Advanced atomic force microscopy techniques V

Edited by Philipp Rahe, Ilko Bald, Nadine Hauptmann, Regina Hoffmann-Vogel, Harry Mönig, Michael Reichling
Cross-sectional Kelvin probe force microscopy on III–V epitaxial multilayer stacks: challenges and perspectives

Mattia da Lisca1,2,3, José Alvarez1,2,3, James P. Connolly1,2,3, Nicolas Vaissiere4, Karim Mekhazni4, Jean Decobert4 and Jean-Paul Kleider1,2,3

Abstract
Multilayer III–V-based solar cells are complex devices consisting of many layers and interfaces. The study and the comprehension of the mechanisms that take place at the interfaces is crucial for efficiency improvement. In this work, we apply frequency-modulated Kelvin probe force microscopy under ambient conditions to investigate the capability of this technique for the analysis of an InP/GaInAs(P) multilayer stack. KPFM reveals a strong dependence on the local doping concentration, allowing for the detection of the surface potential of layers with a resolution as low as 20 nm. The analysis of the surface potential allowed for the identification of space charge regions and, thus, the presence of several junctions along the stack. Furthermore, a contrast enhancement in the surface potential image was observed when KPFM was performed under illumination, which is analysed in terms of the reduction of surface band bending induced by surface defects by photogenerated carrier distributions. The analysis of the KPFM data was assisted by means of theoretical modelling simulating the energy bands profile and KPFM measurements.

Introduction
The development of photovoltaic (PV) technologies has progressed significantly over the past twenty years as a result of considerable advancements in solar cell engineering and material science. As a consequence, solar cells have turned into complex structures containing numerous layers and interfaces [1]. The capability to conduct local investigations at the nano-
scale level that provide information on the electrical properties of materials and along physical interfaces is becoming crucial for solar photovoltaic device efficiency improvement [2].

Electrical measurements based on scanning probe microscopy (SPM) allow for the analysis of two-dimensional (2D) features at the surface and along a physical cross section of nanoscale semiconductor structures. Among the wide variety of SPM techniques available [3], Kelvin probe force microscopy (KPFM) is an application of the atomic force microscope (AFM) for the evaluation of the surface potential with nanometric resolution. KPFM is a valuable investigative approach for the study of work functions via the measurement of the contact potential difference \( V_{\text{CPD}} \), that is, the difference between the electrostatic potential at the surface of the investigated structure and that of the KPFM probe [4].

KPFM has been extensively used in the PV field [5-7]; more specifically, by the analysis of interfaces in a solar device [8,9], it can reveal the presence of unintentional potential barriers or pn junctions, which hinder the extraction of the photogenerated charges. III–V-based solar devices belong to the PV technology of thin and ultrathin films in which layers with widths of the order of a few nanometres are often integrated for an optimal surface passivation or for better carrier extraction, considerably enhancing device efficiency [10,11]. Consequently, the experimental demonstration of the sensitivity of KPFM to the narrower layers can be crucial for the investigation and comprehension of local surface properties and charge transport mechanisms at interfaces [12].

Within this context, this work presents a study about the capability of cross-sectional KPFM for the study of a III–V multilayer stack under ambient conditions. In particular, we have investigated an InP/GaInAs(P) multilayer structure with layers of different widths and doping concentrations.

The first objective of this analysis is the evaluation of the spatial resolution of our KPFM setup under ambient conditions. The second objective is a full understanding of the \( V_{\text{CPD}} \) results combined with a description of the principal factors that affect KPFM measurements with the application of Kelvin probe (KP) numerical modelling. This enables the interpretation of the KPFM data, specifically to investigate the effect of space charge regions, surface defects, and illumination on \( V_{\text{CPD}} \) [13].

**Experimental**

**Sample preparation**

The structure of the studied sample is summarized in Table 1. This multilayer stack structure was epitaxially grown using a MOVPE process in an AIXTRON “Close Coupled Showerhead” reactor (6” × 2") at three different surface temperatures (580/600/640 °C). The n-type AXT substrate doping was typically in the range of \( 3 \times 10^{18} \) to \( 5 \times 10^{18} \) cm\(^{-3} \) with a thickness of 500 μm. Trimethylindium (TMIn), trimethylgallium (TMGa), phosphine (PH\(_3\)), and arsine (AsH\(_3\)) were the source materials, with hydrogen (H\(_2\)) as a carrier gas. Diethylzinc (DEZn) was used as a source of Zn for p-type doping the InP:Zn and the phosphorus-based quaternary (GaInAsP:Zn) and GaInAs:Zn layers. The precursor flow was varied to cover a doping level range from \( 1 \times 10^{18} \) cm\(^{-3} \) to \( 2.5 \times 10^{19} \) cm\(^{-3} \). The first part of the structure was used to measure the growth rate of the non-intentionally doped InP layers (InP:nid) at surface temperatures of 600 and 640 °C. The reflectance signal, monitored with an in situ Laytec EpiCurve TT tool, did not show any difference between the growth rates at the two surface temperatures, which were around 2.13 μm·h\(^{-1}\). The second part of the structure corresponds to the Zn calibration stack used for the p-type clad-

---

**Table 1**: Full structure of the investigated multilayer stack sample.

<table>
<thead>
<tr>
<th>Layer</th>
<th>Material</th>
<th>Doping concentration (cm(^{-3}))</th>
<th>Thickness (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>substrate</td>
<td>InP:S</td>
<td>((3-5) \times 10^{18})</td>
<td>500 μm</td>
</tr>
<tr>
<td>buffer</td>
<td>InP</td>
<td>nid</td>
<td>100</td>
</tr>
<tr>
<td>interlayer</td>
<td>GaInAs</td>
<td>nid</td>
<td>5</td>
</tr>
<tr>
<td>buffer</td>
<td>InP</td>
<td>nid</td>
<td>300</td>
</tr>
<tr>
<td>interlayer</td>
<td>GaInAs</td>
<td>nid</td>
<td>5</td>
</tr>
<tr>
<td>buffer</td>
<td>InP</td>
<td>nid</td>
<td>250</td>
</tr>
<tr>
<td>cladding</td>
<td>InP:Zn</td>
<td>(2 \times 10^{18})</td>
<td>500</td>
</tr>
<tr>
<td>cladding</td>
<td>InP:Zn</td>
<td>(1.50 \times 10^{18})</td>
<td>750</td>
</tr>
<tr>
<td>cladding</td>
<td>InP:Zn</td>
<td>(1 \times 10^{18})</td>
<td>500</td>
</tr>
<tr>
<td>transition</td>
<td>GaInAsP:Zn</td>
<td>(6 \times 10^{18})</td>
<td>20</td>
</tr>
<tr>
<td>contact</td>
<td>GaInAs:Zn</td>
<td>(2.50 \times 10^{19})</td>
<td>200</td>
</tr>
</tbody>
</table>
duling of the multiple quantum well-based structure. The doping concentration of the InP:Zn layers was varied from $2 \times 10^{18}$ to $1 \times 10^{19}$ cm$^{-3}$. The three Zn doping levels of InP layers were purposely inverted along the growth direction to facilitate electrochemical capacitance–voltage (ECV) characterization due to the strong Zn diffusion. The InP:Zn and the GaInAsP:Zn layers were epitaxially grown at a surface temperature of 600 °C. Note that the GaInAsP:Zn layer is an intermediate layer with a doping concentration of $6 \times 10^{18}$ cm$^{-3}$ with the purpose to smooth the InP:Zn/GaInAs:Zn transition bandgap and to reduce contact resistances. Finally, a GaInAs:Zn contact layer was made at a lower temperature of 580 °C in order to reach a higher doping level around $2.5 \times 10^{19}$ cm$^{-3}$.

Before starting the KPFM analysis, the sample was cleaved, and a surface cleaning was carried out to expose a clean cross section. We performed a chemical treatment based on sequential ultrasonic baths of acetone, ethanol, and deionized water. The sample was then placed in 1% HF solution for 30 s to etch the top oxide layer. This step was followed by a rinsing with deionized water and drying in air. This procedure was necessary for an optimal KPFM analysis since the presence of a native oxide surface layer on top can lead to the measurement of a misleading $V_{\text{CPD}}$ value [14].

**Kelvin probe force microscopy**

The following KPFM experimental procedures closely follow those described in [12]. KPFM evaluates the contact potential difference ($V_{\text{CPD}}$) between the surface of metallic and semiconductive samples and a conductive AFM tip, which at equilibrium can be related to the work functions as:

\[
qV_{\text{CPD}} = \phi_{\text{tip}} - \phi_{\text{sample}},
\]

where $\phi_{\text{sample}}$ and $\phi_{\text{tip}}$ are the work functions of the sample and of the tip, respectively [4]. The $V_{\text{CPD}}$ value is acquired by evaluating the DC voltage required to compensate for the electrostatic force generated between the tip and the sample, which, in turn, defines the KPFM signal [15]. KPFM was performed using a scanning probe microscopy system from AIST-NT (TRIOS platform) under ambient conditions and operated in the frequency-modulated KPFM (FM-KPFM) mode using a two-pass scanning mode, where the second pass was performed at a constant distance of 10 nm from the sample surface. Topographical data were collected on the first pass, whereas $V_{\text{CPD}}$ was measured during the second one. The schematic of our KPFM setup is depicted in Figure 1.

The FM-KPFM mode was chosen over the amplitude-modulation mode (AM-KPFM) since it is well known that it provides better spatial resolution. In particular, in AM-KPFM the electrical force between the tip and the sample is directly evaluated, whereas in FM-KPFM the gradient of the force is analysed. As a result, FM-KPFM is more sensitive to local tip apex–sample surface interactions; therefore, long-range electrostatic interactions of the cantilever are reduced, as well as the effect of parasitic capacitances [16]. Additionally, in FM-KPFM, surface potential measurements are less dependent on the lift-height tip–sample distance than in AM-KPFM since this mode is less sensitive to static offsets induced by capacitive coupling or crosstalk [17].

The laser beam deflection system in our AFM employs a laser wavelength of 1310 nm, which is well below the bandgap of our sample; therefore, the parasitic laser absorption, which may interfere with the KPFM measurement, is reduced to negligible levels [13]. Highly doped n$^+$-Si ARROW EFM tips (radius < 25 nm) with a conductive Pt/Ir coating at a resonance frequency of 75 kHz were used.

During KPFM measurements under ambient conditions, tip contamination is likely to occur because of pollutants that may be present on the sample surface causing a variation of $\phi_{\text{tip}}$ [18]. Hence, $\phi_{\text{tip}}$ was evaluated periodically in the course of the analysis using Equation 1 by measuring the $V_{\text{CPD}}$ value of a freshly exfoliated surface of highly ordered pyrolytic graphite (HOPG) with $\phi_{\text{sample}}$ being equal to 4.6 eV [19]. The successively measured $\phi_{\text{tip}}$ values showed only small variations with values ranging between 5.65 and 5.75 eV.

![Figure 1: Schematic diagram of the KPFM system employed in this analysis. While an ac + dc potential is applied, the KPFM tip scans across a surface. The ac signal is sinusoidal with a frequency that equals the mechanical resonance of the cantilever. The four-quadrant detector gives feedback in order to minimize cantilever oscillation modifying the dc signal providing the sample surface potential relative to that of the tip. Figure 1 was reproduced from [13] © 2019 C. Marchat et al., published by EDP Sciences, distributed under the terms of the Creative Commons Attribution 4.0 International License, https://creativecommons.org/licenses/by/4.0).](image-url)
KP FM measurements were performed under dark conditions and under illumination on the cross section of the sample. The acquisition of \( V_{\text{CPD/light}} \) enables the evaluation of the surface photovoltage (SPV), which is defined as the light-induced change of the contact potential difference at the surface of a photoactive material [20]. Since the surface potential of the tip is assumed to be unaffected by illumination, the difference between \( V_{\text{CPD/light}} \) and \( V_{\text{CPD/dark}} \) is equal to the change in surface potential of the sample between illumination and dark, which defines the surface photovoltage:

\[
\text{SPV} = V_{\text{CPD/light}} - V_{\text{CPD/dark}}.
\]  

(2)

It is important to mention that although KPFM is primarily a surface technique, the SPV can be sensitive to the presence of buried interfaces and/or deep charge trap states that may be present far from the surface in the bulk of semiconductors. Therefore, in our study the white light coming from the camera connected to the microscope was used. The white-light wavelength range is 400 to 700 nm, and for these wavelengths the penetration depth in GaInAs ranges between 10 and 100 nm. This makes our measurements mainly sensitive to the surface states and surface band bending. Additionally, a uniform illumination of the surface cross section was achieved thanks to the wide light spot.

Finally, the power density was 750 W·m\(^{-2}\) as measured by a thermal power sensor S401C from Thorlabs, which has a flat spectral response in the white-light range of wavelengths. This relatively low power density allows one to minimize the Dember effect since its contribution becomes significant only under high-injection conditions [20].

**KP modelling**

In order to analyse the experimental characterization, scanning KP simulation was performed using the ATLAS software from Silvaco Inc. [21], controlled by the in-house software KELSCAN [13], which evaluates the contact potential and surface photovoltage as a function of the position.

The Silvaco ATLAS model solves the Poisson equation self-consistently coupled to carrier continuity and transport equations in the well-known drift diffusion model, which is given detail in [22] and not repeated here for brevity. The solution presented in this work assumes ohmic contacts and, therefore, Dirichlet boundary conditions fixing potential and carrier concentrations at the boundaries, as reported in section 3.5 of the SILVACO ATLAS manual. The ATLAS module solves semiconductor transport and continuity equations numerically in two dimensions and includes flexible descriptions of bulk and surface defect distributions. KELSCAN simulates the experimental setup by sequentially moving the AFM tip across the surface of the sample, statically solving the semiconductor equations at each position, and then evaluating the contact potential at each position from the field distribution calculated by ATLAS and exported to KELSCAN.

In order to replicate the experimental conditions, the radius of the tip is set at 25 nm, the distance between the tip and the sample cross section is set at 10 nm, and the \( \phi_{\text{tip}} \) value is set at 5.7 eV, that is, the value measured on our tip as reported above. Note that KELSCAN allows one to simulate \( V_{\text{CPD}} \) measurements either under dark conditions or under illumination. In the case of “under illumination” simulations, the power density described in the above section was used.

KP FM is a surface technique; therefore, KPFM measurements are strongly influenced by the presence of surface defects. In order to provide a quantitative analysis of the experimental results, KELSCAN allows for the introduction of defects in a surface layer of arbitrary depth. The model of defects extending into the volume is physically more appropriate than a simpler two-dimensional surface distribution [23]. The introduced defect volume density of states (DOS), \( N(E) \) (eV\(^{-1}\)·cm\(^{-3}\)), is assumed to be homogeneous throughout the thickness of the defective layer, \( t_{\text{DL}} \), which we took equal to 1 nm. This can be translated into a surface density of states \( N_{\text{os}}(E) \) (eV\(^{-1}\)·cm\(^{-2}\)): \( N_{\text{os}}(E) = N(E) \times t_{\text{DL}} \), with \( t_{\text{DL}} = 1 \times 10^{-7} \text{ cm} \). In addition, the DOS consists of the sum of two distributions of monovalent donor and acceptor states, \( N_{\text{D}}(E) \) and \( N_{\text{A}}(E) \), respectively: \( N(E) = N_{\text{D}}(E) + N_{\text{A}}(E) \). These determine the charge neutrality level (CNL) of the surface defects. That is, when the Fermi level \( (E_F) \) at the surface coincides with the CNL, there is no net charge coming from the surface defects. In contrast, when \( E_F \) is above (below) the CNL, surface defects are overall negatively (positively) charged. Here, to illustrate the effect of the defects on the band bending and on the measured surface potential profile, we introduced a simple constant DOS for both donor and acceptor states. The CNL is thus easily deduced from the ratio of the constant donor and acceptor DOSs. If they are chosen equal, the CNL is set at mid-gap, whereas it is moved towards the valence (conduction) band if the ratio of acceptor to donor DOS is larger (smaller) than 1 [24].

**Results**

**KP FM cross-sectional investigation under dark conditions**

The cross section of the sample was first investigated by KPFM under dark conditions, immediately after the chemical cleaning step. The topography and the associated \( V_{\text{CPD}} \) image are reported in Figure 2a and Figure 2b, respectively.
Figure 2: KPFM measurement under ambient conditions on the surface cross section of the sample under dark conditions: (a) topography and (b) $V_{\text{CPD}}$ image. A vertical coloured bar is included to ease the identification of the different layers. The profile in (c) corresponds to the region identified by the dotted white segments in (b), each point of the profile (vertical) direction being an average of 207 points over a width of 0.7 μm along the $x$ axis. Several regions along the structure have been highlighted using different colours (see text). Two black arrows indicate the space charge regions at the interfaces of the InP:Zn region.

Note that the origin (0;0) is identified as a point in the InP substrate. Moving along the positive direction of the $y$ axis, one will reach the end of the sample, that is, the surface of the 2D wafer (e.g., around 3.09 μm in Figure 2). In order to achieve a successful KPFM analysis, a low surface roughness is essential to obtain high-quality images since surface inhomogeneities can cause a topographical image imprint on the surface potential image. With sufficiently low surface roughness, the topographic influence on the measurement is minor, and the observed contrast of the $V_{\text{CPD}}$ map is dominated by the surface potential such that topographic artefacts can be neglected.

A first look at the $V_{\text{CPD}}$ image and the extrapolated profile (Figure 2c) allows for a qualitative analysis. KPFM successfully detects the n-InP substrate (from 0 to 0.46 μm), the InP: nid/ GaInAs: nid region (from 0.46 to 1.12 μm), the InP:Zn region (from 1.12 to 2.87 μm), and the GaInAsP:Zn/GaInAs:Zn region (from 2.87 to 3.09 μm).

KPFM demonstrated a strong sensitivity on the local doping concentration as reported in a number of publications [12,25]. However, a clear identification of the 5 nm GaInAs: nid interlayers among the InP: nid buffer layers is not achieved in the $V_{\text{CPD}}$ image. Nevertheless, their presence was still detected and represented in the $V_{\text{CPD}}$ image by the dark and blue lines at 0.61 and 0.91 μm, respectively. The low resolution of the interlayers can be attributed either to their narrowness or to the experimental conditions since the two GaInAs: nid layers are well resolved in the topography image. Certainly, the width of these layers is narrower than the radius of the tip (<25 nm), and the operating conditions, namely the tip–surface distance and ambient measurements, negatively affect the resolution of KPFM measurements [26]. In particular, KPFM under ambient conditions is affected by the tip-averaging effect due to the long-range nature of the electrostatic force. The tip can sense multiple layers with different properties simultaneously, resulting in the detection of an averaged $V_{\text{CPD}}$ at the interfaces [27].

During KPFM measurements, the tip scans the cross section from the n-InP substrate to the end of the sample; consequently, it will sense the surface potential variation along the structure. The progression of the $V_{\text{CPD}}$ profile shows that four different slopes are present considering the region from the last InP: nid buffer layer to the GaInAs:Zn contact layer (from 0.86 to 3.09 μm). In particular, the first is located between the last InP: nid buffer layer and the first InP:Zn layer (from 0.86 to 1.17 μm), the second in the InP:Zn region (from 1.17 to 2.76 μm), the third between the last InP:Zn layer and the GaInAsP:Zn transition layer (from 2.76 to 2.87 μm), and the fourth between the GaInAsP:Zn transition layer and the GaInAs:Zn contact layer (from 2.87 to 3.09 μm). These regions have been identified with the colours red, green, blue, and light blue in the $V_{\text{CPD}}$ profile, respectively.

The green profile represents the InP:Zn region; because of the comparable doping concentration of the three InP:Zn layers, a
small variation of $V_{\text{CPD}}$ of the order of 20 mV is expected to be measured along this region. However, the experimental $V_{\text{CPD}}$ profile presents a $V_{\text{CPD}}$ variation of the order of 50 mV along the InP:Zn region (from 1.13 to 2.87 $\mu$m). Several factors can influence KPFM measurements leading to this experimental evidence, namely the sample preparation, the experimental conditions, and the presence of surface defects. All these aspects have an impact on the surface potential, as we will see in the Discussion section (“KPFM experimental conditions and sample preparation”).

