_{ac}^2}{2} \right] \]
Figure 1. KPFM modes. (a) The cantilever frequency shift displays a quadratic dependence as a function of the tip-sample electrostatic potential difference. Applying an ac voltage (with angular frequency \( \omega_{\text{mod}} \)) causes periodic oscillations in the cantilever resonance frequency. In FM-KPFM, the surface potential (\( V_s \)) or contact potential difference (CPD) is obtained by minimizing (with a proper dc bias, \( V_{\text{dc}} \)) the amplitude of the modulated frequency shift at the first harmonic (\( \Delta f_{\omega_{\text{mod}}}, \text{main text, equation 3b} \)). The second harmonic channel (\( 2\omega_{\text{mod}} \)) yields a measurement of the tip-sample capacitance gradient -derivative. (b) Side-bands exist due to the frequency mixing between the electrical bias modulation and the cantilever mechanical oscillation (depicted here at its first eigenmode, \( \omega_0 \)). \( V_s \) is obtained by minimizing the amplitude of the first side bands (\( \omega_0 \pm \omega_{\text{mod}} \)). In AM-heterodyne KPFM, \( \omega_{\text{mod}} \) is selected in order to shift the first right side-band (\( \omega_0 + \omega_{\text{mod}} \)) to the second eigenmode frequency (\( \omega_1 \)). (c) In all cases, a static electrostatic force component proportional to the capacitance gradient and the square of the modulated bias amplitude remains. To perform a correct topographic measurement, one needs to apply the KPFM compensation dc bias (\( V_{\text{dc}} \)) without adding the modulated bias. (d) Principle of the two-dimensional z-spectroscopy. In each pixel of the surface, the scan is stopped. The KPFM dc bias loop and the modulated bias are maintained during a first integration/stabilization delay (\( \Delta t_1 \)). The dc bias is subsequently ‘frozen’ by a sample and hold circuit. After a second delay (\( \Delta t_2 \)) the bias modulation is switched off, during a time-lapse \( \Delta t_3 \). All components of the electrostatic force are now suppressed. \( \Delta t_3 \) is set to exceed the z-feedback time constant: the tip-sample distance has enough time to stabilize itself to its minimum. The bias modulation is turned on again, and the KPFM dc bias loop is reactivated after a fourth delay (\( \Delta t_4 \)). The scan resumes after a last delay (\( \Delta t_5 \)).

\[
F_{z_{\text{inst}}} = C''_z(V_{\text{dc}} + V_{\text{CPD}}) V_s \cos(\omega_{\text{mod}} t) \quad (2b)
\]

\[
F_{z_{\text{mod}}} = \frac{1}{4} C''_z V_{\text{inst}}^2 \cos(2\omega_{\text{mod}} t). \quad (2c)
\]

Note that an alternative formulation of these equations in terms of difference between the tip bias and an ‘effective’ electrostatic surface potential (\( V_s \)) can be used, it is described in the supplementary information.

Instead of using the force, it is preferable to perform a force gradient detection (which minimizes the contribution of long-range electrostatic interaction) by using the cantilever frequency shift (\( \Delta f \)). The components of interest become:

\[
\Delta f_{\text{dc}} = \frac{1}{2} C''_z \left( V_{\text{dc}} + V_{\text{CPD}} \right)^2 + \frac{V_{\text{inst}}^2}{2} \quad (3a)
\]

\[
\Delta f_{\omega_{\text{mod}}} = C''_z (V_{\text{dc}} + V_{\text{CPD}}) V_s \cos(\omega_{\text{mod}} t) \quad (3b)
\]

\[
\Delta f_{\omega_{\text{mod}}} = \frac{1}{4} C''_z V_{\text{inst}}^2 \cos(2\omega_{\text{mod}} t), \quad (3c)
\]

where \( C''_z \) is the capacitance second \( z \)-derivative. In frequency-modulated KPFM (FM-KPFM), the first harmonic component (equation 3b) is demodulated and injected as an
input in the KPFM compensation potential feedback loop (figure 1(a)), which minimizes it by adjusting \( V_{dc} \). Demodulating the second harmonic (equation 3c) yields a measurement of the tip-sample capacitance second \( z \)-derivative.

In side-band KPFM, the electrostatic information is obtained through the amplitude of lateral side bands (figure 1(b)). They stem from a heterodyning effect (or frequency mixing) between the electrical bias modulation and the cantilever mechanical oscillation (usually performed at the first eigenmode, with an angular frequency \( \omega_0 \)). It can be simply shown (see the supporting information) that here, too, the signal is proportional to the force gradient. Amplitude modulated heterodyne-KPFM [16] (hereafter simply referred to as heterodyne-KPFM) is an interesting variant of side-band KPFM, in which the first side-band is shifted at the second cantilever eigenmode (frequency \( \omega_1 \)) by performing the electrical excitation at \( \omega_{mod} = \omega_1 - \omega_0 \). The sensitivity is thus boosted by performing the amplitude detection at the second resonance.

Whatever the detection scheme, the existence of a static electrostatic force component (equation 2a) remains an issue. It is still with us, even when the tip dc bias matches finally the surface potential. This is a fundamental limitation of bias-modulated KPFM: to probe the surface potential one has no choice but to generate an additional ‘extrinsic’ electrostatic force. This situation is illustrated in figure 1(c). In other words, it is ultimately incorrect to claim that one nullifies the tip-sample electrostatic interaction by using an active KPFM loop.

As we have already pointed out, this should especially be a matter of concern if the tip-sample capacitance displays spatial variation; in that case, topographic artefacts seem unavoidable. Fortunately, these effects should be mitigated by working with small bias modulation amplitudes. One shall indeed remember here that the dc component of the force—or its gradient—is proportional to the square of the bias modulation amplitude. In the following, we will first check to what extent reducing the bias modulation amplitude allows performing a correct estimation of the thickness of TMD flakes grown by chemical vapor deposition (CVD) on silicon oxide. We will then demonstrate how ‘electrostatic free’ measurements can be performed by implementing a dedicated \( z \)-spectroscopy protocol (figures 1(c) and (d)).

2. Results

With the idea of reducing as much as possible the modulated bias amplitude, heterodyne-KPFM shall be an asset. We are indeed going to see that, thanks to its sensitivity, it allows reducing \( V_{ac} \) down to a few tens of mV while preserving a good potential resolution. It is also worth mentioning that, contrary to conventional amplitude-modulated KPFM, heterodyne KPFM is not affected by artefacts due to long-range electrostatic forces [16, 17]. This stems from the fact that the electrostatic force component at the origin of the lateral side bands is proportional to the second capacitance \( z \)-derivative (see the supporting information). In short, heterodyne-KPFM somehow combines the advantages of AM-KPFM and FM-KPFM (in terms of sensitivity and lateral resolution, respectively). Nothing, however, is perfect: by shifting the first side band at the second eigenmode, we deprive ourselves of mapping the capacitive variations with a second harmonic demodulation.

Before going any further, it can thus be helpful to perform a first characterization of the samples under consideration by ‘conventional’ FM-KPFM. In that case, we can rely on a dual harmonic demodulation to perform a simultaneous mapping of the surface potential and of the capacitance-related signal. In this work, the samples consist in MoS\(_2\) flakes grown by CVD on doped-silicon substrates, covered by a 150 nm thick thermal silicon oxide layer (figure 2(a)). The CVD process parameters have been set to obtain MoS\(_2\) monolayers. Basic topographic characterizations carried out by AFM in ambient conditions suggest that the TMD growth performed as expected. However, the effective stacking height deduced from these measurements (ca. 0.3 nm, see figure S1 in the supplementary information) is much lower the expected value for one MoS\(_2\) layer. This highlights the limitations of routine.

Figure 2. (a) Scheme of the samples (CVD-grown MoS\(_2\) flakes on SiO\(_2\)/Si) and experimental configuration. Both dc (\( V_{dc} \)) and modulated bias (\( V_{mod} \)) voltages are applied to the tip, the sample is grounded. KPFM data are presented as the tip dc bias (compensation potential, \( V_{tip} = V_{dc} = V_{KPFM} \)), that matches the surface potential (SP) ((b)–(d)). Topography, surface potential and capacitance second \( z \)-derivative images acquired by FM-KPFM. 2000 × 2000 nm, 300 × 300 pixels. \( V_{ac} = 620 \text{ mV}, \omega_{ac} = 1140 \text{ Hz} \).
AFM topographic characterizations, when investigating atomically flat 2D materials on SiO\(_2\).

Now, let us look at the flake thickness from the vantage of nc-AFM/nc-FM-KPFM imaging. The images in figures 2(b) and (c) display the topography and the surface potential of a representative area of the sample, where MoS\(_2\) flakes can easily be identified. The flakes display typical triangular shapes, and appear as dark patches (i.e. more negative) in the surface potential images. Interpreting that electrostatic contrast in terms of effective work function may not be straightforward, because the MoS\(_2\) domains have been grown on an insulator. It is enough to state that they appear as negatively charged.

As highlighted before, it is just as important, to put it mildly, to investigate the capacitance variations when moving the AFM tip from the SiO\(_2\) to the MoS\(_2\). The second harmonic channel image (figure 2(d)) confirms indeed that this parameter displays a significant change: it is much larger over the TMD flake. Consequently, the AFM tip undergoes a stronger attractive force, that the z-feedback loop compensates by retracting the tip away from the surface. Indeed, an effective stacking height of approximately 6 nm nanometers is deduced from the topographic image z-values histogram (not shown): this exceeds almost by one order of magnitude the value expected for one monolayer.