Regarding the other slopes pointed out above, their detection is attributable to the formation of space charge regions among the different layers along the structure [28]. Specifically, the $V_{\text{CPD}}$ progression reflects the band bending present in the presence of depletion and accumulation regions. In particular, undoped InP crystals always contain different unintentional impurities due to the growth processes. The InP:nid layers fabricated at III–V Lab usually present an intrinsic n-type doping of the order of $10^{15}$ cm$^{-3}$, which results in shallow donor energy levels within the energy gap. Since the intentional Zn p-type doping concentration is much greater than this residual n-type doping present in the InP:nid buffer, the space charge region is expected to be located almost exclusively in the buffer layer.

Similarly, two Zn doping concentration gradients are present from the last InP:Zn layer to the GaInAsP:Zn transition layer (from $1 \times 10^{18}$ to $6 \times 10^{18}$ cm$^{-3}$) and from the GaInAsP:Zn transition layer to the GaInAs:Zn contact layer (from $6 \times 10^{18}$ to $2 \times 10^{19}$ cm$^{-3}$). This results in two space charge regions situated almost completely in the InP:Zn layer and in the GaInAsP:Zn transition layer, respectively.

It is worth to mention that the band bending induced by the different space charge regions along the structure depends on the doping concentration (e.g., number of involved charge carriers) and on the width of the layers. Consequently, the corresponding $V_{\text{CPD}}$ variation will depend on the same parameters [12].

In order to investigate the effect of the space charge on the measured $V_{\text{CPD}}$, we have implemented theoretical modelling to this work. As a first step, we have simulated through ATLAS/Silvaco software [21] the energy bands profile of the analysed structure in the ideal case in which no surface defects are considered, qualitatively reproducing the expected energy bands profile in our sample. The widths and doping concentrations of the layers were chosen as reported in Table 1, whereas the other physical parameters (e.g., energy gaps) are present in the Silvaco database [21]. Note that in order to simulate the InP:Zn region, we have specified just one Zn doping concentration of $1.5 \times 10^{18}$ cm$^{-3}$. Furthermore, in order to replicate the experiment, we have included a metal layer on the left of the n-type InP substrate. Under these conditions, the metal layer represents the contact between the sample holder and the n-type InP substrate. Finally, the work function of the metal was set to be equal to that of the substrate to guarantee an ohmic contact. The simulated energy bands profile confirmed our hypothesis showing the induced band bending along three space charge regions at the InP:nid/InP:Zn, the InP:Zn/GaInAsP:Zn, and the GaInAsP:Zn/GaInAs:Zn interfaces, as shown in Figure 3a.

![Figure 3](image)

**Figure 3:** (a) Cross-sectional profile at equilibrium of the surface band energies (black: valence band maximum, $E_V$, and red: conduction band minimum, $E_C$) along the structure assumed free of any surface defects. The constant Fermi level, $E_F$, is taken as the energy reference (blue horizontal line). (b) $V_{\text{CPD}}$ evolution along the same simulated structure obtained by KP modelling. Note that both figures present an inset detailing the InP:Zn/GaInAsP:Zn/GaInAs:Zn interfaces close to the external surface of the sample.
In particular, because of the low doping concentration of the InP:nid layer compared to the adjacent n-InP substrate and the InP:Zn region, a space charge extends over its complete width. The \( V_{\text{CPD}} \) profile across the InP:Zn/GaInAsP:Zn/GaInAs:Zn interfaces results from the different work functions. The work function of GaInAsP:Zn is slightly larger (by 0.04 eV) than that of InP:Zn, and it is substantially larger (by 0.22 eV) than that of the GaInAs:Zn contact layer, which leads to a decrease and an increase of potential, respectively. It is important to note that due to the narrowness of the GaInAsP:Zn transition layer (20 nm), the space charges at the two neighbouring heterojunctions overlap in this layer, leading to an asymmetric U-shape of the \( V_{\text{CPD}} \) profile. The asymmetric U-shape is also present in the experimental profile in Figure 2c (dark blue and light blue parts emphasizing the decrease and increase in potential, respectively). The mismatch of the conduction and valence bands between these materials then leads to the peculiar band energy diagram. Insets have been added to Figure 3a and Figure 3b to zoom in this region. Additionally, KP modelling [13] was used to simulate the \( V_{\text{CPD}} \) profile along the same structure assumed to be free of any surface defects for a quantitative evaluation of the effect of space charge on the surface potential (Figure 3b). \( V_{\text{CPD}} \) is proportional to the difference between the vacuum level and \( E_G \); therefore, the changes in the energy bands profile will be reflected in the simulated \( V_{\text{CPD}} \) profile.

The simulated \( V_{\text{CPD}} \) profile shows the same qualitative progression as the experimental profile reported in Figure 2c. However, several important differences can be noted by the comparison between the experimental and simulated \( V_{\text{CPD}} \). In particular, the experimental \( V_{\text{CPD}} \) profile (Figure 2c) seems to show that a part of the first space charge extends into the first InP:Zn layer (from 1.12 to 1.20 \( \mu \)m); similarly, the second space charge seems to extend more into the last InP:Zn layer than the modelling predicts (from 2.76 to 2.87 \( \mu \)m). These two regions are indicated by the two black arrows in Figure 2c. Additionally, the simulated \( V_{\text{CPD}} \) shows a flat profile a few nanometres inside the GaInAs:Zn contact layer, whereas a flat surface potential is not obtained experimentally. In other words, experimental surface potential variations occur over distances larger than one may expect solely from the extrinsic Debye lengths calculated from the nominal doping densities, which are only a few nanometres [29]. As a consequence, the lack of a sharp transition among the interfaces can cause difficulties in the identification of the position of the metallurgical junctions in the \( V_{\text{CPD}} \) image [28]. In particular, one reason can be found in the aforementioned tip-averaging effect: The tip still senses parts of the space charge in the InP:nid buffer layer and in the GaInAsP:Zn transition layer although being already on the first InP:Zn layer and on the GaInAs:Zn contact layer, respectively. Similarly, the tip starts to sense prematurely parts of the space charge inside the last InP:Zn layer. Furthermore, non-ideal abrupt junctions may contribute to this effect, for instance, because of dopant interdiffusion, as will be described in the following section.

Finally, the simulated \( V_{\text{CPD}} \) progression predicts an overall surface potential change of the order of around 1.34 V from the n-type InP substrate to the InP:Zn region. Conversely, this \( V_{\text{CPD}} \) variation in our experimental results is of the order of around 0.18 V. This is a first indication that the experimental surface potential is modified by the presence of surface states induced by surface defects since we know that KPFM is a surface technique and that the simulated \( V_{\text{CPD}} \) variation at this stage is based solely on bulk material properties and is not affected by any surface defects. Therefore, the experimental surface potential results to be less pronounced than in the “gedanken profile” that occurs far from the surface. This will be fully addressed in the Discussion section (“KPFM experimental conditions and sample preparation”).

KPFM cross-sectional investigation under illumination

In order to study the effect of the illumination on the sample cross section, we have performed KPFM measurements under white-light illumination. The topography and the associated \( V_{\text{CPD}} \) image are reported in Figure 4a and Figure 4b, respectively. The \( V_{\text{CPD/}} \text{light} \) image of Figure 4b shows a significant contrast enhancement due to the interaction with the light compared to \( V_{\text{CPD/dark}} \) of Figure 2b. As a consequence, \( V_{\text{CPD/light}} \) results to be more homogenous along the cross section than \( V_{\text{CPD/dark}} \), as shown in the corresponding \( V_{\text{CPD/light}} \) profile reported in Figure 4c. Moreover, the improvement of contrast also facilitates the identification of the narrower interlayers and of the position of the metallurgical junctions at the InP:nid/InP:Zn and the InP:Zn/GaInAsP:Zn interfaces, which were more undefined in the previous \( V_{\text{CPD/dark}} \) image.

Overall, the \( V_{\text{CPD/light}} \) profile follows the same evolution as the profile of \( V_{\text{CPD/dark}} \). In this case, four different \( V_{\text{CPD}} \) slopes are present in the profile. In particular, the first is located between the last InP:nid buffer layer and the first InP:Zn layer (from 0.83 to 1.25 \( \mu \)m), the second in the InP:Zn region (from 1.25 to 2.78 \( \mu \)m), the third between the last InP:Zn layer and the GaInAsP:Zn transition layer (from 2.78 to 2.85 \( \mu \)m), and the fourth between the GaInAsP:Zn transition layer and the GaInAs:Zn contact layer (from 2.85 to 3.07 \( \mu \)m). These regions have again been identified with the colours red, green, blue, and light blue in the \( V_{\text{CPD}} \) profile, respectively.

Notably, the \( V_{\text{CPD/light}} \) profile along the InP:Zn region between 1.25 and 2.78 \( \mu \)m is flatter compared to that of \( V_{\text{CPD/dark}} \). This \( V_{\text{CPD/light}} \) profile is more consistent with what the modelling
Figure 4: KPFM measurement under ambient conditions on the surface cross section of the sample under illumination: (a) topography and (b) $V_{CPD}$ image. A vertical coloured bar is included to ease the identification of the different layers. The profile in (c) corresponds to the region identified by the dotted white segments in (b), each point of the profile (vertical) direction being an average of 207 points over a width of 0.7 μm along the x axis. Several regions along the structure have been highlighted using different colours (see text). The black arrow indicates the space charge region at the InP: nid/InP: Zn interface.

predicts for such small variations in the Zn doping concentration along the InP: Zn region. Conversely, at the beginning of the InP: Zn layer, from 1.10 to 1.25 μm (indicated by the black arrow), the $V_{CPD}$ profile presents a steeper slope suggesting that the tip is still sensing the band bending induced by the space charge between the last InP: nid and the first InP: Zn layer. However, the tip-averaging effect alone cannot explain the detection of a space charge that extends for around 0.16 μm inside the first InP: Zn region. As a matter of fact, the diffusion of Zn impurities is likely to occur due to the high temperatures required for the growth of the material and the high diffusion coefficient of Zn in InP [30]. Therefore, the true spatial extent of the space charge region is not trivial to determine and may differ from what would be expected given the nominal structure of the sample. Conversely, the width of space charge region between the last InP: Zn layer and the GaInAsP: Zn transition layer is reduced and closer to the modelled one. Additionally, the detected surface potential change related to the space charge region at the GaInAsP: Zn/GaInAs: Zn interface is higher and closer to the simulation.

As described in the Experimental section (“Kelvin probe force microscopy”), the SPV can be calculated by applying Equation 2 to the experimental values of $V_{CPD/light}$ and $V_{CPD/dark}$. The SPV along the structure is reported in Figure 5.

The SPV progression along the structure shows an overall negative SPV. For highly doped semiconductors in the absence of surface states (or for surface state densities small enough so that they cannot introduce significant surface band bending) a SPV signal close to zero is expected to be measured [20]. We therefore expect a vanishing SPV signal in the highly doped n-type InP substrate, which is degenerately doped at $5 \times 10^{18}$ cm$^{-3}$ with respect to the InP effective conduction band density of states ($5.7 \times 10^{17}$ cm$^{-3}$ [31]). Experimentally the uncertainty on extracted SPV values can be evaluated at ±20 mV. Hence, the obtained value of around −10 mV in the highly doped n-type InP substrate is in good agreement with the theoretical expectation of vanishing SPV.

Furthermore, a negative SPV of around −95 mV is estimated for the InP: Zn region, which is consistent with the fact that a negative SPV is expected for a p-type semiconductor because of surface band bending due to surface states produced by surface
defects. In particular, the detection of a negative SPV implies that a downward band bending is present in the vicinity of the surface [32]; this aspect will be fully addressed in the Discussion section (“Effect of the illumination on the V$_{CPD}$”). Finally, it is worth mentioning that after illumination the initial conditions are restored, which excludes the presence of long-lived charge accumulation along the different junctions.

Discussion

In this section the principal factors that affect KPFM measurements will be addressed in order to develop a methodology of analysis and apply it to experimental results.

KPFM experimental conditions and sample preparation

Several factors can influence KPFM measurements, namely the experimental conditions and the status of sample surface and AFM tip. Additionally, as pointed out in the Results section (“KPFM cross-sectional investigation under dark conditions”), the presence of surface non-idealities (e.g., surface defects) has an effect on the surface potential and, thus, on the measured $V_{CPD}$. All these aspects can lead to surface inhomogeneities, which result in $V_{CPD}$ variations compared to an otherwise constant measurement on bulk material.

KPFM analysis was carried out under ambient conditions, which result in surface oxidation and in the adsorption of water molecules on the sample surface due to the humidity present in air [18]. Furthermore, a non-optimal deoxidation procedure may result in an inhomogeneous removal of the surface oxide. Additionally, the condition of the tip during the numerous scans along the sample cross section must also be considered. In particular, contamination of the tip is likely to occur due to pollutants (e.g., nano- and/or micrometre-size dust grains), which may be present on the sample surface leading to a variation of the tip surface potential.

The tip-averaging effect represents an important aspect of KPFM under ambient conditions, as revealed in the Results section (“KPFM cross-sectional investigation under dark conditions”). Even at extremely short tip–sample distances (5 nm), the tip-averaging effect can lower the lateral resolution as well as the measured KPFM signal [25]. This is especially evident in KPFM under ambient conditions, where typical tip–surface distances are of the order of tens of nanometres because of the vibrating tip amplitude necessary to achieve an acceptable signal-to-noise ratio.

Finally, it is well documented in the literature [20] that the cleavage procedure produces surface defects, which strongly impact the $V_{CPD}$. In order to study the effects of surface defects on the $V_{CPD}$, we have extended the energy band simulations to a non-ideal case in which constant distributions of acceptor-like and donor-like defects have been introduced at the surface, as described in the Experimental section (“KP modelling”). In order to clarify the analysis and focus on essentials, we have simulated a simpler structure with respect to the analysed multilayer sample, in which we did not include the 5 nm InGaAs:ni interlayers and the final InGaAs(P):Zn transition and contact layers. Specifically, we have compared the ideal structure free of surface defects to three different cases in which identical acceptor-like and donor-like surface defects densities of $1 \times 10^{12}$, $1 \times 10^{13}$, and $5 \times 10^{13}$ eV$^{-1}$cm$^{-2}$ (taken to be constant throughout the bandgap) were introduced at the surface. The results are reported in Figure 6. In this specific case, the charge neutrality level of surface defects is set at mid-gap. Thus, increasing the surface defect densities will produce a pinning of the Fermi level at the neutrality level of the surface states and the energy of valence and conduction bands will appear symmetric with respect to mid-gap position [24]. In particular, it is possible to observe this trend even at relatively low surface defects densities ($2 \times 10^{12}$ eV$^{-1}$cm$^{-2}$, see Figure 6b) in the InP:ni layer because of the low doping concentration ($1 \times 10^{15}$ cm$^{-3}$) compared to the other two layers. Conversely, in the n-InP substrate and in the InP:Zn layer, this trend is only well evidenced when high surface defects densities (above $10^{13}$ eV$^{-1}$cm$^{-2}$) are introduced at the sample surface; the trend is already visible for $2 \times 10^{13}$ eV$^{-1}$cm$^{-2}$ and really clear for $1 \times 10^{14}$ eV$^{-1}$cm$^{-2}$ in Figure 6c and Figure 6d, respectively.

Increasing the surface defect densities leads to an increase in the valence and conduction band energies within the n-InP substrate and to a decrease in the InP:Zn layer, so that the overall potential drop across the junctions is significantly reduced, from 1.42 V in Figure 6a to 0.15 V in Figure 6d. Specifically, to an increase of energy corresponds a decrease of surface potential, which reflects the upward band bending induced by the presence of surface defects. Conversely, a decrease of energy corresponds to an increase of surface potential, which reflects the downward band bending induced by the presence of surface defects.

We conclude that the presence of surface defects can explain the overall experimental $V_{CPD}$ variation along the structure that is less pronounced than in the simulated ideal case of a defect-free surface, as described in the Results section (“KPFM cross-sectional investigation under dark conditions”). This conclusion on the overall mitigation of the $V_{CPD}$ variation is not changed if we choose other surface defect density distributions (not constant vs energy) that produce different charge neutrality levels in the energy gap (which is not presented here for brevity).
However, large surface defect densities not only mitigate the overall change in $V_{CPD}$, but they are also responsible for strong changes in the shape of the surface potential. For instance, in Figure 6d the surface potential appears flat along the simulated structure with the exception of very narrow transition regions at the two layer interfaces. In other words, large surface defect densities also decrease the effective screening lengths compared to the ones calculated exclusively from the nominal doping densities, due to the extra charges directly provided by the surface states. The essentially constant flat profile in the InP:nid buffer layer strongly departs from the progressively decreasing profile observed experimentally in Figure 2c. In order to provide an explanation for the observed experimental profile that is both mitigated and progressively decreased in this buffer layer, it is necessary to decrease the surface defect density in the buffer layer, while keeping a very large value in the external n-InP substrate and p-InP:Zn layer. Therefore, the n-InP substrate and the p-InP:Zn layer require a high value of $N_{SS} = 1 \times 10^{14}$ eV$^{-1}$ cm$^{-2}$, whereas the InP:nid layer requires a lower value of $N_{SS} = 2 \times 10^{12}$ eV$^{-1}$ cm$^{-2}$. Furthermore, in order to provide a more quantitative explanation of the experimental profile of Figure 2c, the GaInAsP:Zn transition and GaInAs:Zn contact layers have been included again in the simulated structure ($N_{SS} = 1 \times 10^{14}$ eV$^{-1}$ cm$^{-2}$). The energy bands and surface potential profiles simulated with these parameters are shown in Figure 7.

The surface potential shown in Figure 7 is in good agreement with the experimental profile of Figure 2c. In particular, the potential drop from the n-InP substrate to the InP:Zn layer is comparable to the 0.18 V obtained experimentally. Additionally, the shape of the surface potential in the InP:nid layer shows a progressive change extending all over the InP:nid buffer layer. Finally, the GaInAsP:Zn transition and GaInAs:Zn contact layers are again consistent with the higher value of $N_{SS} = 1 \times 10^{14}$ eV$^{-1}$ cm$^{-2}$. In particular, the potential difference between the InP:Zn and the GaInAs:Zn contact layers is also attenuated with respect to the ideal case shown in Figure 3b.
in the experimental $V_{CPD}$ profile of Figure 2c. Overall, this approach demonstrates that the surface defect density variations provide good agreement with the experimental surface potential profile of Figure 2c.

In conclusion, a quantitative description of the accurate surface defects distributions that characterize the surface of semiconductors materials is a complex task as it is not always certain that surface defects are homogeneously distributed across the entire cross section. This is particularly true in our case since the several layers present different physical properties because of varying doping types and concentrations [33].

In order to overcome these challenges related to the operating conditions and to the cleaving process presented in this paragraph, KPFM measurements can be performed in ultrahigh vacuum (UHV) at an optimal surface–tip distance of the order of a few nanometres [34] with particular attention to the sample preparation either in the deoxidation and cleaving process.

**Effect of the illumination on the $V_{CPD}$**

In the Results section (“KPFM cross-sectional investigation under illumination”), we have pointed out the enhancement of contrast in the $V_{CPD}$ image under white-light illumination of the sample cross section. In particular, since the bulk lattice periodicity is interrupted at the surface of a cleaved semiconductor, surface reconstruction and formation of dangling bonds of surface atoms may occur, creating surface states within the energy bandgap. For instance, these surface states can pin the Fermi level and cause downward (upward) band bending from the bulk to the surface in a p-type (n-type) semiconductor in the case of the formation of a depletion (or inversion) space charge layer imposed by the charge neutrality condition [32,35].

By illuminating the sample, a SPV is generated by the drift and diffusion of photogenerated carriers towards the surface, which counteracts the defect-induced band bending energy variations [20]. As illustrated in Figure 8, in the case of downward surface band bending in a p-type semiconductor, photogenerated holes are repelled from the surface, while photogenerated electrons flow in the direction of the surface, balancing the positive charges corresponding to empty donor-type surface states. This results in a reduction of surface band bending and a decrease of surface potential, that is, a negative SPV.

Conversely, in the case of upward surface band bending in an n-type semiconductor, photogenerated electrons are repelled from the surface, while photogenerated holes flow towards the surface, balancing the negative charges corresponding to ionized occupied acceptor-type surface states, that is, a positive SPV.