It is therefore absolutely imperative to reduce, as much as possible, the amplitude of the modulated bias. Now is the moment to take advantage of the heterodyne-KPFM capabilities. A series of images acquired with that mode on the same area than the FM-KPFM data is presented in figure 3.

![Figure 3. Series of images acquired in heterodyne-KPFM (2000 × 2000 nm, 300 × 300 pixels), for decreasing bias voltage modulation amplitudes. $w_{ac} = w_1 - w_2 \approx 394 \, 900 \, \text{Hz}$. (a), (c), (e), (g) Topography (b), (d), (f), (h) surface potential. (a), (b) $V_{ac} = 600 \, \text{mV}$. (c), (d) $V_{ac} = 400 \, \text{mV}$. (e), (f) $V_{ac} = 200 \, \text{mV}$. (g), (h) $V_{ac} = 50 \, \text{mV}$. (i), (j) Histograms of the images z-values for $V_{ac} = 600 \, \text{mV}$. (i) and $V_{ac} = 50 \, \text{mV}$ (j). (k) Black squares: MoS\(_2\) stacking height on SiO\(_2\) (deduced from z-histograms) as a function of $V_{ac}$. The open circle corresponds to the data obtained by FM-KPFM (shown in figure 2(b)). The red line shows the output of an adjustment of the data obtained by heterodyne-KPFM by a second order power law.](image-url)
During these experiments, the modulation bias amplitude has been progressively reduced (image per image) from a few hundreds of mV to a few tens of mV (four of six sets of data are displayed as images). The same colour scale has been used to map both topographic and potentiometric data, whatever the $V_{ac}$ value. It appears clearly that the apparent stacking height experiences a dramatic decrease when the modulation bias amplitude is reduced. In turn, the surface potential images display almost identical features (both in terms of potential levels and contrasts). This confirms—if it was needed—that the topographic dependence as a function of $V_{ac}$ is not related to an artefact in the surface potential compensation by the KPFM loop. Tip height histograms have been analysed for each image (two of them are shown in figures 3(i) and (j)), allowing to plot the dependence of the apparent stacking height as a function of $V_{ac}$. The data can be nicely adjusted using a quadratic equation, yielding a zero intercept value of $0.75\pm0.04$ nm. Doing so, one extrapolates the stacking height that would be measured in the absence of any perturbative electrostatic force. The interpolated value is fully consistent with what is expected for a single layer of MoS$_2$ in van der Waals interaction with the underlying substrate.

It is also worth mentioning that, even without performing a comprehensive analysis of the z-histogram $V_{ac}$-dependence, stacking height values below 1 nm would have been deduced from the data acquired with modulation amplitudes equal or below 100 mV (see figure 3(k)). Thus, in our case, working with low $V_{ac}$ would have been sufficient to confirm the monolayer nature of the MoS$_2$ flake. However, there is no assurance that fixing the modulation amplitude below 100 mV will always allow assessing the number of monolayers of any kind of TMD, stacked on any kind of oxide. Depending on the system under investigation, several parameters can indeed affect the tip-sample capacitance and how it varies when moving from the bare oxide to the TMD. To name just a few examples, there is every reason to believe that depending on the tip apex geometry, on the oxide thickness, and on the metallic, semiconducting or insulating nature of the TMD, the situation may differ.

In view of this, we need to go a step further. To do so, the only way is to remove all components of the electrostatic force during the topographic measurement (figures 1(c) and (d)). At first glance, this seems impossible: the tip-sample potential difference cannot be compensated if one does not use a modulated bias to measure it. It is however possible to overcome this apparent deadlock by performing the surface potential measurement and electrostatic force cancellation in a sequential manner. In a first step, the KPFM controller is operated in a standard manner. Once the compensation potential has been generated by the KPFM feedback loop ($V_{dc} = V_{KPFM}$), it is maintained to a fixed value by using a sample and hold stage. Then, it is possible to switch off the modulated bias (because the output of the hold circuit stays equal to the compensation bias). At this stage, since $V_{dc} = V_s$ and $V_{ac} = 0$, the electrostatic force has been totally cancelled. In practice, spectroscopic curves of the tip vertical displacement as a function of time are recorded in each image pixel.

The spectroscopic acquisition is synchronized with two pulse trains generated by an arbitrary waveform generator. The first pulse channel drives the sample and hold stage (built around an analogic LF198 circuit from Texas Inst.). The second channel controls the application of the modulated bias via an analogic multiplication stage (based on an AD835 4-quadrant multiplier from Analog Devices). Additional information can be found in the supplementary information (figure S2). Finally, it must be ensured that enough time is given to the topographic feedback loop to track properly the z-change after $V_{mod}$ switching off. The time-lapse during which $V_{ac} = 0$ ($\Delta r_1$ in figure 1(d)) is thus set to exceed the z-feedback time constant. Additional delays can be set at the beginning and the end of the spectroscopic sequence, in particular the first delay ($\Delta r_1$ in figure 1(d)) can be extended to improve the signal-to-noise ratio on the compensation KPFM potential ($V_{dc}$).

The performances of this electrostatic compensated z-spectroscopy have been put to the test on a second MoS$_2$ sample; here again the CVD-process was performed to obtain monolayers on SiO$_2$. As we shall see, however, this sample feature defects that can be used to illustrate furthermore the crucial need to perform a fully ‘electrostatic-compensated’ topographic imaging.

As before, it is preferable to carry out a preliminary scan in standard nc-AFM/FM-KPFM, the results of which are presented in figure 4. Here again, the surface potential is shifted towards more negative values and the capacitance second derivative signal is in overall higher over the MoS$_2$ domains. So, it is not surprising that once again, the TMD appear much thicker in the $z$-images than it should be. Despite these similarities, the topographic images show significant differences with respect to the ones recorded on the former sample. The domain tip and some areas at the periphery along the edges display indeed a lower effective height, which is correlated with a specific contrast in the capacitance signal. More precisely, these areas are characterized by lower $C''/z$ values, which account for the topographic contrast.

If not careful, one might be tempted in view of the topography to conclude that the MoS$_2$ flake is covered in its most part by a contamination layer. We will see, thanks to the outputs of electrostatic-free imaging that the opposite happens. Figure 5 displays the outputs of a first 2D $z$-spectroscopy scan, which has been performed in heterodyne-KPFM on rectangular area that spreads on both sides of the TMD edge (highlighted by dotted contours in figure 4). The first series of images (figures 5(a), (b)) correspond to the data acquired in the scan phase during which both the modulated bias ($V_{mod}$) and the compensation bias ($V_{dc}$) are applied (see figure 1(d)). The second series of images (figures 5(d), (e)) has been obtained from the matrix of spectroscopic curves (a selection of curves is shown in figures 5(g), (h)), by mapping the $z$ values (figure 5(d)) and tip compensation bias (figure 5(e)) values recorded during the time-lapse where $V_{mod} = 0$, and after allowing time to the AFM tip to reach a minimum $z$-level. During each spectroscopic acquisition, this time-interval falls between $t = 100$ ms and $t = 120$ ms, as shown in figure 5(g). Two curves acquired at different

Nanotechnology 34 (2023) 215705
A Arrighi et al
locations (over the TMD and over the bare substrate) are presented (figure 5(g)), along with a curve of the surface potential value (recorded over the TMD). It is easy to see that the relative z-level difference between both curves strongly decreases when the modulation bias is switched off. Accordingly, the topographic image contrast undergoes a dramatic change (compare figures 5(a) and (d)), while the surface potential channel (figure 5(b) vs figure 5(e)) stays almost perfectly constant; that is, the tip dc bias is fixed to the proper value by the sample and hold circuit when $V_{\text{mod}} = 0$. 

Figure 4. (a), (b), (c) Topography (a), surface potential (b) and capacitance second z-derivative $C'_z$ (c) images acquired by FM-KPFM on a second MoS$_2$-SiO$_2$/Si sample. 4000 × 4000 nm, 300 × 300 pixels. $V_{\text{ac}} = 1.1$ V, $\omega_{\text{ac}} = 1140$ Hz. The arrows labeled by greek characters highlight three different areas within the TMD domain. $\alpha$: apparent topographic level and capacitive signal (with respect to the bare substrate) similar to the ones of the former sample. $\beta$: ‘anomalous’ area with lower $C'_z$. $\gamma$: multilayer area. The dotted rectangle indicates the location of the area where a subsequent 2D z-spectroscopy will be performed (figure 5).