As shown in Figure 5, an overall negative SPV was calculated along the structure, and a SPV of −95 mV was obtained in the InP:Zn region, which seems in good agreement with the expected trend in a p-type layer with surface defects. However, in case of pn junctions, the SPV can also include the contribution of the open-circuit voltage ($V_{OC}$) of the pn junction due to the splitting of the quasi-Fermi levels of electrons and holes and the related charge separation at the junction. In our case, because...
the n-type side of the junction (substrate) is grounded, we expect a positive SPV contribution from the $V_{OC}$ of the pn junction at the surface of the p layer outside the space charge region of the pn junction. Therefore, the SPV measured in the InP:Zn region should be a trade-off between the negative contribution due to the flattening of surface defect-related band bending and the positive contribution of $V_{OC}$. As a consequence, the slightly negative SPV value of $-95$ mV measured in the InP:Zn region indicates a weaker contribution of the pn junction ($V_{OC}$) compared to the change in surface band bending related to surface defects.

In order to provide a quantitative analysis of this experimental evidence, we have calculated the conduction and valence band energy shift induced by the illumination simulating two simple structures. The first one is metal/n-InP/air, the n-type InP simulates our n-type substrate with a doping concentration of $5 \times 10^{18}$ cm$^{-3}$, and the second one is metal/InP:Zn/air, with InP:Zn having a p-type doping concentration of $1.5 \times 10^{18}$ cm$^{-3}$, similarly to the p-doped layer in our sample. In these simulations, the back metal/InP contact was assumed to be ohmic in both structures. We introduced unequal donor-like and acceptor-like surface defect densities. Specifically, the donor-like defect density was chosen equal to $1 \times 10^{13}$ eV$^{-1}$cm$^{-2}$, and the acceptor-like was 20 times lower, $5 \times 10^{11}$ eV$^{-1}$cm$^{-2}$, resulting in a charge neutrality level very close to the conduction band of InP.

Under these conditions, a SPV close to zero and a negative SPV are expected for the n-type InP substrate and for the InP:Zn layer, respectively. The simulated results gave a SPV close to zero (very slightly positive) and a negative SPV of $-356$ mV for the n-type InP substrate and for the InP:Zn layer, respectively.

In this specific case, a $V_{OC}$ of 261 mV would have been produced across the pn junction considering the experimental SPV result of $-95$ mV. This surprisingly low $V_{OC}$ value could be explained either by a poor material quality of the sample, in which a high density of bulk defects is responsible for reducing the carrier lifetime, or by the lack of a true ohmic contact between the sample holder and the n-type InP substrate during the KPFM measurement. In the second case, a potential barrier would be present at the metal contact/n-InP substrate interface, which could reduce the overall $V_{OC}$. Nevertheless, these considerations need further investigations and further support from modelling.

Conclusion

In this contribution, it is shown that KPFM under ambient conditions is a valuable tool to investigate III–V multilayer stacks with high spatial resolution of down to 20 nm. The verified sensitivity of our KPFM setup to the narrower layers will be crucial for the study of the cross sections of operating solar device in future works.

The analysis of the surface potential profile identified the presence of space charge regions and, thus, the formation of several junctions along the stack. The complexity of the analysed structure combined with the ambient operating conditions caused challenges in the identification of the real position of the junctions in the $V_{CPD}$ image.

KPFM measurements are significantly affected by surface defects and other surface inhomogeneities. In particular, numerical modelling and analysis indicated that surface defects are responsible for a significant departure of the magnitude of the surface potential from the value in the bulk material. Also, we showed that the observed potential profile along the cleaved surface of the n-InP/InP: nid/p-InP:Zn heterojunction stack can be explained by large surface defect densities in the highly doped n-InP and p-InP:Zn layers, with a much lower defect density in the InP: nid buffer layer.

With further characterization and analysis, we have shown that white-light illumination reduces the surface band bending induced by surface defects, providing an enhancement of the contrast in the $V_{CPD}$ image. The analysis of the SPV variation along the structure cross section further suggests that either bulk defects or a non-ohmic contact between the metallic sample holder and the n-type InP substrate may exist. For future work, it will be necessary to assure a good ohmic contact between the sample holder and the sample and to carry out complementary characterization of the optoelectronic properties of the layers to refine the analysis of the results.

ORCID® iDs

Mattia da Lisca - https://orcid.org/0000-0002-1549-319X
Nicolas Vaissiere - https://orcid.org/0000-0003-3568-1670
Jean-Paul Kleider - https://orcid.org/0000-0003-4388-6326

References

Spatial mapping of photovoltage and light-induced displacement of on-chip coupled piezo/photodiodes by Kelvin probe force microscopy under modulated illumination

Zeinab Eftekhari1, Nasim Rezaei1, Hidde Stokkel1, Jian-Yao Zheng1, Andrea Cerreta2, Ilka Hermes2, Minh Nguyen1, Guus Rijnders1 and Rebecca Saive1

Abstract

In this work, a silicon photodiode integrated with a piezoelectric membrane is studied by Kelvin probe force microscopy (KPFM) under modulated illumination. Time-dependent KPFM enables simultaneous quantification of the surface photovoltage generated by the photodiode as well as the resulting mechanical oscillation of the piezoelectric membrane with vertical atomic resolution in real-time. This technique offers the opportunity to measure concurrently the optoelectronic and mechanical response of the device at the nanoscale. Furthermore, time-dependent atomic force microscopy (AFM) was employed to spatially map voltage-induced oscillation of various sizes of piezoelectric membranes without the photodiode to investigate their position- and size-dependent displacement.

Introduction

Light has been recognized as a versatile external energy source to actuate micro/nanorobots with outstanding merits of wireless, remote, and precise controllability [1-4]. Light-driven micro/nanorobots convert light into mechanical motion and are able to perform precise motion with high resolution. This offers promising possibilities for biomedical, environmental, and micro/nanoengineering applications [5,6]. Various types of design and actuation mechanisms have been developed in recent years [7,8]. A primary requirement to unlock the better performance of these micro/nano devices is to scrutinize their structure and the interaction between their different components. This can be done by high-resolution characterization techniques that simultaneously probe dynamic properties of different parts of the device. This enables the decoupling of the roles
of each function of the components on the overall motion behavior.

A variety of characterization techniques, such as white light interferometry, laser Doppler vibrometry (LDV), and double-beam laser interferometry (DBLI) have been used to determine the displacement of piezoelectric membranes [9,10]. However, the working principle of these techniques is based on optical interferometry mapping which can be challenging for light-sensitive devices. Furthermore, it can be advantageous to employ a method that also allows for mechanical contact and manipulation. Atomic force microscopy (AFM) [11-14] is a powerful and versatile technique to study fundamental and functional characteristics of materials and devices at the nanoscale, with application in physics, materials science, engineering, and biology. It can operate in either static (contact mode) or dynamic (tapping and noncontact mode) modes with atomic vertical resolution. In several studies, AFM has been used to determine photo-induced height/topography variation in organic–inorganic lead halide perovskites [15], nanosheets [16], and photosensitive polymers [17].

Kelvin probe force microscopy (KPFM), an electrostatic variant of AFM, can be used to measure contact potential difference (CPD) between the tip and the sample [18-20]. In particular, time-dependent KPFM [21-23] allows us to determine temporal changes of CPD and understand the dynamic behavior of functional devices at the nanoscale. Kelvin probe force microscopy in combination with illumination has been used to investigate photo-generated charge carriers of photovoltaic materials and devices. This is done by determining the CPD shift under illumination known as surface photovoltage (SPV) by calculating SPV = CPD_{light} − CPD_{dark}, whereas CPD_{dark} is the CPD in the dark and CPD_{light} is the CPD under illumination in that same location [24-27]. In some studies, KPFM has been employed for simultaneous study of structural and optoelectronic properties of materials and functional devices [28-30]. For example, the topography and SPV of illuminated photostrictive materials have simultaneously been examined through KPFM to determine the generated photovoltage and the following lattice change of the material [31].

Here, we present a KPFM study involving modulated illumination to investigate local height changes (vertical displacement) and the correlative SPV of the light-driven piezo/photodiode device over time. Employing modulated illumination enabled us to quantify precisely the device displacement due to improved signal-to-noise ratio, which could not be achieved by continuous illumination. The configuration of the hybrid piezo/photodiode device has previously been developed and reported by our group [32].

In further investigations, we used time-dependent AFM to determine the voltage-induced displacement of solely piezoelectric membranes without the photodiode. This experiment was performed to probe the local electromechanical properties of the piezoelectric membrane as a reference sample, which can reveal its contribution to the piezo/photodiode device.

Methodology
Sample fabrication
The device type-I employed in this study is a piezo/photodiode device, fabricated following a previously reported procedure [32], where the piezoelectric material, lead zirconate titanate (PZT), was integrated onto a silicon photodiode. The PZT layer was sandwiched between two lanthanum nickelate (LNO) electrodes and ultimately the backside of the silicon substrate was etched to enhance the motion of the membrane. More detailed information on the fabrication and cross-sectional scanning electron microscopy images can be found in [32]. The top view of the piezo/photodiode device is given in Figure 1a, where the inset represents the cross section of the device stack. Owing to the integration of PZT with silicon processing and operation at low voltages, this device can be actuated by either modulated illumination or electrical bias.

The device type-II used in this study had the same configuration as the device type-I only without the photodiode. A series of devices with different sizes were fabricated in which the active device dimensions were (7.6 × 7.6), (5.2 × 5.2), (2.8 × 2.8) and (1.4 × 1.2) mm² labeled as A, B, C, and D, respectively. In the process of fabrication, a 100 nm thick layer of LNO as the bottom electrode was first deposited, using pulsed laser deposition (PLD) technique, on a single crystal silicon wafer. Then, an 850 nm lead barium zirconia titanate (PBZT) and a 150 nm LNO as the top electrode were deposited. The wafer was patterned by a standard photolithographic process, starting with the application and patterning of the photoresist mask for defining the device areas. Subsequently, the excess PBZT and LNO were removed by a wet etching process with a diluted BHF:HNO₃:H₂O solution and a HCl solution, respectively. To avoid shunting of the device, a SiO₂ insulating layer was deposited. Patterned aluminum (Al) contacts which connect to the top and bottom electrodes of the PBZT were fabricated through a lift-off process. The fabrication was finalized by etching circular holes from the backside of the wafer to obtain thin membranes. The sizes of these holes were defined by applying and patterning a photoresist on the backside of the wafer, which was then anisotropically etched by deep reactive ion etching (DRIE) using SF₆, O₂, and C₄F₈ gases. This final step was carried out to minimize the clamping effect of the actuator on the silicon substrate, thus enhancing the movement of the membrane.
Figure 1: (a) Schematic illustrating the connection diagram of sideband KPFM measuring the piezo/photodiode device under modulated illumination. The top view of the device is shown where the inset represents the cross section of the device stack. (b) Time-dependent topography scan showing height variation under alternating illumination, and (c) corresponding time-dependent CPD under alternating illumination. (d) Temporal behavior of displacement and CPD obtained from averaging multiple linear profiles selected from b and c.
Kelvin probe force microscopy under modulated illumination

In this experiment, we used KPFM with modulated illumination to study device type-I, namely the piezo/photodiode device. The device was illuminated from the top surface using a laser diode at a wavelength of 628 nm. The light source was installed inside the AFM chamber, and the light beam was aligned towards the active area of the device. The illumination source was modulated by a square waveform voltage at an adjustable frequency, operated through a function generator (GWInstek, SFG-1013). Here, the selected modulation frequency was 1 Hz. It should be noted that the active area of the device stack of piezoelectric layer (PZT) and LNO electrodes is transparent and thus the incoming light from the top reached the Si p–n junction and generated electron–hole pairs, building a potential difference across the junction. The generated photovoltage was applied to the piezoelectric capacitor through the photolithographically defined contacts and induced mechanical displacement in the piezoelectric stack. Kelvin probe force microscopy was employed to measure the photoinduced voltage simultaneously with the displacement at the surface of the top LNO electrode as the bottom electrode was grounded. These measurements were performed with a Park Systems NX10 AFM microscope equipped with Pt/Ir-coated silicon probes (ARROW-EFM from nanoworld). Topographical measurements were performed in amplitude-modulated (AM) AFM. The KPFM measurements were carried out in single-pass sideband mode [33], which is a technique that detects electrostatic force gradients. The connection diagram of the sideband KPFM shown in Figure 1a illustrates multiple lock-in amplifiers employed to excite the cantilever both mechanically and electrically at the same time, and to retrieve simultaneously the amplitude and phase of the movement of the cantilever at different frequencies. The cantilever is excited at its mechanical resonance frequency ($f_0$) executed by the lock-in amplifier 1 and the generated topography signal is controlled by the Z feedback. A sinusoidal AC bias ($V_{AC}$) with drive of 1 V and frequency ($f_{AC}$) of 5 kHz is applied to the tip through lock-in 2, generating a signal with a frequency of $f_0 \pm f_{AC}$ near the cantilever resonance. Modulating the tip with $V_{AC}$ while the cantilever is oscillating near its resonance frequency leads to frequency mixing and intermodulation of the two frequencies ($f_0 \pm f_{AC}$) [34]. The lock-in amplifiers 2 and 3 are fed with the vertical deflection signal of the cantilever to measure the sideband signals at $f_0 + f_{AC}$ and $f_0 - f_{AC}$. Then, their average is used for the KPFM feedback to adjust the DC bias. If $f_{AC}$ is chosen to be small enough, such that the sideband peaks are close to $f_0$, the amplitude of these peaks will be enhanced by the mechanical resonance of the cantilever leading to a better signal-to-noise ratio. The feedback applies a DC bias ($V_{DC}$) matching the potential difference between the tip and the sample, which compensates for the electrostatic force. Therefore, the sidebands disappear. The value of $V_{DC}$ corresponds to the contact potential difference.

Measurements of modulated topography and CPD were conducted at the center of the membrane, where the AFM tip was positioned at a single point (zero scan size) to avoid any effect of the topography on the results. In conventional AFM images, each pixel represents the value of a specific signal relative to its position within a defined surface region. Herein, the acquired topography and CPD images shown in Figure 1b and Figure 1c were represented in the time domain. Therefore, the horizontal scale of the images indicates the time at which a given pixel has been acquired in one line, while the vertical scale indicates the temporal evolution of this timeline throughout the measurement process. These scans indicate the reproducibility of acquired displacement and photovoltage under modulated illumination at a single point. To analyze them, we extracted 10 line profiles depicted in blue and red for topography and CPD as a function of time, respectively. The average value of the peak-to-peak amplitude was calculated over the collectively selected profiles. The extracted profiles in Figure 1d were fit using a sinusoidal function in which their peak-to-peak amplitude represents the displacement and the photovoltage. The CPD profile in Figure 1d shows a 50 mV baseline in the dark, which can be attributed to the generation of charge carriers due to the stray light from the super luminescent diode (SLD) of the AFM. The wavelength of the SLD beam employed in the measurements is 830 nm, which can be absorbed by the Si photodiode and lead to a nonzero baseline. However, it does not affect the photovoltage as the peak-to-peak potential was calculated. Comparative measurements over a micrometric area of the sample were performed (see Supporting Information File 1). The CPD of a 1 $\mu$m$^2$ area at the center of the sample was measured in the dark, under continuous and modulated illumination, respectively. The obtained results indicate that the difference between CPD in the dark and under continuous illumination is similar to that under alternating illumination. It is important to note that the acquired photovoltage for the micrometric measurement is comparable to the locally measured photovoltage. However, we were not able to quantify precisely the displacement of the membrane by conventional imaging since a temperature-induced drift occurs under illumination. Therefore, we modified the method in the point scan mode.

The basic principle of our method lies in the acquisition of light-modulated CPD and vertical displacement at a single point on a two-dimensional grid to unveil the 3D motion of the membrane and the corresponding SPV map. To facilitate light alignment on the sample during measurements, we divided the active area of the device ($5.6 \times 5.6 \text{mm}^2$) into four quadrants. Initially,
one of the quadrants was subdivided into a grid consisting of 25 points with steps of 0.7 mm in both x and y directions, where the displacement and SPV of each point were recorded one after another. To ensure that the cantilever or the AFM head does not block the light from reaching the sample, the sample was manually rotated, and the measurement was performed on the second quarter of the device using the same procedure. As all four quadrants of the sample surface were mapped, the points located at the quadrant boundaries were measured twice during each rotation. Therefore, we took the average of the readout signals for each quadrant boundary. Lastly, all the acquired data for displacement and photovoltage of the four quadrants were stitched together and presented in color maps.

Time-dependent AFM to measure voltage-driven properties

In this experiment, we studied type-II devices (which do not include the photodiode), and the piezoelectric membrane was excited by an external bias. Time-dependent AFM was employed to determine the voltage-induced displacement of the piezoelectric layer. The AFM measurements were carried out in tapping mode, where the tip was located at a single point of the membrane. The external bias with an amplitude of 2.5 V and frequency of 2 Hz in a square waveform provided by the function generator was applied to the top and bottom Al contacts of the piezoelectric device. The height change of a specific point at the center of the membrane was recorded over time for the utilized voltage and frequency. We selected 10 line profiles from the modulated topography image, took the average over the selected lines similarly to the previous case, and fitted these with a sinusoidal function. The peak-to-peak value of the averaged and fitted data represented the displacement of the membrane for a given point. The cantilever was lifted and moved to the next point and the same measurement was performed. By this approach, spatial mapping of the active area was conducted for four piezoelectric actuators of varying sizes, namely A, B, C, and D. Only one-quarter of the devices were mapped, considering their symmetry. The experiment focused on studying the size-dependent displacement of these devices.

Simulations

We used COMSOL Multiphysics for the finite element method (FEM) simulations of our devices. Solid mechanics and electrostatics modules were coupled to facilitate the piezoelectricity calculations. As shown in Figure 2, the symmetry condition is used to reduce the computation cost of the simulations. Analogous to our AFM and KPFM experiments, the sample edges are fixed. Additionally, the effect of gravity on the displacement is taken into account. The voltage excitation signal is introduced to the LNO terminals as shown in the inset of Figure 2.

The material properties of PZT and LNO thin films were derived from the literature and are summarized in Table 1. The strain-charge form is employed for the piezoelectric material.

Results and Discussion

The optoelectronic and mechanical responses of the piezo/photodiode device (device type-I) measured by the KPFM technique are presented in Figure 3. As expected, the maximum displacement is obtained at points positioned at the center of the

Figure 2: Unit cell of the piezo/photodiode device as simulated in COMSOL.
Table 1: Properties of PZT [35,36] and LNO films [37]. Compliance matrix elements (elastic compliance constants, \(S_{ij}\)) and coupling matrix elements (piezoelectric coefficients, \(d_{ij}\)) have the units of \(1/T\text{Pa}^2\) and \(\text{pm/V}\), respectively.

<table>
<thead>
<tr>
<th>Material</th>
<th>Relative permittivity</th>
<th>Poisson's ratio</th>
<th>Elastic compliance constants</th>
<th>Piezoelectric coefficients</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>(S_{11})</td>
<td>(S_{12})</td>
</tr>
<tr>
<td>PZT</td>
<td>600</td>
<td>0.32</td>
<td>13.8</td>
<td>-4.07</td>
</tr>
<tr>
<td>LNO</td>
<td>(\infty)</td>
<td>0.27</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Figure 3: Device type-I corresponding color map of (a) light-induced displacement determined at each point of a predefined grid over the surface of the device. A total of 81 points on the surface active area of 5.6 × 5.6 mm² are mapped. The dashed black circle marks the hole etched on the back-side of the silicon substrate. (b) The surface photovoltage of each measured point. (c) Displacement normalized to the corresponding photovoltage at each point. (d) Simulation results of the same sample.

membrane with a maximum of 946 pm, while decreasing to a few picometers at the side edges. The decay of displacement from the center to the edge is expected from the clamping effect at the edges, where the Si substrate is thicker [38]. The measured CPD shift in Figure 3b indicates that the photovoltage stays nearly constant regardless of the scanned position, and is comparable with the open-circuit voltage \(V_{OC}\) of the photodiode (270 mV, measured by a multimeter). By inspecting the displacement and photovoltage color maps it is possible to confirm that the drum-like displacement of the device is due to the flexible center of the membrane and clamped edges, and it is not attributed to the variation of induced photovoltage. The simulation results of the same device (Figure 3d) confirm the shape and range of displacement mapping over the active area. It is instructive to note that ideally the measured photovoltage over the LNO contacts is equal to the \(V_{OC}\) of the photodiode. However, as can be seen in Figure 3b, this value varies between 100 and 232 mV. This can be attributed to multiple factors, including i) the resistance of the contacts, ii) damages to various points on the top LNO layer from previous measurements or the etching process and hence its lower conductivity, and iii) other factors such as improper light alignment or SPV underestimation by KPFM.