Figure 5. 2D z-spectroscopy on the second MoS$_2$-SiO$_2$/Si sample. The data have been acquired on the location delimited by dotted-contours in figure 4. (a), (b) Topographic (a) and potentiometric (b) images acquired during the scan with an active bias modulation (heterodyne KPFM, $V_{\text{ac}} = 500$ mV), 300 × 100 pixels. 1500 × 500 nm. (c) Histogram of the topographic image z-values with $V_{\text{ac}} = 500$ mV. Square (in the $\alpha$ area), triangle (in the $\beta$ area), circle (at the edge) and diamond (over the bare substrate) symbols indicate the correspondence between the Gaussian peaks and different sample areas. (d), (e) Topographic (d) and surface potential (e) images reconstructed from the 2D matrix of spectroscopic data for $V_{\text{mod}} = 0$. (f) Histogram of the topographic image z-values with $V_{\text{ac}} = 500$ mV. Square (in the $\alpha$ area), triangle (in the $\beta$ area), circle (at the edge) and diamond (over the bare substrate) symbols indicate the correspondence between the Gaussian peaks and different sample areas. (g) Spectroscopic curves of the tip height (g) and tip dc bias voltage (h). The data have been recorded at the locations highlighted by crosses labelled 1 (over the MoS$_2$ area) and 2 (over the SiO$_2$ substrate) in image (a). In (h), the dc bias curve is only shown for marker 1.
By carrying out an analysis based on the histograms of the z-levels, it turns out that the average stacking height of the TMD on the underlying substrate varies from ca. 3.5 nm when $V_{ac} = 500$ mV to ca. 0.8 nm when $V_{ac} = 0$ mV. For the sake of completeness, we also repeated a series of measurements following our first protocol, i.e. by recording a series of data for decreasing $V_{ac}$ values (see figure S3 in the supplementary information). The outputs of both experiments are fully consistent, but it is worth noting that in this case, reducing the bias down to 100 mV is not sufficient to reach a sub-nm stacking height value (see figure S3). As previously evoked, it turns out that the best measurements are achieved when the electrostatic force is fully suppressed.

The sub-nm stacking height value deduced from the data acquired under zero bias modulation confirms that, here too, the CVD process yielded in average a MoS$_2$ monolayer. However, we still have to understand what the origin of the odd topographic contrasts is (i.e. the contrasts observed under the influence of the dc electrostatic component). A careful examination of the data might provide a clue to understanding the nature of the phenomenon at play. As highlighted before, the MoS$_2$ flake displays specific features near its edges. In figure 5(a), the area highlighted by a triangle (‘β kind’ in reference to figure 4(a)) lies lower than the domain interior (‘α kind’, highlighted by a square), and the average z-level just at the edge (indicated by a circle) falls in between. Remarkably, the first two areas (α and β) become completely levelled when one performs the correct topographic height measurement (see figure 5(d), and compare z-histograms in figures 5(c) and (f)), and only a narrow band at the edge (red circle) continues to appear as a locally raised elevation.

As the last scan was performed on a restricted sample area, one might wonder if our last observation applies to the entire flake. A subsequent 2D z-spectroscopic mapping has therefore been performed on a larger scale (figure 6). The conclusion is clear: the topography is almost completely perfectly levelled when the electrostatic contributions are removed from the force field (i.e. identical topography over α and β areas). This unambiguously demonstrates that the whole flake is constituted by a single MoS$_2$ monolayer, except for a central multilayer area (labeled γ in figure 4), and for the protrusion at the flake edge (labeled by a red circle in figure 5(d), and highlighted by an arrow in figure 6(b)). A question then remains: what is the phenomenon at the origin of the contrasts observed on this sample in ‘standard’ nc-AFM/KPFM imaging? Some defects could be at play. CVD is well-established as a powerful technique to grow high-quality TMD monolayers, in particular MoS$_2$ [19–22]. However, it relies on a large number of experimental parameters (growth temperature, annealing and cooling rates, inert gas flux and pressure, type and amount of sulfur and metal precursors, substrate preparation, use or not of molecular growth promoters [23], furnace geometry, etc.). For each parameter, small perturbations can lead to drastic modifications in the properties of the grown TMD flakes such as shape, size, crystalline quality, doping and number of layers. Growth inhomogeneity not only concerns different batches, but most importantly, at the single synthesis level, significant flake-to-flake and intra-flake inhomogeneity are common. Typical defects include atomic scale defects (in particular sulfur vacancies) and grain boundaries [20, 21], charge fluctuations associated with the former defects and with trapped charges in the substrate, symmetry breaking at edges[24], oxidation sites [25], adsorbates, growth nucleation sites and/or multilayer areas, molecules intercalated between the TMD and substrate and mechanical strain [26]. Studies using Raman and photoluminescence mapping [21, 22, 25, 27–32] often report that
the edges and tips of crystalline TMD flakes behave differently from the core region. In particular, in CVD-based samples, it is well-established that mechanical strain resulting from the difference in thermal coefficient of the TMD and the substrate is a major cause of intra-flake inhomogeneity of the optical properties [27, 30–32]. This strain, accumulated during the cooling stage of the CVD synthesis, is differentially relaxed at edges, lips and grain boundaries. In addition, it is also well recognized that at the post-growth stage, water intercalates between TMDs and hydrophilic substrates [28] (such as the SiO2 used in this study).

In view of what precedes, interesting conclusions can be drawn. The ‘electrostatic free’ images (figure 6(b) and zoom in figure 5(d)) show that wherever within the flake (i.e. α or β area), the defects have a negligible impact on the real sample stacking height. It matches everywhere the sub-nm value expected from one MoS2 monolayer. Only the flake edges (red circle in figure 5(d)) continue to display an ‘extra’ corrugation in the absence of electrostatic artefacts. Although there is no definitive evidence, these last features may possibly be attributed to intercalated water at the SiO2/MoS2 interface, for the samples have been handled in air prior to invacuum measurements. One could also propose that the edges are decorated at the top surface by contaminants.

With regards to the flake interior, it seems much more unlikely that there is a huge amount of intercalated molecules, or chemical contaminants at the MoS2 surface. Again, this would go against the measured stacking height (ca. 0.8 nm everywhere in the ‘corrected’ mode). In turn, what our findings unambiguously show is that the effective conductivity displays significant variations. To make this clear, it is necessary to keep in mind that the tip-sample capacitance is modified by the 2D layer only if the MoS2 displays a certain level of electronic conductivity. To account for both the contrasts observed under the impact of the static electrostatic force component (higher C’α over α area resulting in a higher z-level, figure 6(a)), and for the homogeneous topographic level when the capacitance-related artefact is removed, we have to seek for a phenomenon that affect the local conductivity, but which impact on the stacking height is negligible.

An hypothesis amongst others could be that the flake periphery is partially oxidized (we here mean the parts corresponding to β areas, not to be confused with the edges). Consequently, it would display a lower conductivity, and act less efficiently as top ‘metallic’ electrode that enhances the effective tip-sample capacitance gradient. Yet to be definitely confirmed, the existence of a partial oxidation is also plausible, for the configuration of many kinds of oxidation sites is compatible with the absence of noticeable impact on the topography (off course we discuss here the ‘true’ topography, i.e. the one that is probed in the ‘electrostatic-free’ mode). For instance, it has been shown [18] that oxygen can exist as substitutional impurities on the MoS2 surface (as tentatively depicted in figure 6(c)).

However, at this stage, the ‘oxidation hypothesis’ is just tentative. Any other model that would allow justifying significant conductivity variations may be considered. For instance, it is well established that the density and spatial arrangement of sulfur vacancies can have a strong impact of the charge carrier mobility in 2D MoS2 [33]. Last, although beyond the scope of this work, we also underline that insight may be gained by achieving a controlled oxidation of CVD grown MoS2 samples [34].

Overall, investigating this inhomogeneous sample allowed us to exemplify how our approach not only solves the issue of accurate thickness measurement but can also help studying conductivity inhomogeneity in MoS2 flakes from a new perspective.

3. Conclusion

We have introduced a simple approach for artefact-free topographic measurements by nc-AFM/KPFM, based on the acquisition of spectroscopic curves of the tip-surface distance in close-loop configuration. Its implementation requires only using a few basic analog circuits to synchronously maintain the compensation bias and switch off the modulation voltage: it should also be easy to develop numeric counterparts directly integrated in last generation digital scanning probe microscope controllers. Like in the case of graphene [15], we have shown that conventional nc-AFM/KPFM measurements cannot assess correctly the stacking height of 2D TMD deposited on silicon-oxide substrates. This further highlights just how the variations of the tip-sample capacitance can affect the topographic measurement, despite the CPD compensation by the KPFM controller. Decreasing the modulated bias amplitude reduces the error, in that sense heterodyne-KPFM appears as a promising alternative to FM-KPFM, thanks to its higher sensitivity. However, as demonstrated, error-free measurements can only be performed if all components of the electrostatic force are removed. This warning is to be taken seriously by the community of researchers working with non-contact AFM under UHV. Indeed, the high quality factors under vacuum boost the cantilever sensitivity to electrostatic forces, and the electrostatic-induced topographic artefacts should accordingly be exacerbated. Our results also prompt us to be very careful when applying nc-AFM/KPFM to defect identification, since we have shown that the topographic contrast can counterintuitively be affected by the variations of the capacitive gradient. By cancelling the total electrostatic force, one can perform a z-regulation based on tip-sample interactions stemming only from van der Waals forces (as long as the nc-AFM is operated in a true non-contact regime). Beyond the case of single TMD monolayers, this ‘van der Waals force microscopy’ should become a tool of choice for the characterization of 2D van der Waals heterostructures, for their opto-electronic properties depend critically upon the number of layers stacked at the atomic scale, and the quality of the interfaces that they form with technological oxide substrates.
4. Experimental

Noncontact-AFM (nc-AFM) experiments were performed with a ScientaOmicron VT-AFM setup in ultra-high vacuum at room temperature. The scanning probe microscope is driven by a Matrix control unit (ScientaOmicron). Topographic imaging was realized in FM mode (FM-AFM) in the attractive regime, with negative frequency shifts of a few Hz and vibrational amplitudes of a few tens of nm. A dual channel lock in (7280, Signal Recovery) was used for FM-KPFM, while heterodyne-KPFM measurements were carried out with a numeric lock-in (MFLI, Zurich Instruments). Pt/Ir-coated silicon cantilevers (PPP-EFM, Nanosensors, resonance frequency in the 45–115 kHz range) were annealed in situ to remove atmospheric contaminants. The KPFM compensation voltage $V_{dc}$ was applied to the cantilever (tip bias $V_{tip} = V_{dc}$). The KPFM data are presented as $V_{dc}$ images also referred to as KPFM potential or surface potential images for simplicity.