Figure 3c presents the mechanical displacement of the membrane normalized to the photovoltage. These values were ob-
Figure 4: Color map of the quarters of the surface area of device type-II, (a) A with dimensions of (7.6 × 7.6) mm$^2$, (b) B with dimensions of (5.2 × 5.2) mm$^2$, (c) C with dimensions of (2.8 × 2.8) mm$^2$, and (d) D with dimensions of (1.4 × 1.2) mm$^2$, where voltage-induced displacement is measured by AFM. The displacement is normalized to the corresponding voltage applied to each point. The measured displacement for each point is normalized to its corresponding voltage, shown in picometer per volt (pm/V). It should be noted that the upper limit of the color bars varies according to the maximal displacement value of each device. The maximal displacement is expected at the center of the device, which is the bottom-right corner of each color map. The expected bulging shape is observed for samples B and C shown in Figure 4b and c, respectively. The smallest sample (D) nonetheless shows a relatively uniform displacement, which can arise from the increased stiffness of the membrane as a result of its minuscule dimension (see Figure 4d). Based on the simulations [39], at an excitation voltage of 0.2 V, for active area values larger than $\simeq 6 \times 6$ mm$^2$, the gravitational force dominates the piezoelectric force, causing the membrane to “cave in” in the middle part. This is consistent with the observations in Figure 4. It can also be related to the backside etching of the substrate with poor selectivity, which can form undercuts, causing thinner edges than the central part of the membrane and restricting the movement of the membrane on top.

Figure 4a–d exhibits the spatial mappings of one-quarter of the voltage-driven piezoelectric actuators (device type-II) with different dimensions from large to small sizes, respectively. The backside etching of the silicon substrate is marked by the dashed line. The measured displacement for each point is normalized to its corresponding voltage, shown in picometer per volt (pm/V). It should be noted that the upper limit of the color bars varies according to the maximal displacement value of each device. The maximal displacement is expected at the center of the device, which is the bottom-right corner of each color map. The expected bulging shape is observed for samples B and C shown in Figure 4b and c, respectively. The smallest sample (D) nonetheless shows a relatively uniform displacement, which can arise from the increased stiffness of the membrane as a result of its minuscule dimension (see Figure 4d). Based on the simulations [39], at an excitation voltage of 0.2 V, for active area values larger than $\simeq 6 \times 6$ mm$^2$, the gravitational force dominates the piezoelectric force, causing the membrane to “cave in” in the middle part. This is consistent with the observations in Figure 4. It can also be related to the backside etching of the substrate with poor selectivity, which can form undercuts, causing thinner edges than the central part of the membrane and restricting the movement of the membrane on top.
smaller size. This may be due to the nonuniform etching of the backside of the sample and thickness variations. While with the presented characterization technique, we cannot fully conclude the reason for the deviation from the expected behavior, the results stress the importance of employing advanced, time-dependent spatial mapping characterization techniques for the development of novel nano/micro-actuators.

Conclusion
In this study, we demonstrated position-dependent, light-induced measurements of the displacement and photovoltage of a piezo/photodiode device. Kelvin probe force microscopy was employed to record topography and CPD concurrently which allows to distinguish optoelectronic and mechanical responses at the nanoscale. The measured displacements of the light-driven membrane are in good agreement with the simulation results. Moreover, time-dependent AFM was used to investigate position-dependent and size-dependent displacement of piezoelectric actuators driven by an electrical bias. Deviations from the expected membrane behavior stress the importance of advanced characterization methods for the design of novel nano/micro-actuators. The method presented here can offer remarkable opportunities to investigate the properties of devices driven with alternating light or bias voltage, properties of nanoscale mechanical systems, and combinations thereof. As one example, the time-dependent AFM technique in contact mode can be implemented to measure energy conversion efficiency by pressing the AFM tip with a defined counter force against the motion of the system. This allows us to calculate the work that the system is performing against the counter force and with knowledge of the input energy (e.g., absorbed light) the energy conversion efficiency can be determined.

Supporting Information
Supporting Information File 1
Additional figures.
[https://www.beilstein-journals.org/bjnano/content/supplementary/2190-4286-14-87-S1.pdf]

Acknowledgements
The authors thank Kai Sotthewes from the University of Twente for his advice.

Funding
This publication is part of the project Piezo-photomotion: light-driven nano piezo-propulsion and agitation with project number VI.Vidi.193.020 of the research programs Vidi and Aspasia, which is financed by the Dutch Research Council (NWO).

References


License and Terms

This is an open access article licensed under the terms of the Beilstein-Institut Open Access License Agreement (https://www.beilstein-journals.org/bjnano/terms), which is identical to the Creative Commons Attribution 4.0 International License (https://creativecommons.org/licenses/by/4.0). The reuse of material under this license requires that the author(s), source and license are credited. Third-party material in this article could be subject to other licenses (typically indicated in the credit line), and in this case, users are required to obtain permission from the license holder to reuse the material.

The definitive version of this article is the electronic one which can be found at: https://doi.org/10.3762/bjnano.14.87
Dual-heterodyne Kelvin probe force microscopy

Benjamin Grévin*, Fatima Husainy, Dmitry Aldakov and Cyril Aumaître

Abstract

We present a new open-loop implementation of Kelvin probe force microscopy (KPFM) that provides access to the Fourier spectrum of the time-periodic surface electrostatic potential generated under optical (or electrical) pumping with an atomic force microscope. The modulus and phase coefficients are probed by exploiting a double heterodyne frequency mixing effect between the mechanical oscillation of the cantilever, modulated components of the time-periodic electrostatic potential at harmonic frequencies of the pump, and an ac bias modulation signal. Each harmonic can be selectively transferred to the second cantilever eigenmode. We show how phase coherent sideband generation and signal demodulation at the second eigenmode can be achieved by using two numerical lock-in amplifiers configured in cascade. Dual-heterodyne KPFM (DHe-KPFM) can be used to map any harmonic (amplitude/phase) of the time-periodic surface potential at a standard scanning speed. The Fourier spectrum (series of harmonics) can also be recorded in spectroscopic mode (DHe-KPFM spectroscopy), and 2D dynamic images can be acquired in data cube mode. The capabilities of DHe-KPFM in terms of time-resolved measurements, surface photovoltage (SPV) imaging, and detection of weak SPV signals are demonstrated through a series of experiments on difference surfaces: a reference substrate, a bulk organic photovoltaic heterojunction thin film, and an optoelectronic interface obtained by depositing caesium lead bromide perovskite nanosheets on a graphite surface. The conclusion provides perspectives for future improvements and applications.

Introduction

Kelvin probe force microscopy (KPFM) is a well-known variant of AFM that allows probing at the nanoscale the electrostatic landscape on the surface of a sample by measuring the so-called contact potential difference (CPD). If one considers a simple junction formed by a metallic AFM tip and a metallic sample, the CPD originates from the tip-sample work function difference. More generally, the CPD stems from the existence of electric charges and/or dipoles in the system under consideration. As a result, the applications of KPFM are extremely broad. It is now used by physicists, chemists, and biologists to charac-
characterize the nanoscale electronic/electrostatic properties of an ever-expanding range of materials, interfaces, and devices, in ambient conditions, under ultrahigh vacuum, or at the liquid–substrate interface.

Since the early 90’s, a variety of approaches have been implemented to improve KPFM performances in terms of spatial, potentiometric, and temporal resolution. Several research teams continue to work in this direction and KPFM is still an evolving technique in many aspects. In particular, the development of KPFM-based approaches specifically designed to investigate photogeneration mechanisms and charge dynamics at the nanoscale in photovoltaic and optoelectronic materials is an active research area.

In photoassisted KPFM, the idea is to probe the surface photovoltage (SPV), which is the illumination-induced change in the surface electrostatic potential (i.e., the opposite of the CPD shift under illumination). To map the SPV, the most basic approach consists in performing a dual-pass experiment. Two CPD maps are recorded, the first in the “dark state” and the second under continuous wave (cw) illumination. An SPV image can eventually be recalculated as the difference between both sets of data [1]. The inherent drawback of this dual-pass method is that the source images used for the SPV calculation may feature misalignments, which is especially unavoidable at room temperature (RT) due to thermal drift [2,3]. Another issue is that some of the SPV components – related to dynamical processes – can remain hidden to this “conventional” SPV imaging [4].

To mitigate the effects of thermal drift, a first alternative consists in performing a data cube acquisition of CPD curves synchronously recorded with the application of a light pulse (i.e., a curve is recorded at each point of the surface along a 2D grid). Again, a differential SPV image can be reconstructed from the matrix of spectroscopic curves [5]. However, this approach is not free from artefacts, in particular the cantilever photothermal bending can significantly modify (depending on the optical power) the tip–surface distance during the spectroscopic measurement (which has to be performed in open z-loop).

Whenever possible, it is preferable to investigate the photoreponse of the sample under modulated or pulsed illumination. Provided that the modulation frequency of the light source is set high enough, it becomes possible to “stabilize” the static bending in a steady state, and photothermal cantilever excitation can be avoided (by setting the optical modulation at a frequency that differs from the cantilever resonance eigenmodes).

Working under modulated illumination also allows direct SPV measurements using special modulation/demodulation schemes, such as the one recently proposed by Miyazaki and co-workers for ac-bias KPFM [6]. In addition, most time-resolved KPFM modes developed so far rely on the use of a pulsed/modulated illumination chain. This is for instance the case of intensity-modulated KPFM [7-9], pump-probe KPFM [4,10,11], or G-mode KPFM [12], to name a few (we refer the readers to review articles for a more comprehensive introduction to AFM-based time-resolved potentiometric and electrostatic modes [13,14]).

Each of these approaches have advantages and disadvantages. Intensity-modulated KPFM implementation is straightforward, since it simply consists in analysing the frequency response of the time-average CPD under modulated illumination. Nevertheless, it is prone to capacitive artefacts [15]. Accurate quantitative measurements can be performed by pump-probe KPFM (pp-KPFM), with a time-resolution down to the sub-nanosecond scale [10]. However, pp-KPFM features a severely limited bandwidth. In the case of our last implementation of pp-KPFM [4], several tens of seconds (to minutes) are needed to record a single spectroscopic curve, and tens of hours to several days are needed to map a 2D matrix of data. Last, G-mode KPFM requires analysis of large datasets acquired with high-speed data capture [12].

A few years ago, Borgani and Haviland presented an interesting alternative for time-resolved SPV measurements [16], which consists in analysing the intermodulation products between the mechanical oscillation of the cantilever and the photogenerated surface potential. In short, intermodulation spectroscopy allows working in the frequency domain (instead of the time domain) by extracting, during a single measurement, quantities that are directly proportional to the Fourier coefficients of the time-periodic surface photovoltage. Unfortunately, the translation of this promising technique from ambient conditions – where it has proven its worth – to ultra-high vacuum poses significant challenges. This is mainly due to the enhanced quality factors under vacuum, which severely limits the frequency window available to increase the amplitude of the intermodulation products (for a more detailed discussion, see [14]).

In this work, we propose to approach the measurement of intermodulation products with non-contact AFM under ultra-high vacuum in a slightly different way. We demonstrate that the Fourier spectrum (modulus and phase coefficients) of the time-periodic electrostatic surface potential generated under optical (or electrical) pumping can be probed, by exploiting a double heterodyne mixing effect between the cantilever mechanical oscillation, the surface photovoltage harmonics, and an ac bias modulation signal. The frequency of the modulated bias
can be set so that any given spectral component of the surface potential (or intermodulation product) can be "transferred" to the second cantilever eigenmode. This transfer or rejection (i.e., a measurement of a Fourier harmonic at the pump frequency through a demodulation at the second eigenmode frequency) is achieved by using two numerical lock-in amplifiers in cascade, which allows the generation of proper phase-coherent combination of reference signals.

Dual-heterodyne KPFM (DHe-KPFM) dramatically enhances the sensitivity to "weak" (i.e., a few mV) surface photovoltage signals, thanks to the amplification by the second resonance mode. Time-resolved measurements can be performed in a lock-in amplifier. The attractive electrostatic force between the tip and the surface can be expressed as:

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

In the above equation, \( C'_z \) stands for the tip–sample capacitive gradient. \( V_{bias} \) represents the external bias voltage applied to the system (including both a dc and an ac component, see hereafter). The plus or minus sign applies if \( V_{bias} \) is applied to the tip (+ sign) or to the sample (− sign), respectively.

The lock-in output provides a modulated ac bias voltage (\( V_{ac} \), amplitude \( U_{ac} \), and angular frequency \( \omega_{ac} \)) that is added to the static dc voltage applied to the tip (or sample), \( V_{bias} = V_{ac} + V_{dc} \).

The electrostatic force displays modulated components, and some are directly proportional to the dc electrostatic potential term (i.e., \( V_{dc} \pm V_{CPD} \)). The idea is to demodulate such a component, and feed it into a loop which controls the dc bias. The KPFM controller (with a zero set point), will eventually adjusts the dc bias to minimize its input, yielding a measurement of the CPD (\( V_{dc} = \pm V_{CPD} \) depending on the setup geometry). In the following, the dc compensation bias provided to the tip by the KPFM controller (in our setup \( V_{dc} = - V_{CPD} \)) will be referred to as either \( V_{dc} \) or KPFM potential. To avoid repetition, this quantity is sometimes also referred to as "surface potential". This is obviously a misuse of language, as KPFM gives a relative measurement of the surface electrostatic potential with respect to that of the tip. However, it is partly justified because in our setup the compensation bias is applied to the tip. Then, provided that the effective work function of the tip remains constant during the measurement, any change in the KPFM compensation potential will strictly follow the change in the surface electrostatic potential without sign inversion (a local positive surface charging corresponds to a positive \( V_{dc} \) change).

Actually, there are many ways to perform the signal demodulation. Amplitude heterodyne KPFM, introduced in 2012 by Sugawara et al. [17], is a very elegant approach. It combines the advantages of frequency-modulated KPFM (FM-KPFM) and amplitude-modulated KPFM (in terms of lateral resolution and sensitivity, respectively). This mode takes advantage of heterodyning effects (frequency mixing) between the electrical bias modulation and the cantilever mechanical oscillation (usually performed at the first eigenmode, angular frequency \( \omega_0 \)). These effects result in the existence of additional modulated component of the electrostatic force (or sidebands) at frequencies \( \omega_0 \pm \omega_{ac} \). They stem from higher harmonic components in the capacitance term [16,18]:

\[ C'_z = K_0 + \sum_{n=1}^{\infty} K_n \cos(n \omega_0 t) = K_0 + K_1 \cos(\omega_0 t) + \ldots \]  

If we restrict ourselves to the first harmonic (\( n = 1 \)), electrostatic force components emerge (we just describe the first set of sidebands, other exist at \( \omega_0 \pm 2 \omega_{ac} \)) which are:

\[ F_{0_0+1_0ac} = \frac{1}{2} K_1 U_{ac} (V_{dc} \pm V_{CPD}) \left[ \cos\left(\left(\omega_0 - \omega_{ac}\right) t\right) \right. + \left. \cos\left(\left(\omega_0 + \omega_{ac}\right) t\right) \right]. \]
It can be shown [18], that the Fourier coefficient at \( n = 1 \) is proportional to the second \( z \)-derivative of the capacitance \( (K_2 = C''_z) \). Consequently, demodulating the amplitude of the sidebands gives access to a term that is proportional to the dc potential difference, and one works (like in frequency-modulation KPFM) on a signal that is proportional to the electrostatic force gradient (through \( C''_z \)). For that reason, this “side-band” KPFM is often referred to as a variant of FM-KPFM.

Amplitude-modulated heterodyne KPFM [17] further improves this approach. The idea is to set the modulated bias angular frequency so that the first right sideband \( (\omega_0 + \omega_{ac}) \) is “rejected” at the second mechanical resonance eigenmode (frequency \( \omega_1 \)) of the cantilever. Implementing this modulation/demodulation scheme is nowadays greatly facilitated by the flexibility offered by last-generation digital lock-in amplifiers, which allow generating (and demodulating) phase-coherent combinations of multiple oscillators (i.e., an excitation at \( \omega_{ac} = \omega_1 - \omega_0 \) and a modulation at \( \omega_1 \)).

Here, it is mandatory to stress a very important point. In all strictness, in the above, we should have written that \( \omega_{ac} = \omega_1 - (\omega_0 + \Delta \omega_0) \), where \( \Delta \omega_0 \) stands for the cantilever frequency shift due to the tip–surface interaction. In heterodyne KPFM, the reference sideband that drives the modulated bias is indeed generated as follows. The frequency of the first source signal (or lock-in internal oscillator) is set to \( \omega_0 \), ultimately it will be used for signal demodulation. The second source signal is obtained by tracking the cantilever resonance frequency at its first eigenmode \( (\omega_0 + \Delta \omega_0) \) with a second oscillator configured as a phase-locked loop (PLL). This tracking is necessary because the first mode is used by the main AFM controller for topographic control (in frequency modulation mode in the case of non-contact AFM under UHV). In other words, it is the AFM controller which generates the source signal at \( \omega_0 + \Delta \omega_0 \) which “excites” the mechanical oscillation of the cantilever. The frequency mixing effect will effectively generate a modulated electrostatic component at \( \omega_0 - \omega_1 \) – phase-coherent with the demodulation chain – only if and only if the frequency shift that the cantilever (at its first mechanical resonance mode) experiences in the tip–surface interaction is taken into account. In FM-AFM, it is impossible to perform a heterodyne-KPFM measurement by setting a “fixed” value for \( \omega_0 \).

### Dual-Heterodyne Kelvin Probe Force Microscopy: Principle

To understand how dual-heterodyne KPFM works, consider the case of a sample subjected to a time-periodic pump that generates a (time-)periodic electrostatic potential. Within the framework of investigations on photoactive materials, of course, the pump will consist of light pulses (in which case one generates a periodic SPV), but DHe KPFM experiments (as shown below) can also be performed under electrical pumping (by applying bias pulses directly to the sample with an arbitrary waveform generator).

The time-periodic electrostatic potential \( V_{mod} \) (or photopotential) generated at the sample under modulated illumination can be described by a Fourier series:

\[
V_{mod} = V_0 + \sum_{n=1}^{\infty} V_n \cos(n\omega_{mod}t + \phi_n) \tag{4}
\]

As in other KPFM modes, a combination of dc \((V_{dc})\) and ac \((V_{ac})\) bias is applied to the AFM tip. The total electrostatic force between the tip and the sample is now:

\[
F_{el} = \frac{1}{2} C''_z \left( (V_{dc} + V_{CPD}) + V_{ac} - V_{mod} \right)^2
\]

with \( V_{ac} = U_{ac} \cos(\omega_{ac} t) \)

Note that in the above, we assumed that the dc potential is applied to the tip (this actually corresponds to the configuration of our setup). \( V_{CPD} \) encompasses the “in-dark” electrostatic potential difference between the tip and the sample. The additional time-averaged shift due to the SPV is accounted for by the first term in the Fourier series \( (V_0) \). The harmonic terms \((n \geq 1 \text{ in Equation 4})\) contain all the information about the time dependence of the SPV. To prevent misunderstanding, it is important to stress that the amplitude spectrum (i.e., the \( V_n \) terms) should not be confused with the amplitude of the time-periodic SPV. Strictly speaking, the \( V_n \) terms correspond to the modulus of complex Fourier coefficients (see Supporting Information File 1). The reader is asked to keep this fact in mind when the \( V_n \) series will be referred to as the amplitude (modulus) spectrum in the following. Obviously, by linearity of the Fourier transform, each component of the “amplitude spectrum” (including the static term) is proportional to the amplitude (or magnitude) of the SPV. We will see later on how static (SPV magnitude) and dynamic (SPV decay time constant) images can be mapped by appropriately fitting the amplitude spectrum.

As with AM-heterodyne KPFM, there is a frequency mixing effect due to the capacitance term, and we restrict ourselves to the first harmonic to describe the time response of the capacitance gradient \( (K_1, \text{Equation 2}) \). Moreover, under periodic pumping, an additional frequency mixing process occurs due to the simultaneous existence of modulated potentials at \( \omega = \omega_{ac} \) and \( \omega = n\omega_{mod} \). In our case, the terms of interest are those resulting from the multiplication of \( V_{ac} \) by \( V_{mod} \) in Equation 5 (in
Before going further, we would like to note that the same result (i.e., Equation 8 and Equations 9–12) would have been obtained by first considering a frequency mixing effect between the mechanical oscillation at \( \omega_0 \) and the modulated components at \( n \omega_{\text{mod}} \), and then a second heterodyning process with the ac bias modulation. This may sound trivial, but considering things in this order may provide a useful way to visualise how harmonics can be “transferred” by properly setting the ac bias modulation frequency at the second eigenmode, as shown in Supporting Information File 1, Figure S4.