MoS$_2$ domains were synthesized by chemical vapor deposition (CVD) as in [35], based on a process initially adapted from [20]. Briefly, sulfur and MoO$_3$ powders were annealed in a nitrogen flow within the quartz tube of a tubular furnace using their respective positions to adjust their temperature (in the 180 °C–220 °C and 700 °C–750 °C ranges for S and MoO$_3$ respectively). The Si/SiO$_2$ substrate, covered with a thin film of polyethylene-3,4,9,10-tetraacarboxylic acid tetrapotassium salt (PTAS) acting as seed promoter was placed at the same temperature as the MoO$_3$ source and kept at the maximal temperature for 10 min.

5. Contributions

BG implemented the z-spectroscopic mode, carried out the nc-AFM/KPFM experiments with AA, and analysed the data. The MoS$_2$ samples were CVD-grown by NU under the supervision of VD BG wrote the manuscript, with inputs from VD and NU for the CVD growth description and discussion of the defects.

Acknowledgments

Financial support by the Agence Nationale de la Recherche (France) with the Matra2D project (ANR-20-CE24-0017) is gratefully acknowledged. CEA-Licsen thanks Quentin Cogoni for his contribution to the MoS$_2$ synthesis during his internship.

Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

ORCID iDs

Aloïs Arrighi @ https://orcid.org/0000-0002-9774-852X
Nathan Ullberg @ https://orcid.org/0000-0002-7264-7992
Vincent Derycke @ https://orcid.org/0000-0002-3272-9694
Benjamin Grévin @ https://orcid.org/0000-0002-6494-8138