Demodulating the amplitude of the second eigenmode (at \( \omega_1 \)) gives thus a direct access to the Fourier coefficients characterizing the \( n \)-th harmonic component of the time-periodic electrostatic potential of interest. It is important to understand that, in practice, such demodulation can only be carried out if phase (time) coherence is maintained between all the signals throughout the modulation/demodulation chain. This requires the use of two numerical lock-in amplifiers in cascade, as shown in Figure 1.

As with AM-heterodyne KPFM, the first lock-in unit performs a combination of two signals to generate a reference at the frequency \( \omega_{\text{ref}} = \omega_1 - (\omega_0 + \Delta \omega_0) \). The frequency of the first source signal (or internal oscillator) is set to \( \omega_1 \), ultimately it will be used for signal demodulation. The second source signal is obtained by tracking the cantilever resonance frequency at its first eigenmode \( \omega_0 + \Delta \omega_0 \) with a second oscillator configured in a PLL configuration.

In conventional AM-heterodyne KPFM, the reference signal at \( \omega_1 - (\omega_0 + \Delta \omega_0) \) is used to perform the electrical excitation. In dual-heterodyne KPFM, it is instead used as an “intermediate” reference signal. It is subsequently fed to the external input of a second digital lock-in, which tracks it with a dedicated PLL. A second internal PLL is used to track a second reference signal generated by an arbitrary waveform generator at \( n \omega_{\text{mod}} \). Actually, this AWG unit generates two in-phase coherent signals. The first channel generates a square-waved modulation (period \( 2\pi/\omega_{\text{mod}} \), duty ratio fixed at the user convenience), which is used to pump the sample (via a digital modulated laser source, or a direct electrical connection to the sample for tests under electrical pumping). The second channel generates a sinusoidal reference signal at \( n \omega_{\text{mod}} \). The modulated bias voltage \( V_{\text{ac}} \) can then be generated by the second digital lock-in by performing a phase-coherent combination of the two reference signals at \( \omega_1 - (\omega_0 + \Delta \omega_0) \) and \( n \omega_{\text{mod}} \). Finally, the amplitude and phase of the second eigenmode are demodulated at \( \omega_1 \) by the first lock-in unit. The schematic diagram in Figure 1 shows how the modulation/demodulation chain is set up.
Figure 1: The implementation of DHe-KPFM. The real geometry of the sample stage (backside or front side illumination depending on the nature of the substrate) and the external optics differ from that of the simplified scheme. The cantilever is mechanically excited by the AFM control unit at its first eigenmode resonance frequency $\omega_0$, shifted by $\Delta \omega_0$ in the tip-surface interaction. The first lock-in unit performs a combination (or sideband generation) to generate a reference sine at $\omega_1 = (\omega_0 + \Delta \omega_0)$. The “intermediate” reference signal at $\omega_1 = (\omega_0 + \Delta \omega_0)$ is subsequently fed to the external input of a second digital lock-in. The second lock-in combines it with another reference sine signal generated by the arbitrary waveform generator (AWG, channel 2) at $n \omega_{mod}$. Then, a modulated bias $V_{ac}$ with an angular frequency $\omega_{ac} = \omega_1 - (\omega_0 + \Delta \omega_0) + n \omega_{mod}$ is generated at the lock-in output and applied to the AFM cantilever. NB: the configuration can be switched (software-controlled toggle of the modulation unit) between DHe-KPFM (DHe) and standard AM-heterodyne-KPFM (He). The AWG also generates the pump source signal (channel 1, i.e., a square-waved modulation with period $2\pi/\omega_{mod}$, duty ratio fixed at the user convenience). The time-periodic SPV displays multispectral components at the frequencies $n \omega_{mod}$ which stem from the dynamics of photoexcited states. Demodulating the normal force at $\omega_1$ yields access to the SPV $n$-th Fourier coefficients (amplitude and phase). Curves of the SPV Fourier spectrum are acquired by sequentially sweeping the output signal from the second channel of the AWG (i.e., $n \omega_{mod}$ with $n = 1, n = 2, n = 3$, etc.). This is achieved by playing a pre-programmed list of waveforms, triggered by TTL pulses generated by the AFM controller.

To sum up, DHe-KPFM allows a selective demodulation of the Fourier coefficients $(V_n, \Phi_n)$ of the periodic electrostatic potential generated at the sample surface under a modulated pump.

The first and most straightforward application consists in mapping a selected component (such as the first harmonic $n = 1$) to obtain a set of images (amplitude/phase) directly related to the SPV generated under modulated/pulsed illumination. Series of images can be acquired for different pump parameters (period and duty ratio), providing a first approach to check the nature of the SPV dynamics. Compared to previous “modulated” SPV imaging techniques, dual-heterodyne KPFM provides an enhanced sensitivity (as demonstrated in the following), thanks to the amplification of the intermodulation products by the second resonance eigenmode.

In addition, alike intermodulation spectroscopy [16], time-resolved measurements can be performed by DHe-KPFM by recording several harmonics of the SPV signal. To that end, we implemented (as detailed hereafter in the “DHe-KPFM implementation” section) a spectroscopic variant which allows recording onto 2D grid curves of the Fourier coefficients $(V_n, \Phi_n)$ as a function of the harmonic number.

As far as the phase is concerned, two points should be stressed. The first is trivial: depending on the sideband used for rejection, a $+$ or $-$ sign must be applied after demodulating the signal (intermodulation products have a phase of $\pm \Phi_n$, see Equation 8). More importantly, the phase measurement is relative, since the demodulation chain introduces an arbitrary phase shift with respect to the “zero” phase of the average component of the
modulated SPV ($V_0$ in Equation 4). To solve that issue, we added a refinement which consists in “switching” (during a selected time window of the spectroscopic sequence) the sideband generation to the standard AM-heterodyne KPFM scheme (i.e., $\omega_{ac} = \omega_1 - (\omega_0 + \Delta \omega_0)$ instead of $\omega_{ac} = \omega_1 - (\omega_0 + \Delta \omega_0) + n\omega_{mod}$ when working with the $4n$-th sidebands). In this configuration, the demodulated component yield access to the “dc” Fourier coefficient $V_0$ and to the reference phase shift $\phi_0$.

Compared to intermodulation spectroscopy [16], our approach has the disadvantage of being “sequential” in the sense that the Fourier components are measured one after the other and not during the same acquisition time window. However, it offers interesting advantages. First, the sideband rejection at the second eigenmode ensures that the transfer function remains exactly the same regardless of the measured harmonic. This allows a quantitative measurement of the Fourier components without the need for cantilever transfer function calibration. More importantly, there is virtually no limit to the number of harmonics that can be probed and the time resolution, other than that imposed by the maximum modulation/demodulation frequencies allowed by the lock-in units and the AWG. Last but not least, DHe-KPFM can be implemented on a non-contact AFM operating under ultra-high vacuum, where the high resonance quality factors should now become an advantage and provide greater sensitivity. In the next section, we will provide some details on the technical implementation of DHe-KPFM on an nc-AFM. We will then demonstrate its ability to detect weak SPV signals and perform time-resolved measurements.

Before ending this section, two final remarks should be made. DHe-KPFM is an “open loop” variant of KPFM. It does not rely on the application of an “active” compensation bias to probe the electrostatic potential of the sample. It yields a measurement of the Fourier spectrum of the time-periodic surface potential, which may be in principle used to reconstruct the signal in the time domain. However, in the current version of our implementation, this retro-conversion process from the frequency domain will only provide data that are proportional to the surface potential (or photopotential). This stems from the fact that the tip–sample capacitance second derivative $C''_{xz}$ ($K_1$ term in Equation 8 and Equations 9–12) remains unknown. In principle, alike in the case of dual-harmonic KPFM [19], it should be possible to perform a quantitative measurement of $C''_{xz}$ by employing a complementary demodulation scheme. For that purpose, one would need to reject at the second eigenmode another set of sidebands ($\omega_0 \pm 2\omega_{ac}$). This point – beyond the scope of the current study – will be the subject of a forthcoming work. In the remainder of this article, for the sake of brevity, we will omit to systematically recall that the measurement of the amplitude coefficients is performed within a multiplication by the factor $K_1$. We will write $V_n$ instead of $K_1 \times V_n$.

The amplitude spectrum data will be given in mV (instead of arbitrary units), as they correspond to the demodulated amplitudes at the output of the locking device. However, once again, a confusion should not be made between these amplitudes (modulus) values and the SPV amplitude itself.

The second comment is also related to the fact that DHe-KPFM is an open variant of KPFM. It cannot be used for an active electrostatic compensation. However, as in the case of pump-probe KPFM [4,10], it is possible to use a second additional FM-KPFM loop which cancels the “time-averaged” dc part of the potential. This feature will not be used in this work, but its implementation has been validated. In the schematic (Figure 1), the dc bias applied to the tip represents the compensation bias of this second loop (it also has its own modulated bias, which is not shown in the schematic). As with pump-probe KPFM, there is no crosstalk between the two modulation/demodulation units because their operating frequency ranges are far apart. In FM-KPFM, the bias is modulated at a few kHz, while in the double-heterodyne scheme, much higher frequencies are used for electrical excitation. This spectral range difference also holds true for signal demodulation, which is performed at a few kHz for the FM-KPFM loop and hundreds of kHz (demodulation at the second eigenmode) for its heterodyne counterpart.

**Dual-Heterodyne Kelvin Probe Force Microscopy: Implementation**

Non-contact AFM (nc-AFM) and KPFM experiments are performed with a VT-beam AFM system (Sciencta-Omicron) at room temperature (RT) under ultra-high vacuum (UHV), driven by a Mitea scanning probe microscope (SPM) controller (SPECs-Nanonis). Topographic imaging is performed in FM mode (FM-AFM) in the attractive regime, with negative frequency shifts of a few Hz and vibration amplitudes of a few tens of nm. All experiments were performed with Pt/Ir coated silicon cantilevers (PPP-EMF, Nanosensors, resonance frequency in the range 45–115 kHz), annealed in situ to remove atmospheric contaminants.

The dual-heterodyne KPFM mode was implemented by combining the SPM unit with two digital lock-ins from Zurich Instruments (lock-in 1: MFLI, lock-in 2: HF2LI). Both are equipped with multiple oscillators, control loops, PLLs, and modulation modules (2 for the HF2LI). The MFLI modulation module is used to generate the intermediate reference signal with an angular frequency of $\omega_1 - (\omega_0 + \Delta \omega_0)$. The reference sidebands for the electrical excitation ($V_{ac}, \omega_{ac}$) are generated by the HF2LI modulation module. As aforementioned, different series of sidebands can be used to probe the signal Fourier spectrum. In this regard, it should be noted that a 180 phase...
shift is added by the HF2LI to its output \( (V_{ac}) \) if one uses the left sideband (with respect to the carrier, as defined in the HF2LI modulation module) instead of the right one. In our case, this additional 180 phase shift is taken into account when the \( n \_1 \) sidebands are used instead of the \( n \_4 \) ones.

The pump (modulated square wave with an adjustable duty ratio and period \( 2\pi/\omega_{mod} \)) and the harmonic reference (sine, angular freq. \( n \times \omega_{mod} \)) are generated by a Keysight 33600 A arbitrary waveform generator. The maximum frequency for the sine signal is 120 MHz, 50 MHz for a square wave with a duty ratio of 25%. On its part, the HF2LI unit can handle signals up to 50 MHz. In principle, these combined features allow up to approximately 10 harmonics to be sampled with a base pump period as small as 200 ns \((10 \times \omega_{mod}/2\pi \sim 50 \text{ MHz})\). It should be noted, however, that other factors may limit measurements at high frequencies (e.g., attenuation of the ac signals transmitted to the cantilever).

Time-resolved measurements are performed by recording curves of the demodulated Fourier components of the time-periodic surface potential \( (V_n, \Phi_n) \) as a function of the harmonic number \((n)\). This is done by sequentially sweeping the output signal from the second channel of the AWG (i.e., \( n \omega_{mod} \) with \( n = 1, n = 2, n = 3 \), etc.). To that end, a pre-programmed list of waveforms is played, and the triggering is done by TTL pulses generated by the AFM controller. The AWG waveform playlist is programmed by using the Keysight benchlink pro software, and the TTL pulses are generated during the course of the spectroscopic ramp by using a user-available high speed digital output of the Mimeo unit.

To measure the “dc” components of the Fourier spectrum \( (V_0 \text{ and the reference phase } \Phi_0) \), the sideband generation is switched during a dedicated time window within the spectroscopic ramps (i.e., from DHe-KPFM to standard AM-heterodyne KPFM configuration). To do so, a Python routine is used to toggle the output configuration of the HF2LI modulation module (see Supporting Information File 1), as a function of a trigger signal sent by the Mimeo unit. The full phase spectrum \((\Phi_n)\) is eventually reconstructed by shifting the data set from \( \Phi_0 \) \((n, 4 \text{ sidebands})\) or \( \Phi_0 + 180^\circ \) \((n, 1 \text{ sidebands})\).

An external fibre-coupled laser source (Omicron Laserage, PhoxX+ at 515 nm) was used for sample illumination through an optical viewport of the UHV AFM chamber. Samples can be illuminated either from the front or from the back using sample holders with on-board mirrors [3]. The latter configuration is used in the case of organic BHJ thin films (processed on transparent substrates, i.e., glass coated with indium thin oxide). The light intensity is adjusted using the laser power control and optical density filters. In the following, for each measurement, the optical power \( P_{opt} \) (maximum pulse intensity in the case of experiments under modulated illumination) is given in the corresponding figure caption. The \( P_{opt} \) value is roughly defined per unit area, taking into account the diameter of the laser beam (approximately 1 mm) and the angle of the optical beam with respect to the plane of the substrate.

**Results and Discussion**

**Dual-heterodyne Kelvin probe force microscopy under electrical pumping: benchmarking**

Similar to the case of pp-KPFM [11], we tested this new implementation by performing DHe-KPFM measurements under electrical pumping on a highly oriented pyrolytic graphite substrate (HOPG). For these tests, the sample was electrically connected to the AWG (channel 1 in Figure 1) by mounting the HOPG substrate onto a sample holder designed with in situ electrical contacts [11]. The results of four measurements with different pump signals are shown in Figure 2. In all cases the pump period was fixed at 100 µs, and the pump shape illustrates a textbook case in the field of Fourier transforms (the Fourier coefficients for all waveforms are derived in Supporting Information File 1).

The results of the first two measurements alone would be sufficient to demonstrate the ability of DHe-KPFM to probe the Fourier spectrum of the time-periodic electrostatic surface potential. The pumps consisted of a square wave with a 50% duty ratio (Figure 2a) and a saw-tooth (Figure 2b). In either case, the amplitude and phase spectra almost perfectly match those expected from a simple Fourier transform of the pump.

In short, the square-wave spectrum has only odd harmonics, while the saw-tooth has all of them. In both cases, the amplitude is inversely proportional to the harmonic number, and the phase shows almost perfect quadrature with respect to the dc reference. This last point already demonstrates the validity of the proposed procedure for an absolute determination of the phase signal.

This conclusion is reinforced by the second test results (Figure 2c and Figure 2d), which have been both carried out with a square wave pump, for which the duty ratio was reduced to 10%. The only difference here is that the second measurement (Figure 2d) has been performed by rejecting the \( n, 1 \) sidebands at the second eigenmode, instead of the \( n, 4 \) ones (Figure 2c). Both spectra are identical, but – as expected (Equations 9–12) – the phases are inverted (i.e., \(-\Phi_n\) instead of \(+\Phi_n\)) with respect to the pump Fourier transform in the case of a
signal demodulation based on the \( n_4 \) sidebands. At the exception of the harmonics directly neighbouring the null component (\( n = 10 \) in the case of a 10% duty ratio pump waveform), the measured phase values match fairly well the ones expected from the pump Fourier transform. For their part, the amplitude spectra are identical, they display the typical cardinal sine (sinc) shape (see Supporting Information File 1) and perfectly match the calculated ones. A figure where all set of data (experimental and calculated) are gathered is provided in Supporting Information File 1 (Supporting Information File 1, Figure S5).

**Dual-heterodyne Kelvin probe force microscopy under optical pumping on an organic solar cell**

To further validate the DHe-KPFM implementation, a second set of measurements was performed under optical pumping on an organic photovoltaic donor–acceptor blend. As in our previous works, we used the PTB7:PC71BM tandem. We refer the reader to our former reports [4,11] and review articles for a detailed introduction to KPFM on organic heterojunctions [20], and to the specificities of the PTB7:PC71BM blend.

We limit ourselves here to recall that in these organic blends, charge photogeneration can be understood, in a first approach, as the result of exciton dissociation into Coulomb bound charge transfer (CT) states at the donor–acceptor interfaces. This event is finally followed by the dissociation of the CT states into delocalized carriers of opposite sign on both sides of the D–A interface.

In the context of this work, it is also worth recalling that KPFM investigations are carried out in an "open circuit voltage" configuration. In such a geometry, the surface photovoltage probed under continuous-wave illumination results from a balance between the processes of photogeneration and carrier annihilation (by electron–hole recombination). In addition, from the venture of time-resolved KPFM under pulsed illumination, the SPV dynamics are mainly governed by the effective carrier mobility and trapping mechanisms. The main factor limiting the photocharging dynamics is indeed the effective mobility of holes and electrons (under the effect of drift diffusion) in the donor and acceptor networks. After the application of a light pulse – and during the duration of the pulse – the charge
mobility limits the rate at which an electrostatic equilibrium can be reached in the sample. Clearly, this parameter also has an impact on the SPV decay dynamics. However, in the latter case, the slower trap release processes are actually the limiting factor. In particular, in the case of the PTB7:PC71BM system, it is now well-established that isolated PC71BM clusters act as electron trapping centres. The blend morphology, phase composition and concentration gradients of the donor and acceptor species (through the film thickness) can therefore have a dramatic impact on the SPV decay dynamics probed by KPFM.

The sample investigated in this work has been specifically processed to display finely intermixed networks of the donor and acceptor species at the scale of a few tens of nanometres. This was achieved by using diiodooctane as a solvent additive [21], following an identical processing protocol than the one described in our former report [11]. The topographic nc-AFM images (Figure 3a, and numeric zoom in Supporting Information File 1, Figure S6) indicate that the thin-film processing was performed as expected. They display a uniform contrast at the hundred-nanometre scale, indicating that a fine intermixing of donor and acceptor species has been obtained. On a smaller scale (see Supporting Information File 1, Figure S6), nanoscale features appear in the form of small topographic elevations.

The contrasts obtained by imaging the first harmonic components of the time-periodic SPV under modulated/pulsed illumination (amplitude in Figure 3b and phase in Figure 3c) clearly

![Figure 3: The SPV imaging of an organic solar cell by DHe-KPFM. Topographic (a) and DHe-KPFM (b,c) images (500 x 500 nm, 256 x 256 pixels) of a PTB7-PC71BM blend acquired under pulsed illumination (λ = 515 nm, Popt = 300 mW cm⁻², illumination in backside geometry): \( \omega_{2n} = 519.3 \text{ kHz}, \) \( \omega_{1} = 63.3 \text{ kHz}, \) \( \Delta \omega = 30 \text{ Hz}, \) \( U_{ac} = 1 \text{ V}. \) \( \omega_{ac} = \omega_{1} - (\omega_{0} + \Delta \omega + n \omega_{mod}) \) with \( n = 1. \) The optical pump consists in a square-shaped signal with a base period of 5 ms (\( \omega_{mod}/2n = 200 \text{ Hz} \)) and a duty ratio of 20 percent (optical pulse duration: 1 ms). The DHe-KPFM data have been acquired by demodulating \( (n,4) \) sideband) the amplitude \( V_{1} \) (b) and the phase \( \Phi_{1} \) (c) of the first \( (n = 1) \) harmonic of the time-periodic SPV. The scan rate was set to 5 s/line. d) Histogram of the phase values.](image-url)
confirm that the phases are segregated at the 10 nm scale. In addition, it is clear that the local topographic protrusions correlate with local minima in the amplitude channel (compare Supporting Information File 1, Figures S6a and S6b).

In all likelihood, the observed contrasts originate from the nanoscale phase segregated donor-acceptor networks. However, it is not possible to perform a phase identification on the sole basis of the harmonic amplitude signal (Figure 3b). Taken alone, that channel gives indeed no information about the polarity of the SPV signal.

In principle, one could use the phase signal for that purpose. Unfortunately, contrary to the case of measurements performed in data-cube spectroscopy (shown hereafter), it is here not possible to determine the phase reference level ($\Phi_0$). It is still possible, however, to draw a partial conclusion from the examination of the phase data. Their values are indeed distributed in a relatively narrow band, as shown by the histogram in Figure 3d. This indicates that regardless of the area of the sample being scanned, the SPV – or more specifically, its first harmonic component – keeps a constant polarity (otherwise, 180 degree reversals should be observed). As shown hereafter, this assumption is confirmed by spectroscopic DHe-KPFM measurements. It is moreover consistent with the results of complementary AM-heterodyne KPFM measurements of the “static” SPV performed by using a differential spectroscopic protocol. These additional data, presented in Supporting Information File 1 (Figure S7), reveal that the SPV is positive over the entire surface, with values ranging from ca. 40 mV to ca. 170 mV (for 95% of the data according to the SPV histogram, see Supporting Information File 1, Figure S7).

Consequently, the local minima in the DHe-KPFM amplitude image (appearing as dark spots in Figure 3b and Supporting Information File 1, Figure S6b) correspond to areas of the sample where the SPV is “less positive”. Thus, from an electrostatic point of view, the most reasonable hypothesis is that these contrasts (and the correlated topographic protrusions) reveal the location of the electron-acceptor (PC$_{71}$BM) sub-network.

These first series of DHe-KPFM measurements has been performed under an optical pump signal featuring a relatively long time-period (5 ms), and 1 ms wide light pulses. This choice of parameters was made according to the results of our previous pp-KPFM measurements on PTB$_7$:PC$_{71}$BM blends [4,11], which showed that the SPV decay time constant can vary from tens of $\mu$s to several hundreds of $\mu$s, depending on the morphology and phase composition. Doing so, we maximized our chances to generate a time-dependent SPV (which first harmonic could be mapped by DHe-KPFM) by choosing a pump time-period higher than a few ms (i.e., the order of magnitude of the longest decay time constants that we observed so far in this system [4]). Naturally, at this stage, the contrasts observed do not allow us to conclude as to the nature of the SPV dynamics (i.e., decay time-constant). In turn, this experiment confirms that DHe-KPFM allows an ac-demodulated imaging of the SPV (to within the $K_1$ scalar constant) with a very high spatial resolution (a lateral resolution of a few nanometres has been achieved according to image cross-sections, not shown), and at a standard scanning speed (here 5 s/line).

It is now time to test the ability of DHe-KPFM to probe the SPV dynamics. Therefore, the 10 first harmonic components (amplitude/phase) were recorded in a data cube spectroscopy experiment under an optical pump, this time operated at a tenfold smaller time scale (100 $\mu$s light pulses repeated over a 500 $\mu$s period). Figure 4a presents one set of spectra (demodulated amplitude and phase at the second eigenmode as a function of the harmonic number) acquired during this 2D data-cube acquisition. Both the phase and amplitude spectra can be adjusted using fit functions, which are obtained from an analytical calculation of the Fourier components for a time-periodic SPV, whose decay dynamics between light pulses follows an exponential time dependence (with a time constant $\tau_0$). An initial approach to the problem consists in neglecting the photocharging dynamics (i.e., making the approximation of an instantaneous sample photocharging as soon as a light pulse is applied). The calculation of these functions and of the Fourier coefficients is given in a dedicated section of Supporting Information File 1.

The results of this data-cube DHe-KPFM experiment and of the post-data acquisition data treatment (automated adjustment of the matrix of spectroscopic curves by batch processing with OriginPro software) are presented in Figure 4, along with the topographic image recorded simultaneously pixel by pixel with the spectroscopic curves. Note that the spectroscopic images displayed in this figure have been treated by applying a Gaussian smooth filter. The raw data are shown in Supporting Information File 1, Figure S8, they display the same features, but with a higher noise level. Remember also that the reference phase ($\Phi_0$) is now measured for each pixel. Accordingly, a post-acquisition correction is applied to the phase data, resulting in absolute values that can be adjusted with the above-mentioned mathematical function (derived from Equation S18 in Supporting Information File 1).

A first sight, both the amplitude and phase data agree reasonably with the calculated Fourier coefficients. The spectroscopic curves (Figure 4b) can be fairly well adjusted, yielding similar
SPV time-constant decay values, ranging from a few µs to a few tens of µs (depending on the sample area). In addition to the SPV decay time constant, a second variable parameter – the SPV magnitude (or amplitude in absolute value) – is required to adjust the amplitude (or modulus) coefficients. Following what precedes, the output of that adjustment is given in arbitrary units (since the amplitude coefficients are all probed to within a multiplication by the same unknown factor, $K_1$).

The calculated SPV magnitude image (Figure 4c) displays contrasts, which definitely confirm our former assumptions. It displays indeed local minima that are correlated with the topographic protrusions. At the same time, the full set of phase data confirms that the SPV polarity remains constant over the entire sample area. Whatever the harmonic, the phase values are indeed distributed in ranges that are incompatible with local polarity inversion (phase images for each harmonic are presented in Supporting Information File 1, Figure S9).

On average, higher decay time constants are observed over the areas associated with the PC$_{71}$BM subnetwork. There are clear correlations between the magnitude minima (Figure 4c) and the decay time constant maxima (Figure 4d and Figure 4e) in several parts of the surface. One of these areas is highlighted by dashed contours in Figure 4c and Figure 4d. This observation is consistent with a well-known fact for fullerene derivative-based heterojunctions: PC$_{71}$BM aggregates act as charge trapping...
centres. The trap release processes become the limiting factor determining the SPV decay dynamics.

It is also important to note that although both sets of data (amplitude/phase) show good agreement, a better data fit was obtained in the case of the amplitude. In fact, although the relative error ($\Delta t_\text{fit}/t_\text{ref}$) is on average slightly smaller for the constants fitted from the phase data (17% instead of 25% for the constants calculated from the amplitude), the fit failed (phase only) for a small fraction of the data (see the images of relative errors and time constant histograms in Supporting Information File 1, Figure S9).

At this stage of our investigations, we have not been able to definitively establish the origin of these differences. A hint can be found by considering the fact that the phase signal obviously shows a higher noise level for the harmonics with the smallest magnitude (e.g., $n = 5$, see the phase image in Supporting Information File 1, Figure S9). The question also arises as to whether a better adjustment could be achieved, by taking into account the photocharging dynamics in the mathematical model used to describe the SPV dynamics.

A first approach consists in checking what the dynamics of the SPV are from the perspective of another technique. To that end, we performed a series of complementary spectroscopic measurements (single data points at selected locations on the surface) by switching the configuration of the setup to perform pump-probe KPFM measurements. We will merely remind that now, the SPV time-measurement proceeds by recording the KPFM compensation potential as a function of a time-delay between the optical pump and the probe. The probe is obtained by restricting the application of the modulation bias to a restricted time window. We refer the reader to our former report [4] for more details; the measurements discussed herein have been realized using exactly the same setup configuration. The pp-KPFM spectra (Figure S10 in Supporting Information File 1) reveal that the SPV decay can be relatively well accounted by a single exponential law, with time-constant values fully consistent with the ones calculated from DHe-KPFM spectra. In addition, the pp-KPFM data show that only a few hundreds of nanoseconds are needed to reach an electrostatic equilibrium once a light pulse has been applied to the sample. This supports the idea that, even if we cannot rule out the possibility of a better fit, neglecting in a first step the photocharging dynamics remains (in the current case) a reasonable approximation. Last, we also note that the pp-KPFM data once again confirm the (positive) SPV polarity.

To conclude this part of the work, it is important to check whether the data obtained for this PTB7:PC$_{71}$BM sample are consistent with the results of our previous investigations on BHJ thin films based on the same donor–acceptor tandem. Considering only the SPV decay dynamics, the current result seems to contradict those of previous investigations on other PTB7:PC$_{71}$BM nanophase-segregated blends. Indeed, previous pp-KPFM studies yielded decay time constant values in the order of hundreds of µs to ms for similar PTB7:PC$_{71}$BM blends processed with diiodooctane additive [4,11]. However, it is important to note that, in contrast to the present case, these earlier series of samples exhibited an overall negative SPV. This shows that although all of these samples are “nanophase segregated”, the morphology of the donor and acceptor subnetworks can show significant variation from batch to batch.

In fact, the decay time constant dynamics we observed here are reminiscent of the SPV dynamics we previously observed in PTB7-enriched regions of blends processed without solvent additive [4]. The comparison seems even more pertinent when one considers that these PTB7-enriched areas also showed a positive SPV [4]. Although the following model remains tentative, the picture that seems to emerge is that the BHJs investigated in this work feature nanophase-segregated networks with a higher concentration of the electron-donor polymer (accounting for the positive SPV), and/or a lower density of non-percolating PC$_{71}$BM clusters (delaying the SPV decay less).

### Imaging weak surface photovoltage signals: CsPbBr$_3$ nanosheets on HOPG

We have just seen that images of SPV magnitude and dynamics can be obtained with high spatial resolution. In this final section, we will show that DHe-KPFM, thanks to the signal enhancement provided by the second eigenmode, can image weak SPV signals that would otherwise be barely detectable.

To illustrate the capabilities of DHe-KPFM in terms of high sensitivity, we have chosen as a model system an optoelectronic interface that can be obtained by depositing caesium lead halide perovskite nanosheets (NSs) on a highly oriented pyrolytic graphite (HOPG) substrate. Lead halide perovskites have emerged recently as materials with unique optical and electronic properties, such as high absorption coefficients, high defect tolerance, and charge mobility. Due to this, they are very promising for the use in many applications, such as LEDs, solar cells, and photodetectors. Reducing their size down to the nanoscale by synthesizing colloidal nanocrystals in solution can allow high control over the perovskite crystallinity and access to various morphologies. Thus, cubic lead halide perovskite nanocrystals have been widely studied and used for various optoelectronic applications [22,23]. More recently, ultra-thin nanoplatelets or nanosheets (several nm thick and hundreds nm large) with very appealing properties were reported [24]. Due to
the 2D quantum confinement in the vertical direction and their smooth surfaces with atomic thickness control, very precise control over the optical gap and exciton energy of NSs can be achieved through chemical synthesis, making them very interesting objects for various studies.

As in previous works [25], the CsPbBr$_3$ nanosheets (NSs) synthesized for our investigations display an orthorhombic phase (confirmed by X-ray diffraction characterizations, not shown), a thickness of a few unit cells, and lateral dimensions of a few hundreds of nanometres (the synthesis protocol is described in the Supporting Information File 1). Complementary characterizations were carried out by photoluminescence spectroscopy (Supporting Information File 1, Figure S11), scanning electron microscopy (SEM, Supporting Information File 1, Figure S12), and AFM in ambient conditions (Supporting Information File 1, Figure S13), on a series of samples obtained by depositing the NSs (by spin coating the hexane solution where they are dispersed) on silicon and HOPG substrates (for SEM and AFM). Note that prior to SEM and AFM investigations, the excess of ligands was removed by immersing the substrates in an anhydrous ethyl acetate solution.

Sometimes we observe by AFM sample areas where a non-negligible fraction of the surface is covered by NSs monolayers (about 4.5 nm according to the topographic cross section profiles, see Supporting Information File 1, Figure S13). In most cases, however, the NSs form stacks on the surface that are tens to hundreds of nanometres high. This is due to the fact that these objects have a natural tendency to aggregate in solution over time. It is on one of these areas of a HOPG substrate that the DHe-KPFM experiments were performed, the results of which are shown in Figure 5, along with preliminary measurements performed by “differential” SPV imaging (panels a,b,c, and f in Figure 5).

This differential imaging proceeds by recording a 2D matrix of curves of the KPFM potential as a function of time (setup configured in standard AM-heterodyne KPFM, and spectroscopic acquisition performed with an open z-loop). During the spectroscopic ramp, the illumination (continuous wave) is turned on during a pre-determined time window. The difference between the KPFM compensation potential values at the end of the light pulse and just before the light is turned on can be calculated for each pixel.

These differential images (Figure 5b) reveal that a negative SPV develops in the NSs stacks under illumination, with an amplitude exceeding several tens of mV in many places. In a first approach, this negative photocharging may be explained by the existence of a built-in electric field at the interface between the graphite substrate and the CsPbBr$_3$ stacks. The KPFM images taken in the "dark state" (Supporting Information File 1, Figure S14) show that the surface potential is in average more positive by ca. 720 mV over the NSs, compared to the bare substrate. A reasonable hypothesis, although not yet definitely confirmed, is that this built-in electric field results from a negative charge transfer mechanism from the CsPbBr$_3$ stacks to the substrate. Consequently, the extra charge carriers generated under illumination undergo a drift process, resulting in a spatial separation of electron and hole populations across the space charge region. In other words, the negative SPV that we observe is consistent with a downward band bending at the graphite/CsPbBr$_3$ interface. This situation is shown in Supporting Information File 1, Figure S14, together with the "in-dark" KPFM image. While this model seems most plausible, we note that other mechanisms could be invoked to explain the observed SPV (such as illumination-induced band flattening at the top of the stacks, as a result of Fermi level pinning by surface states).

Trapping processes are also clearly involved, as shown by the time course of the KPFM potential (Figure 5c). After each illumination, it takes several seconds for the KPFM potential to return to its initial state (note that an additional 500 ms delay was added between each spectroscopic acquisition, which accounts for the observed difference between the signals at $t=0$ and $t=5$ s). Compared to the case of the organic BHJ, the trap release processes now take place on time scales that are several orders of magnitude higher.

A closer examination of the entire set of spectroscopic curves reveals that, in some areas of the sample, a certain fraction of the negative charges may be released more rapidly than in other areas. In fact, some curves exhibit a sharp rise just after the light pulse stops, while others show only a smooth slope increase. Two curves showing this different behaviour, labelled 1 and 2 (corresponding to the locations where they were recorded, as indicated by the markers in Figure 5a and Figure 5b), are shown in Figure 5c.

It turns out that when using DHe-KPFM to map the sample photosresponse under modulated illumination, these specific sample areas become clearly visible. The results of that second data acquisition in DHe-KPFM are presented in Figure 5e (along with the topography in Figure 5d), which displays the amplitude of the first Fourier harmonic ($V_1$) recorded under a 10 ms periodic square-wave modulated illumination (i.e., a 50% duty ratio). The demodulated signal peaks at exactly the same location (highlighted by an arrow in Figure 5e) where the spectroscopic KPFM(t) curves indicate that part of the photopotential is decaying at a faster rate. Again, it is not possible to
Figure 5: Imaging the photoresponse of a CsPbBr₃:HOPG interface. (a,b,c,f) Data acquired by differential SPV imaging with the setup configured for AM-heterodyne KPFM (ω₂ = ω₁ − (ω₀ + Δω₀)). (d,e) DHe-KPFM measurements (ωₐc = ω₁ − (ω₀ + Δω₀) + nωₘ₀ with n = 1). For all measurements, λ = 515 nm, P_{opt} = 1.5 mW·cm⁻². ω₀/2π ≈ 63.6 kHz, ω₁/2π ≈ 401.7 kHz. a,b) Topography a) and SPV b) images (2.1 μm x 2.1 μm). For this measurement, Δω₀/2π = -4 Hz, ω₁ = ω₀ + Δω₀, U_{ac} = 0.5 V. The SPV map is reconstructed from the 2D matrix (96 x 96 pixels) of KPFM(t) curves (see text). c) Two curves of the KPFM compensation potential as a function of time (200 pixels), recorded on the locations indicated by markers (labelled 1 and 2) in the topographic and SPV images. For each spectroscopic acquisition, a single 500 ms long light pulse (equivalent to a continuous wave illumination) is applied during the 2.25 s < t < 2.75 s time window. Note that an extra 500 ms delay is set between each spectroscopic measurement (i.e., from one image pixel to the next). d,e) Images of the topography d) and amplitude of the first Fourier harmonic e) mapped by DHe-KPFM (256 x 256 pixels, 4 μm x 4 μm). For this measurement, Δω₀/2π = -12 Hz, ω_{ac} = ω₁ = ω₀ + Δω₀ = nωₘ₀ with n = 1, U_{ac} = 1 V. The optical pump consists in a square-shaped signal with a base period of 10 ms (ωₘ₀/2π = 100 Hz) and a duty ratio of 50 percent (optical pulse duration: 5 ms). The dotted contours in d) delimit approximately the area investigated by differential SPV imaging. The arrow in e) pinpoints the location corresponding to the KPFM(t) curve labelled 1 in c). f) Zooms on the KPFM(t) curve labelled 1. The aim is to highlight what happens immediately after the light pulse is applied, and after its extinction. Extrapolating the photoresponse to the DHe-KPFM case (modulated illumination with a 10 ms time-period) shows that the modulated SPV magnitude (i.e., V₁, panel e) cannot exceed a few mV.

provide a truly quantitative measurement of the harmonic amplitude V₁ (since the measurement is performed within the multiplicative factor K₁). However, since both series of images were acquired at the same location, a direct comparison can be made between the DHe-KPFM data and the KPFM curves recorded in the time domain.

For that purpose, let us zoom in on the parts of the KPFM(t) curves that correspond to the start and end of the “long” light pulses applied for the differential SPV imaging (Figure 5f). These zooms show that, depending on whether one is interested in the SPV growth or decay regime, the electrostatic potential cannot be changed by more than 10 mV or 4–5 mV in a 10 ms time-lapse. Thus, under modulated illumination, the “modulated SPV” magnitude is limited by the slower decay dynamics, and cannot exceed a few mV. The 4–5 mV value appears really as a maximum, since instead of a 10 ms timescale, it would be more rigorous to consider only the 5 ms periods corresponding to the interval between the light pulses used for the DHe-KPFM experiment.

The very high sensitivity of DHe-KPFM is fully demonstrated by the simple fact that clear contrasts are also observed even on sample areas where the magnitude of the modulated SPV is smaller. According to the comparison with the time domain spectroscopic data corresponding to the sample location labelled 2, a resolution at the mV limit may have been achieved. Further investigations would be needed to precisely quantify the
magnitude of the modulated SPV component. At the very least, complementary measurements performed under electrical pumping (see Supporting Information File 1, Figure S15) confirm that modulated components as small as a few mV can be detected.

Conclusion
We have introduced DHe-KPFM as a new approach to measure the Fourier spectrum (or intermodulation products) of a time-periodic surface potential with an atomic force microscope. It has been specially designed for experiments with an nc-AFM under UHV conditions, where the high resonance quality factors of the cantilever are an obstacle to the application of a direct intermodulation scheme [16]. Through a series of experiments on model systems, we have demonstrated the ability of DHe-KPFM not only to probe the Fourier harmonics under optical or electrical pumping, but also to detect modulated components within the resolution limit of other reported KPFM methods. This was made possible by exploiting the amplification of the signal by the second eigenmode of the cantilever. In this sense, DHe-KPFM is the first step towards an open-loop generalization of the AM-heterodyne KPFM method. The only drawback – at this stage – is that the measurement of the amplitude spectrum is achieved within a multiplication by a scalar constant. We have good reason to believe that this issue will soon be solved. Preliminary tests have indeed shown that it is also possible to demodulate other series of sidebands through the second eigenmode, which yields access to the capacitance gradient harmonics. In the short term, it will thus be possible to apply a fully automated retro-conversion process to reconstruct truly quantitative (photo)-potential data in the time domain. This will also provide a simple path for dual-harmonic open-loop KPFM measurements [19], without the need to calibrate the transfer function of the system (keeping in mind that whatever the sideband is, the signal is detected at the fixed second eigenmode frequency).

To conclude this work, we would like to emphasize that beyond time-resolved measurements, perhaps the greatest contributions of DHe-KPFM will come from its ability to detect very weak photomodulated signals. In some cases, this may make it possible to reveal phenomena that would otherwise remain inaccessible to other KPFM-based SPV imaging modes. This applies to any type of system where the net density of spatially separated photogenerated charges is insufficient to generate an electrostatic potential difference greater than a few mV. This situation may for instance occur in some cases in hybrid perovskite thin films when the internal electric fields at the interfaces (with the substrate or the vacuum) are too weak. This could also be the case for molecular heterojunctions in the single layer limit.