References

[1] Nonnenmacher M, O’Boyle M P and Wickramasinghe H K 1991 Kelvin probe force microscopy Appl. Phys. Lett. 58 2921–3
[2] Sadewasser S and Ch L-S M 2003 Correct height measurement in noncontact atomic force microscopy Phys. Rev. Lett. 91 266101
[3] Nörenberg T, Wehmeier L, Lang D, Kehr S C and Eng L M 2021 Compensating for artifacts in scanning near-field optical microscopy due to electrostatics Appl. Photon. 6 036102
[4] Okamoto K, Sugawara Y and Morita S 2002 The elimination of the ‘artifact’ in the electrostatic force measurement using a novel noncontact atomic force microscope/electrostatic force microscopy Appl. Surf. Sci. 188 381–5
[5] Naitou Y and Ogiso H 2011 Capacitive imaging of graphene flakes on SiO$_2$ substrate Japan. J. Appl. Phys. 50 066602
[6] Thakar K and Lodha S 2020 Optoelectronic and photonic devices based on transition metal dichalcogenides Mater. Res. Express 7 014002
[7] Ottaviano L et al 2017 Mechanical exfoliation and layer number identification of MoS$_2$ revisited 2D Mater. 4 045013
[8] Jin Y and Yu K 2021 A review of optics-based methods for thickness and surface characterization of two-dimensional materials J. Phys. D: Appl. Phys. 54 393001
[9] Nemes-Incze P, Osváth Z, Kamarás K and Biró L P 2008 Anomalies in thickness measurements of graphene and few layer graphite crystals by tapping mode atomic force microscopy Carbon 45 1435–42
[10] Shearer C J, Slattery A D, Stapleton A J, Shapter J G and Gibson C T 2016 Accurate thickness measurement of graphene Nanotechnology 27 125704
[11] Lee C, Yan H, Brus L E, Heinz T F, Hone J and Ryu S 2010 Anomalous lattice vibrations of single and few-layer MoS$_2$ ACS Nano 4 2695–700
[12] Lee H and Park J Y 2019 Height determination of single-layer graphene on mica at controlled humidity using atomic force microscopy Rev. Sci. Instrum. 90 103702
[13] Barboza A P M, Chacham H, Oliveira C K, Fernandez T F D, Ferreira E H M, Archanjo B S, Batista R J C, de Oliveira A B and Neves B R A 2012 Dynamic negative compressibility of few-layer graphene, h-BN, and MoS$_2$ Nano Lett. 12 2313–7
[14] Cowie M, Plougmann R, Benkirane Y, Schué L, Schumacher Z and Grütter P 2022 How high is a MoSe$_2$ monolayer Nanotechnology 33 125706
[15] Ritz C, Wagner, T and Stemmer A 2020 Measurement of electrostatic tip–sample interactions by time-domain Kelvin probe force microscopy Beilstein J. Nanotechnol. 11 911–21
[16] Sugawara Y, Kou L, Ma Z, Kamijo T, Naitoh Y and Li Y J 2012 High potential sensitivity in heterodyne amplitude-modulation Kelvin probe force microscopy Appl. Phys. Lett. 100 223104
[17] Axt A, Hermes I M, Bergmann V W, Tausendpfund N and Weber S A L 2018 Know your full potential: quantitative Kelvin probe force microscopy on nanoscale electrical devices Beilstein J. Nanotechnol. 9 1809–19
[18] Kc S, Longo R C, Wallace R M and Cho K 2015 Surface oxidation energetics and kinetics on MoS2 monolayer J. Appl. Phys. 117 135301
[19] Lee Y-H et al 2012 Synthesis of large-area MoS2 atomic layers with chemical vapor deposition Adv. Mater. 24 2320–5
[20] Najmaei S, Liu Z, Zhou W, Zou X, Shi G, Lei S, Yakobson B I, Idrobo J-C, Ajayan P M and Lou J 2013 Vapour phase growth and grain boundary structure of molybdenum disulphide atomic layers Nat. Mater. 12 754–9
[21] van der Zande A M, Huang P Y, Chenet D A, Berkelbach T C, You Y, Lee G-H, Heinz T F, Reichman D R, Muller D A and Hone J C 2013 Grains and grain boundaries in highly crystalline monolayer molybdenum disulphide Nat. Mater. 12 554–61
[22] Lee Y-H et al 2013 Synthesis and transfer of single-layer transition metal disulfides on diverse surfaces Nano Lett. 13 1852–7
[23] Ling X, Lee Y-H, Lin Y, Fang W, Yu L, Dresselhaus M S and Kong J 2014 Role of the seeding promoter in MoS2 growth by chemical vapor deposition Nano Lett. 14 464–72
[24] Yin X, Ye Z, Chenet D A, Ye Y, O’Brien K, Hone J C and Zhang X 2014 Edge nonlinear optics on a MoS2 atomic monolayer Science 344 488–90
[25] Gao J, Li B, Tan J, Chow P, Lu T-M and Koratkar N 2016 Aging of transition metal dichalcogenide monolayers ACS Nano 10 2628–35
[26] Najmaei S, Yuan J, Zhang J, Ajayan P and Lou J 2015 Synthesis and defect investigation of two-dimensional molybdenum disulfide atomic layers Acc. Chem. Res. 48 31–40
[27] Liu Z et al 2014 Strain and structure heterogeneity in MoS2 atomic layers grown by chemical vapour deposition Nat. Commun. 5 5246
[28] Zheng C, Xu Z Q, Zhang Q, Edmonds M T, Watanabe K, Taniguchi T, Bao Q and Fuhrer M S 2015 Profound effect of substrate hydroxylation and hydration on electronic and optical properties of monolayer MoS2 Nano Lett. 15 3096–102
[29] Lee Y, Park S, Kim H, Han G H, Lee Y H and Kim J 2015 Characterization of the structural defects in CVD-grown monolayered MoS2 using near-field photoluminescence imaging Nanoscale 7 11909–14
[30] Kataria S, Wagner S, Cusati T, Fortunelli A, Iannaccone G, Pandey H, Fiori G and Lemme M C 2017 Growth-induced strain in chemical vapor deposited monolayer MoS2: experimental and theoretical investigation Adv. Mater. Interfaces 4 1700031
[31] Kolesnichenko P V, Zhang Q, Yun T, Zheng C, Fuhrer M S and Davis J A 2020 Disentangling the effects of doping, strain and disorder in monolayer WS2 by optical spectroscopy 2D Mater. 7 025008
[32] Xin H, Zhang J, Yang C and Chen Y 2022 Direct detection of inhomogeneity in CVD-grown 2D TMD materials via K-means clustering raman analysis Nanomaterials 12 414
[33] Gali S M, Pershin A, Lherbier A, Charlier J-C and Beljonne D 2020 Electronic and transport properties in defective MoS2: impact of sulfur vacancies J. Phys. Chem. C 124 15076–84
[34] Kang S et al 2021 Enhanced photoluminescence of multiple two-dimensional van der waals heterostructures fabricated by layer-by-layer oxidation of MoS2 ACS Appl. Mater. Interfaces 13 1245–52
[35] Henrotte O, Bottein T, Casademont H, Jauwen K, Bourgetteau T, Campidelli S, Derycke V, Jousselme B and Cormut R 2017 Electronic transport of MoS2 monolayered flakes investigated by scanning electrochemical microscopy ChemPhysChem 18 2777–81