Supporting Information

Fourier coefficient calculation and derivation of the formulas used to fit the spectroscopic DHe-KPFM data acquired under optical pumping on the organic BHJ solar cell (text and Figures S1, S2 and S3). Schematic illustration of the dual frequency mixing effect (Figure S4). Python routine for switching the demodulation configuration. Comparison between the data acquired under electrical pumping with n_4 sidebands, n_1 sidebands, and calculated Fourier coefficients (Figure S5). Numeric zooms from the images acquired by DHe-KPFM on the PTB7:PC71BM blend (Figure S6). Complementary measurements on the PTB7:PC71BM blend by differential SPV spectroscopy (Figure S7). DHe-KPFM data-cube spectroscopy on the PTB7:PC71BM blend: unfiltered (raw-data) images and error images (Figure S8). Images of the first ten harmonic phase signals recorded on the PTB7:PC71BM blend (Figure S9). Complementary measurements on the PTB7:PC71BM blend by pump-probe KPFM (Figure S10). CsPbBr3 nanosheets: synthesis protocol (text); CsPbBr3 nanosheets: photoluminescence spectroscopy (Figure S11). CsPbBr3 nanosheets: complementary characterization by SEM imaging (Figure S12). CsPbBr3 nanosheets: complementary characterization, by “tapping-mode” AFM imaging (Figure S13). CsPbBr3 nanosheets on HOPG: in dark KPFM data and built-in interface electric field model (Figure S14); detecting weak modulated components: complementary DHe-KPFM measurements under electrical pump (Figure S15).

Supporting Information File 1
Supporting information.
[https://www.beilstein-journals.org/bjnano/content/supplementary/2190-4286-14-88-S1.pdf]

Funding
The HF2LI numeric lock-in has been acquired thanks to a fund by the French National Research Agency (ANR), under the project TRAPPER (ANR19-CE05-0040). Research on CsPbBr3/HOPG interfaces have been carried out in the frame of the Matra2D project (ANR20-CE24-0017).

Author Contributions
BG implemented the DHe-KPFM setup, carried out the nc-AFM/(DHe)-KPFM experiments, processed the data, and proposed physical interpretations accounting for the results. CA processed the PTB7:PC71BM blend. FH synthesized and processed the CsPbBr3 NSs under the supervision of DA, and carried out complementary characteriza-

License and Terms
This is an open access article licensed under the terms of the Beilstein-Institut Open Access License Agreement (https://www.beilstein-journals.org/bjnano/terms), which is identical to the Creative Commons Attribution 4.0 International License (https://creativecommons.org/licenses/by/4.0/). The reuse of material under this license requires that the author(s), source and license are credited. Third-party material in this article could be subject to other licenses (typically indicated in the credit line), and in this case, users are required to obtain permission from the license holder to reuse the material.

The definitive version of this article is the electronic one which can be found at: https://doi.org/10.3762/bjnano.14.88
A multi-resistance wide-range calibration sample for conductive probe atomic force microscopy measurements

François Piquemal¹1, Khaled Kaja¹, Pascal Chrétien²,³, José Morán-Meza¹, Frédéric Houzé²,³, Christian Ulysse⁴ and Abdelmounaim Harouri⁴

Full Research Paper

https://doi.org/10.3762/bjnano.14.94

Open Access

Received: 13 June 2023
Accepted: 09 November 2023
Published: 22 November 2023

This article is part of the thematic issue "Advanced atomic force microscopy techniques V".

Guest Editor: P. Rahe

© 2023 Piquemal et al.; licensee Beilstein-Institut.
License and terms: see end of document.

Abstract

Measuring resistances at the nanoscale has attracted recent attention for developing microelectronic components, memory devices, molecular electronics, and two-dimensional materials. Despite the decisive contribution of scanning probe microscopy in imaging resistance and current variations, measurements have remained restricted to qualitative comparisons. Reference resistance calibration samples are key to advancing the research-to-manufacturing process of nanoscale devices and materials through calibrated, reliable, and comparable measurements. No such calibration reference samples have been proposed so far. In this work, we demonstrate the development of a multi-resistance reference sample for calibrating resistance measurements in conductive probe atomic force microscopy (C-AFM) covering the range from 100 Ω to 100 GΩ. We present a comprehensive protocol for in situ calibration of the whole measurement circuit encompassing the tip, the current sensing device, and the system controller. Furthermore, we show that our developed resistance reference enables the calibration of C-AFM with a combined relative uncertainty (given at one standard deviation) lower than 2.5% over an extended range from 10 kΩ to 100 GΩ and lower than 1% for a reduced range from 1 MΩ to 50 GΩ. Our findings break through the long-standing bottleneck in C-AFM measurements, providing a universal means for adopting calibrated resistance measurements at the nanoscale in the industrial and academic research and development sectors.
**Introduction**

Since its introduction thirty years ago by Murrell et al. [1], conductive probe atomic force microscopy (C-AFM) has evolved into a unique and powerful technique for measuring local electrical quantities (i.e., current and resistance) at the nanoscale. In C-AFM, a micro-machined conductive probe with a sharp nanometer-sized tip acts as a top electrode brought into contact with the surface of a sample while applying a potential difference relative to a back electrode. The small currents flowing through the system are measured using a current amplifier, typically ranging from 100 fA to 10 µA for most commercially available microscopes [2,3]. By sweeping the potential difference while the tip is fixed in contact with the sample, current versus voltage (I–V) curves are acquired. I–V curves are essentially used to extract resistance values or to characterize the electric behavior of components and devices [4]. Alternatively, current variation maps are acquired at a given applied voltage by scanning the AFM tip in contact mode across a defined sample surface area [5]. Owing to its versatility and high resolution in probing the local conductivity of materials, C-AFM has been extensively used in studying semiconductors [6,7], two-dimensional materials [8-10], memristive devices [11-15], photovoltaic systems [16-18], dielectric films [19-23], molecular electronics [24-29], organic and biological systems [30-34], and quantum devices [35-37]. Various technical methods have been developed in C-AFM to cope with the diversity of its applications, including advanced sensors and low-noise preamplifiers [2,38-40]. Nevertheless, quantifying the measured currents and resistances remains a bottleneck issue in C-AFM, inhibiting an effective comparison of results to comprehend experimental processes.

C-AFM measurements are prone to environmental and experimental factors that heavily affect their stability, reproducibility, repeatability, and exactness [41,42]. The formation of a humidity-induced water meniscus at the tip–sample interface, the presence of surface contamination, and thermal drifts induce significant instabilities in C-AFM measurements [42,43]. Moreover, local overheating and anodic oxidation phenomena are commonly observed in C-AFM because of highly localized electric fields at the tip apex leading to structural damage considerably affecting the measurement reliability. These effects are further amplified during scanning in contact mode due to shear forces and strong mechanical stress imposed on the tip apex [44]. Therefore, it is common to measure sudden alterations in local currents and resistances in C-AFM unrelated to the sample’s physical properties [43]. The combination of the effects above makes it difficult to quantify and reproduce the measured values in C-AFM experiments, which degrades the method’s efficiency in advancing the understanding of many processes in materials sciences and industrial developments.

Despite the widely experienced difficulties, no universal solution to ensure the calibration and traceability of C-AFM measurements has been proposed in the literature. So far, only personalized custom approaches have been adopted that are restricted to specific setups or experiments [20,45].

In this paper, we propose a multi-resistance reference sample covering a wide range of values from 100 Ω to 100 GΩ, enabling a universal calibration approach to quantitative measurements in C-AFM applicable to all systems and setups.

**Results and Discussion**

Our approach consists of three main steps performed in a one-month timeframe. First, we calibrate the resistors employed in the fabrication of the reference sample using probe station measurements. Second, we use C-AFM imaging to obtain resistance maps and identify the error sources associated with the imaging-mode measurements. Finally, we apply spectroscopic C-AFM measurements to extract current versus voltage (I–V) curves for each resistance value on the sample. We undertake a comprehensive analysis to compare resistance values obtained by C-AFM imaging and I–V curves measurement to define the conditions for calibrated measurements.

**Calibration sample design and fabrication**

The sample developed in this work consisted of a square fused silica substrate (11 mm wide, 2 mm thick), on which gold connection lines and pads were fabricated by standard photolithography, using a mask aligner (MA6, Karl Suss, Germany), and conventional deposition techniques. Following a resist (about 1 µm thick) development process, a 2 inch diameter wafer was placed in a vacuum chamber for electron beam deposition of a 200 nm thick titanium/gold layer. Subsequently, a lift-off process in acetone was employed to reveal the gold pattern. Finally, square samples were cut to match the dimensions of the measurement setup. We hand-soldered thick-film surface-mounted-device (SMD) resistors onto the connection gold pads on the surface using small soldering paste droplets (F42240, lead-free solder paste – class 5, CIF, France). The fused silica substrate was placed on a heating plate set to 270 °C, which required around 3 min to reach the melting temperature of the solder droplets (217 °C), as observed under an optical microscope. Upon cooling, 16 SMD resistors were fixed on the sample surface, creating a set of 15 resistance values, as shown in Figure 1a. The substrate was fixed onto a circular metallic plate (15 mm diameter), which acts as a back electrode connected to all resistances using a peripheral gold line and dashes of silver paste deposited on the sample edges. Each resistance was connected to an intermediate gold pad (300 µm × 470 µm) designed for microcontacting using a probe.
station setup, as shown in Figure 1a,b. Furthermore, the contacts were extended to the central area (60 µm × 60 µm) of the sample, forming a set of 15 small (i.e., 5 µm wide) electrode arms designed for local C-AFM imaging and spectroscopic measurements. The gold lines’ dimensions were characterized for calculating their intrinsic resistances using the gold resistivity value.

**Calibration of SMD resistors and gold lines**

Before conducting C-AFM measurements, the resistance values of the SMD resistors and the gold connection lines should be determined using calibrated equipment. To this end, the intermediate gold pads were used as terminals to calibrate the corresponding resistance values relative to the back electrode. We used a probe station (Cascade Microtech MPS150) coupled to a programmable voltage source (Marconi 104A) and a high-precision ammeter to measure the resistance values of the SMD devices in an electromagnetically shielded environment under stabilized air temperature (22.9 ± 0.1) ºC and relative humidity (40.7 ± 0.3)%. Two different calibrated ammeters were used depending on the range of the expected resistance values. As shown in Figure 1, a digital voltage multimeter (DVM) (Keysight 3458A) was used for the resistance range between 100 Ω and 1 GΩ, while a very low noise (fA/Hz$^{1/2}$) current amplifier (Femto DDPCA-300) was associated with the same DVM for the upper resistance range between 1 GΩ and 100 GΩ. The DVM and the current amplifier were calibrated at the French National Metrology Institute (LNE) following the highest standards in metrology (see Supporting Information File 1, section S1).

Table 1 compares the nominal resistance values with those measured for each resistor, $R_{\text{meas}}$, at the rectangular pads using probe station measurements with the combined uncertainties. All uncertainties in the paper are given at one standard deviation corresponding to a 68% confidence level in the case of a normal distribution [46]. All measured values were in excellent agreement with the nominal ones within the tolerance limit indicated by the manufacturer, except for the first three pads. Owing to their low values, these three resistances ($R_{1,\text{meas}}$, $R_{2,\text{meas}}$, and $R_{3,\text{meas}}$) were corrected by accounting for the resistances of the connection line segments, $R_{\text{seg}}$, in the central zone of the sample, and the resistance of the wiring, $R_{\text{wire}}$, between the two probes and the DVM. Considering the dimensions of the line segments and the measured resistivity of the deposited gold lines ($\rho = (31.4 \pm 0.4) \times 10^{-9} \Omega \cdot m$), we calculated three correction resistances $R_{1,\text{seg}} = 21.2 \Omega$, $R_{2,\text{seg}} = 20.1 \Omega$, and $R_{3,\text{seg}} = 22.4 \Omega$ for the first three pads, respectively. The measured value of the supplementary resistance due to the wiring (including the resistance of the two probes and the cable resistances) was determined at $R_{\text{wire}} = 1.8 \Omega$ (see Supporting Information File 1, section S2).

The combined uncertainty values in Table 1 were calculated using the root-sum-square method (RSS) from uncertainties related to the sample, the environmental conditions, the measurement circuit, and the measurement repeatability. The uncertainties were estimated using the reference evaluation methods [46]. The major uncertainty components originated from the sample temperature and voltage effects, ranging from 1.1 parts in $10^3$ to 1 part in $10^4$ with decreasing resistance values. The
Table 1: Nominal ($R_{i,\text{nom}}$) and measured ($R_{i,\text{meas}}$) values for the 15 pads and combined uncertainties $u_i$ in relative values (%). The uncertainties are given at one standard deviation. The tolerance on the values of the mounted resistors and the measurement date are given.

<table>
<thead>
<tr>
<th>$i$ (pad index)</th>
<th>$R_{i,\text{nom}}$ (Ω) (resistor)</th>
<th>Tolerance (%)</th>
<th>$R_{i,\text{meas}}$ (Ω) (pad)</th>
<th>$u_i$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>$1 \times 10^2$</td>
<td>0.5</td>
<td>$1.672 \times 10^2$</td>
<td>0.03</td>
</tr>
<tr>
<td>2</td>
<td>$1 \times 10^3$</td>
<td>1</td>
<td>$1.068 \times 10^3$</td>
<td>0.03</td>
</tr>
<tr>
<td>3</td>
<td>$1 \times 10^4$</td>
<td>0.05</td>
<td>$1.007 \times 10^4$</td>
<td>0.03</td>
</tr>
<tr>
<td>4</td>
<td>$1 \times 10^5$</td>
<td>0.1</td>
<td>$1.000 \times 10^5$</td>
<td>0.03</td>
</tr>
<tr>
<td>5</td>
<td>$1 \times 10^6$</td>
<td>1</td>
<td>$1.000 \times 10^6$</td>
<td>0.03</td>
</tr>
<tr>
<td>6</td>
<td>$5 \times 10^6$</td>
<td>1</td>
<td>$5.011 \times 10^6$</td>
<td>0.03</td>
</tr>
<tr>
<td>7</td>
<td>$1 \times 10^7$</td>
<td>1</td>
<td>$0.998 \times 10^7$</td>
<td>0.03</td>
</tr>
<tr>
<td>8</td>
<td>$5 \times 10^7$</td>
<td>1</td>
<td>$4.975 \times 10^7$</td>
<td>0.03</td>
</tr>
<tr>
<td>9</td>
<td>$1 \times 10^8$</td>
<td>1</td>
<td>$0.998 \times 10^8$</td>
<td>0.03</td>
</tr>
<tr>
<td>10</td>
<td>$5 \times 10^8$</td>
<td>5</td>
<td>$5.043 \times 10^8$</td>
<td>0.06</td>
</tr>
<tr>
<td>11</td>
<td>$1 \times 10^9$</td>
<td>10</td>
<td>$1.000 \times 10^9$</td>
<td>0.09</td>
</tr>
<tr>
<td>12</td>
<td>$5 \times 10^9$</td>
<td>10</td>
<td>$4.610 \times 10^9$</td>
<td>0.13</td>
</tr>
<tr>
<td>13</td>
<td>$1 \times 10^{10}$</td>
<td>30</td>
<td>$0.972 \times 10^{10}$</td>
<td>0.13</td>
</tr>
<tr>
<td>14</td>
<td>$5 \times 10^{10}$</td>
<td>30</td>
<td>$3.611 \times 10^{10}$</td>
<td>0.17</td>
</tr>
<tr>
<td>15</td>
<td>$1 \times 10^{11}$</td>
<td>30</td>
<td>$0.784 \times 10^{11}$</td>
<td>0.17</td>
</tr>
</tbody>
</table>

other main uncertainties did not exceed 4 parts in $10^4$, which were related to the calibrations of the measurement instruments (particularly the current amplifier gain), the leakage resistances, and the measurement noise (see Supporting Information File 1, sections S3 and S4).

Resistance values in C-AFM imaging mode

Following the calibration of the SMD resistors, C-AFM imaging measurements were conducted by scanning the central zone of the sample. Experiments were performed using a Multi-mode 8 AFM system with a Nanoscope V controller (Bruker, USA) operated in contact mode with CDT-FMR diamond-coated probes (Nanosensors, USA). Resistance maps ($512 \times 512$ pixels) were recorded using a recently developed custom-built external wide-range current measuring device (WCMD), connected to the AFM system operating under ambient environmental conditions (no shielding and no air conditioning system). The WCMD device consists of a current amplifier with an automatic gain regulation. It allows for, under usual AFM scanning conditions, current and resistance mapping as well as $I$–$V$ spectroscopy over a wide range of current measurement (from 100 µA to less than 100 fA) (see Supporting Information File 1, section S1). Previous experiments have shown diamond-coated tips to be most suitable for imaging gold surfaces in ambient air. A DC bias voltage of 1 V was applied to the sample, while the scanning speed was set to 12 µm·s$^{-1}$ and the scan orientation was parallel to the cantilever’s central axis.

The resistance map in Figure 2 was acquired over the central zone of the sample, showing 15 electrode arms corresponding to the end of the gold connection lines linked to the intermediate gold pads previously measured in Table 1. The imaging result shows a distinguishable resistance contrast for the values expected between 10 kΩ and 100 GΩ, which validates the applicability of the developed sample for the calibration of C-AFM measurements in scanning mode. To extract quantitative values comparable to those listed in Table 1, the surface of each electrode was individually imaged at different locations using the same operating parameters, that is, scan speed, scan orientation, applied force, and bias voltage. A histogram was extracted for each resistance map, and the data were fitted to Gaussian distributions. The results showed that the mean value of measured resistances deviates significantly from the expected value in Table 1 by more than 100% for the first three electrode arms.
$i = 1$ to $i = 3$ (i.e., $100 \Omega$, $1 k\Omega$, and $10 k\Omega$). In this case, the significant deviation was attributed to the high resistance of the AFM tip (ca. $10 k\Omega$, nominal value from the manufacturer), which prevents a correct measurement of small resistance values. For the remaining electrode arms $i = 4$ to $i = 15$ (i.e., $100 k\Omega$ to $100 G\Omega$), the measured values from the resistance maps deviated by 20% to 28% compared to those determined in Table 1. This error was partly related to an erroneous reading from the AFM controller unit, which systemically added an offset to the measured values, as identified by injecting external test DC voltage signals to the controller. Thus, further measurements were conducted by shortcutting the AFM controller and recording resistance values measured directly by the WCMD device. Nonetheless, a remaining deviation of the resistance values obtained in C-AFM imaging mode relative to the values in Table 1 was still observed of the order of 8%.

Resistance values from C-AFM $I-V$ curves

To comprehend the origin of this remaining error, we proceeded into removing any possible contamination of the tip apex by repeatedly scanning over a fixed line (typically a few tens of nanometers) on the sample surface (i.e., by disabling the slow-scan axis). The effective contamination removal was associated with a stable measurement of a minimal resistance value. Then, we positioned the tip at a fixed location in contact with the electrode’s surface with an applied force of 900 nN to extract $I-V$ curves by sweeping the applied voltage between $-1$ V and $+1$ V. This approach mitigates the difficulties related to surface contamination on the gold electrodes during scanning. Resistance values for each electrode arm were determined from the slopes of the $I-V$ straight lines using a regression model. For each value, the coefficient of determination ($R^2$) was equal to 1 (see Supporting Information File 1, section S5 and Figure S1). The results were globally found within a 2.5% deviation relative to the resistance values in Table 1.

In comparison, an excellent agreement (within 1%) was obtained for the specific range of $1 M\Omega$ and $50 G\Omega$, as shown in Figure 3. The resistance values for the electrode arms $i = 3$, 4, and 5 (i.e., $10 k\Omega$, $100 k\Omega$, and $1 M\Omega$, respectively) were corrected by accounting for the tip resistance, which was measured on a copper film at $R_{tip} = 6591 \Omega$ with a relative
uncertainty of 1% (conservative value). It is worth noting that, for higher resistance values up to 100 GΩ, the correction accounting for the tip resistance value becomes largely insignificant. Despite the reduced uncertainty for the resistance values determined from the $I–V$ curves, those obtained from the imaging results still showed a non-negligible deviation. In addition, we noticed that all $I–V$ straights did not pass through zero, which introduced a shift in the measured currents leading to an increase in the resistance values by a constant amount of $(+8 \pm 1)\%$, which agrees very well with the deviations observed from the image values (taken at a bias voltage of $+1$ V).

The origin of $I–V$ curves not going through zero is commonly associated with photovoltaic effects, which was indeed validated by the disappearance of this observation when the laser of the AFM setup was switched off. Although, a photovoltaic effect might be intriguing in current measurements on gold pads, this observation was systematically made for the $I–V$ curves measured on all gold electrode arms. Through further investigations, we were able to associate this observation with the use of worn AFM diamond tips, especially formed by a p-type diamond coating on a highly doped n-type Si core. Thus, the photovoltage effect observed in our paper is solely related to the tip apex and does not depend on the measured sample. We were able to confirm this aspect by running $I–V$ curves using new probes with intact apexes, which showed no shift around zero even with the AFM laser on. This effect is currently under thorough investigations for a future publication. Accordingly, a new set of images was acquired for the electrodes $i = 3$ to $i = 15$ at two bias voltages of $+1$ V and $-1$ V, and the corresponding resistance value was determined by their mean value. For each electrode, this imaging protocol was repeated at three to five zones to enhance statistical values. The final resistance of an electrode corresponded to the average value of the three to five measurements. Figure 3 shows an excellent agreement between the resistance values obtained from C-AFM images and those from $I–V$ curves with a maximum global deviation of 1%. However, the electrode arm $10^4$ Ω ($i = 3$) showed 5.7% deviation, which is well within the corresponding uncertainty.

Our findings show that the multi-resistance reference sample developed in this work enables a universal calibration of C-AFM measurements in both imaging and spectroscopic (i.e., $I–V$ curves) modes with a 1% achievable relative uncertainty level in the range between $10^6$ Ω and $5 \times 10^{10}$ Ω. The protocols adopted in this study highlight several routes for further improvements. Using platinum as metallic material instead of gold for the small electrode arms would help reduce surface contamination-related issues. Consequently, measuring the lowest resistance values would become accessible using low-resistance metallic probes (e.g., Pt-coated or full bulk Pt probes). However, using such probes will require limiting the current (typically 100 μA) to avoid excessive Joule heating within the nanocontact.

**Conclusion**

We have designed a multi-resistance wide-range reference for calibrating the complete C-AFM measurement circuit over a resistance range from 100 Ω to 100 GΩ. A set of operating protocols have been demonstrated for measuring resistance in C-AFM within the range from 10 kΩ to 100 GΩ with deviations lower than 2.5% relative to values calibrated at the macroscale using probe station measurements. The design of the proposed calibration sample features access to a wide range of resistance values (nine decades) within a single AFM scan, calibration of these resistances at the macroscale using a probe station, compatibility with any commercially available AFM system, and the possibility of positioning a device under test (DUT) on the reference sample. Further efforts are underway to develop another sample version featuring easier access to C-AFM measurements of the lowest resistances (from 100 Ω to 10 kΩ) and an expanded resistance range up to 1 TΩ. The outcome of the present work is expected to promote the applicability of C-AFM for the local measurements of DC resistances and currents at the nanoscale, which constitutes an essential requirement for coping with the ever-increasing shrinkage of technological devices. It is worth noting that the authors are closely working with the International Electrotechnical Commission (IEC-TCI13) for the creation of documentary standards regarding resistance measurements in C-AFM.

**Supporting Information**

Supporting Information File 1
Additional experimental information.
[https://www.beilstein-journals.org/bjnano/content/supporting/2190-4286-14-94-S1.pdf](https://www.beilstein-journals.org/bjnano/content/supporting/2190-4286-14-94-S1.pdf)

**Acknowledgements**

Part of this work was done at the C2N micro nanotechnologies platforms and was partly supported by the RENATECH network and the General Council of Essonne. The authors are grateful to José Alvarez for fruitful discussions, Emmanuel Patois for calibration assistance, and Djamel Ziane for software assistance.

**Funding**

This research work was carried out in the framework of the ELENA project (EMPIR 20IND12), which is supported by the European Metrology Programme for Innovation and Research.
The EMPIR initiative is co-funded by the European Horizon 2020 research and innovation program and the EMPIR Participating States.

Competing Interests
The authors declare no competing interests.
41. Sumaiya, S. A.; Martini, A.; Baykara, M. Z. Nano Express 2020, 1, 030023. doi:10.1088/2632-959x/abcae0

License and Terms
This is an open access article licensed under the terms of the Beilstein-Institut Open Access License Agreement (https://www.beilstein-journals.org/bjnano/terms), which is identical to the Creative Commons Attribution 4.0 International License (https://creativecommons.org/licenses/by/4.0). The reuse of material under this license requires that the author(s), source and license are credited. Third-party material in this article could be subject to other licenses (typically indicated in the credit line), and in this case, users are required to obtain permission from the license holder to reuse the material.

The definitive version of this article is the electronic one which can be found at:
https://doi.org/10.3762/bjnano.14.94
Spatial variations of conductivity of self-assembled monolayers of dodecanethiol on Au/mica and Au/Si substrates

Julian Skolaut*1, Jędrzej Tepper2, Federica Galli2, Wulf Wulfhekel1,3 and Jan M. van Ruitenbeek2

Full Research Paper

Address:
1Institute for Quantum Materials and Technology, Karlsruhe Institute of Technology, Hermann-von-Helmholtz-Platz 1, 76344 Eggenstein-Leopoldshafen, Germany, 2Huygens-Kamerlingh Onnes Laboratorium, Leiden University, Niels Bohrweg 2, 2333 CA Leiden, Netherlands and 3Physikalisches Institut, Karlsruhe Institute of Technology, Wolfgang-Gaede-Straße 1, 76131, Karlsruhe, Germany

Email:
Julian Skolaut* - jskolaut@uni-mainz.de

* Corresponding author

Keywords:
Au/mica; Au/Si; conductive atomic force microscopy; dodecanethiol; self-assembled monolayers

Abstract
Determining the conductivity of molecular layers is a crucial step in advancing towards applications in molecular electronics. A common test bed for fundamental investigations on how to acquire this conductivity are alkanethiol layers on gold substrates. A widely used approach in measuring the conductivity of a molecular layer is conductive atomic force microscopy. Using this method, we investigate the influence of a rougher and a flatter gold substrate on the lateral variation of the conductivity. We find that the roughness of the substrate crucially defines this variation. We conclude that it is paramount to adequately choose a gold substrate for investigations on molecular layer conductivity.

Introduction
For decades, the need for miniaturization of electronics has pushed the research field into the direction of bottom-up, rather than top-down, approaches. In this research field, molecular electronics [1-3] has always held a central role, as the flexibility and control over the structure of molecules is unmatched. One of the fundamental parts of devices employing a bottom-up approach combined with molecular electronics is comprised of metal electrodes and molecular layers deposited onto them.
For the use in applications, the properties of such layers of molecules and the interface they form with the metal substrate have to be investigated carefully and systematically. In order to achieve comparability between different types of molecules, ordered layers are favorable, which makes self-assembled monolayers (SAMs) a perfect test bed for studies on molecular layers.

With the idea of molecular electronics in mind, most studies have been aimed at studying the conductivity of SAMs. In previous studies, the contacting of SAMs has been achieved in various ways [4]. We focus here on the contacting of molecular layers between a metal surface and a locally probing electrode. In early studies using this approach, the layers were contacted by a mercury droplet at the end of an electrode, which was then placed on top of the SAM [5-7]. Applying a voltage and, therefore, a current to the substrate and the mercury electrode yields the conductivity of the SAM, averaged over the contact area of the mercury droplet. In such studies, one of the crucial problems was mercury filling out defects in the SAMs, which leads to short circuits and unreliable currents running through the microcontact.

This was avoided in later experiments by using eutectic GaIn (eGaIn) droplets [8-11]. These are much more viscous, to the point that they are almost solid. This reduces the amount of leak currents significantly and makes studies on the conductivity of SAMs much more reliable. A more widely applied method uses conductive atomic force microscopy (CAFM). In this technique, a conductive probe is used in an AFM, which allows for imaging the surface topography (and other characteristics such as adhesion and stiffness) with lateral resolution while simultaneously being able to measure current characteristics. Moreover, the probes used in CAFM are significantly sharper compared to, for example, mercury droplets or eGaIn, which makes it possible to avoid short circuits to the metallic surface relatively easily.

In previous studies, CAFM has been used to investigate the conductivity of surfaces and SAMs, including many studies performed recently on SAMs of helical oligopeptides studying chiral-induced spin-selectivity [12-15]. Here, we re-examine the information that is obtained from CAFM, and we demonstrate that the nature of the metallic substrate is of critical importance. The lateral variation of current characteristics strongly depends on the substrate chosen to deposit the SAM onto. For this study, we employ alkane thiols, which are allowed to form a SAM on different types of Au substrates. We have chosen dodecanethiol (DDT) molecules and study them on commercially available Au substrates consisting of thin Au layers of different surface roughness. We compare granular Au films deposited on Si wafers with epitaxial (flat) Au films on mica.

**Experimental**

Before the experimental results are presented, this section focuses on the preparation of the samples under study and the setup used to carry out the measurements. As mentioned above, two types of Au substrates were used, that is, Au-coated Si (Au/Si) and epitaxially grown Au on mica (Au/mica), bought from Sigma-Aldrich and Phasis, respectively. The Au thicknesses are 200 nm for Au/mica and 100 nm for Au/Si substrates. The Au/mica substrates were used directly out of the box without any further cleaning steps. Au/Si was additionally cleaned by boiling in acetone followed by ethanol for 20 min under a fume hood. It was then dried in a glovebox in N₂ atmosphere, exposed to ozone to remove organic contaminants, and finally rinsed with warm ethanol.

DDT SAMs were deposited onto these substrates by immersing them in a 10 mM solution of DDT in ethanol with subsequent incubation for 24 h. After transfer into a glovebox, the samples were rinsed with ethanol and dried. To improve the order of the SAMs, they were again immersed in 10 mM DDT/ethanol solution and heated to ≈ 80 °C for 1 h. After gradual cooldown, the samples were again rinsed and dried in N₂ atmosphere in the glovebox.

The obtained samples were studied using a commercially available JPK NanoWizard® 3 AFM setup. The setup has been upgraded by a CAFM tip holder with an integrated preamplifier, whose feedback resistor of 1 GΩ fixes the maximum measurable current to 12 nA, sets the amplification to 10⁹ V/A, and allows one to measure currents down to few tens of picoamperes.

In the studies presented here, two types of CAFM-probes were used. For the studies on DDT SAMs on Au/mica, Bruker MESP-V2 (CoCr-coated Si) probes were used, whereas, for the remaining measurements, Rocky Mountain Nanotechnology RMN-25PT300B probes with solid Pt wire as tips were used. The latter have the advantage that they do not oxidize easily and remain conductive, as there is no fragile metal coating on a non-conductive probe in contrast to the CoCr-coated Si probes. This is at the cost of lateral resolution due to the larger radius of the probe apex.

All measurements presented here were carried out in the Quantitative Imaging (QI™) mode by JPK. A sketch of the procedure is shown in Figure 1. In this mode of CAFM operation, a force–distance curve is measured at every pixel of the image. The tip is approached until a certain bend of the cantilever is
Figure 1: In QI™ mode, the probe measures force and conductance curves at a raster of points on the surface, shown here for a row along the x direction. The probe is moved from pixel to pixel in a retracted position far away from the surface. At each point, a force–distance curve is measured while simultaneously acquiring the current. Current maps show the currents extracted as the extremal value of each current curve.

reached, corresponding to the force setpoint $F_{\text{setpoint}}$. Plotting the $z$ position at which the force setpoint is reached provides the topographic information, which we represent here as a yellow–blue color map. During the whole measurement, a bias voltage $U_{\text{bias}}$ is applied between tip and sample. Simultaneously to the force–distance curve, the current is acquired. As it can be seen from the example curves in Figure 1, the extremal current is usually found close to the force setpoint, and both are correlated. The small shift of the position of the extremal current towards larger $z$ distance can be explained by the bandwidth of the preamplifier (specified as 2 kHz). The relatively high rate of 40 approach/retraction cycles per second was chosen as a compromise between bandwidth distortion and total measurement time.

Plotting the extremal current yields the current maps shown here in gray scale and provides a measure to compare the conductive properties in different areas of the surface. Using the QI mode is particularly advantageous in our study, since it measures topography and current simultaneously and reduces wear effects on the tips.

Results and Discussion

We divided the results obtained with the methods described above into two main sections. These are studies on (i) the bare substrates and on (ii) the DDT SAMs on these substrates. The bare substrates were investigated as a reference for the measurements thereafter. They show topographies and current maps characteristic for Au/Si and Au/mica. Subsequently, it was observed how these characteristics change with SAMs deposited onto the surface. A strong resemblance between bare and SAM-covered surfaces was observed. This bears important consequences for the choice of substrates for studies on molecular SAMs; flat substrates are advantageous for such studies.

Bare Au/Si and Au/mica substrates

As mentioned above, two types of Au substrates were investigated, namely Au/Si and Au/mica. The measurements on bare substrates presented here serve as a reference for the studies on the lateral variation of the conductivity of DDT SAMs on said substrates. The reference helps in identifying how much of the SAM’s lateral variation of conductivity stems from the substrate.

Figure 2a and Figure 2b show the topography and the current map, respectively, for a Au/mica substrate. The $300 \times 300 \text{nm}^2$ topography map shows that the Au/mica substrate has large flat areas on which the height does not change significantly. The overall change in height throughout the image is approximately 4 nm, and the most significant changes in height occur at the boundaries between different flat areas.

The corresponding current map (Figure 2b) shows a nearly homogeneous distribution of the current throughout the whole
Figure 2: (a, b) Topography and current map, respectively, of the bare Au/mica substrate. The large flat areas provide a homogeneous current distribution throughout large parts of the image. The sudden change in current in the lower part of the image can be attributed to a tip change. (c, d) The same data for a Au/Si substrate. The topography shows more substructures, which is reflected in more extreme current values in the current map ($F_{	ext{setpoint}} = 50 \text{nN}, U_{	ext{bias}} = 100 \text{mV}, \text{FMN probe}$).

In contrast to the Au/mica surface, the Au/Si substrate exhibits a rougher surface, as seen in Figure 2c, in agreement with the difference in growth mode of Au films on the two substrates. For mica, epitaxial growth is obtained [16,17], while Au on Si/SiO$_2$ forms a granular film [18]. Although the overall height variation is not very different from that observed for the Au/mica substrate (approximately 5 nm), the Au/Si surface shows much more substructures and no flat terraces. Compared to the flat terraces of Au/mica, Au/Si has more peaks and valleys, which is also reflected in the current map in Figure 2d. Here, most of the current map is either at the lower limit of the measurable current (few tens of picoamperes) or at the top end of the current range (high-nanoampere regime) (see Supporting Information File 1, Figure S2b). The transition from low to high currents takes place on rather small length scales of tens of nanometers.

The areas of high current appear to coincide with areas of lower topography, slightly skewed to the bottom right of areas with higher topography. This happens all over the image and indicates an effect of the probe influencing the occurrence of high-current areas. The higher currents found in the valleys likely
result from varying surface-normal load forces. They are smaller if the probe contacts the surface on a flat area and larger if the contact is on a slope in the topography. As the load force only controls the force component normal to the sample plane, this leads to larger variations in the local normal force when the tip lands on a slope. Therefore, the rougher topography is likely influencing the occurrence of high- and low-current areas. More specifically, this means that the conductance can appear higher on slopes and rough surfaces, as the tip contacts the surface laterally.

This rationalizes the large systematic difference between the two substrates regarding their topography and lateral current variation. The Au/mica substrate shows a flatter topography accompanied by a more homogeneous current distribution. Generally, this is favorable for current measurements on SAMs, as it provides larger areas of comparable current to study the conductive properties of molecular SAMs and their lateral variation. With the lateral variation of the current of the bare substrates being known, a well-founded description of the changes after SAM deposition can be made.

Overall, five areas were investigated on Au/mica and three for Au/Si, which all showed consistent images.

**Dodecanethiol SAMs on Au/mica**

Figure 3 shows images of the DDT-covered Au/mica surface obtained after the deposition procedure described above. In
total, four different areas on two DDT/Au/mica samples were investigated, yielding consistent results. In Figure 3a, the topography is similar to that obtained for the bare Au/mica surface, that is, relatively large flat areas, only small height differences throughout the image, and small roughness of the surface. By means of topography alone, the surface cannot be distinguished from that of the bare Au/mica surface.

Also, upon looking at the current distribution, many features are similar to those of the bare Au/mica surface, including its homogeneous current distribution, for this specific case (Figure 3) around 800 pA. It is sensible that the average current is higher compared to the measurements on the bare Au/mica substrate (Figure 2b), as force setpoint and bias voltage are higher. The average current value of 800 pA is again well measurable and allows for a rough estimation of the resistance of each molecule. Such an estimation can be done without consideration of the resistance of the bare Au substrate, as its resistance is much lower than the SAM’s resistance. Assuming that approximately 1000 molecules are contacted [4] and all contacted molecules are connected in parallel, the total resistance of $R_{\text{tot}} = U_{\text{bias}}/I = 1.25 \times 10^3 \, \text{M}\Omega$ results in a resistance for one molecule of $R_{\text{mol}} = 1.25 \times 10^6 \, \text{M}\Omega$. Comparing this value to the literature value ranging between $10^6$ and $10^7 \, \text{M}\Omega$ per molecule, as presented in [4], shows reasonable agreement.

In addition to the features observed for the bare substrate, including its homogeneous distribution around well-measurable current values, more features are visible in the current map (Figure 3b). First, finer topographic details, namely shallower terraces and boundaries between flat areas of the topography, possibly step edges between single atomic steps of the Au surface, become clearly observable. Second, dark spots on the terraces of the current map appear, which can be seen clearly in the expanded-scale image in Figure 3d. These can be attributed to so-called etch pits that arise from the growth of sulfur-bound SAMs on Au surfaces [19,20]. These etch pits are monotonically deep holes in the Au surface. They are produced in the process of SAM formation by sulfur–gold bonds, which result in removing Au atoms from the top layer. This leaves the surface with Au atom vacancies that arrange into small islands of a few nanometers in size. This size matches the darker areas observed in the current maps after DDT SAM formation. The presence of a well-ordered SAM on the surface was confirmed by scanning tunneling microscopy (STM) images on alkane-thiol-covered Au surfaces prepared in the same way, in which the individual molecules can be resolved, shown in Figure S4 in Supporting Information File 1. The etch pits serve as evidence that the SAMs form in an ordered fashion. The abovementioned features can also be seen clearly in the 3D view of the surface in Figure 3c, where the color coding indicates the measured current at each point. The 3D view also underlines the direct correspondence between features in the current map and the topography.

A further indication that the SAM has formed correctly is the observation that it can be thinned by imaging smaller areas with high load forces. As shown in Figure S5 in Supporting Information File 1, after three consecutive imaging runs performed on the same area, the center square of the image appears lower in topography compared to the sides when the scanning area is widened. Also, the measured current increases from image to image, while the etch pits remain intact, indicating that the Au surface structure remains unaffected. We attribute lower topography and increased current to a thinning of the SAM by pushing aside molecules with the probe. Another effect contributing to the thinning of the SAM is molecules being picked up by the probe during the measurement. The effect we observe here is most likely a combination of both processes. All these indications lead to the conclusion that ordered DDT SAMs form on the surface with the chosen deposition technique. More importantly, the current maps in Figure 3 show that the substrate and measurement technique are suitable for obtaining information on the conductivity of a molecular SAM, as the measured currents show a homogeneous distribution and large areas without change in the topography, allowing for comparison between the currents measured on these areas. For quantitative information, it is also important to reduce the load force as suggested by the observed removal of part of the SAM by the tip during imaging. Studies of the extent and type presented here can be used as the basis for well-founded statements concerning electronic properties such as the current–voltage characteristics of the molecular SAM. To this purpose, the characteristics should only be averaged over comparable areas, excluding terrace boundaries and other edges. As the Au/mica substrates provide large areas of this kind, they are favored for the use in studies of the conductive properties of SAMs.

**Dodecanethiol SAMs on Au/Si**

The SAM formation technique used for the Au/mica substrates was also used for the Au/Si substrates. As it seems to be suitable for Au/mica substrates, it should also yield densely packed molecular SAMs on Au/Si substrates, allowing for the evaluation of the influence of the substrate on the lateral variation of the conductive properties of SAMs.

For comparison, Figure 4 presents measurements of DDT SAMs on a Au/Si substrate. Comparing topography (Figure 4a) and current map (Figure 4b) to the ones of the bare Au/Si substrate, close similarities can be seen. After coverage of the surface by the SAM, the surface retains the same roughness with
only small flat areas. Although in Figure 4 this is slightly distorted by a probe effect duplicating features, the systematic difference in surface structure between Au/Si and Au/mica, already observed in the bare substrates, is reproduced.

Just as for the bare Au/Si, the substructures of the substrate lead to strong variations in the corresponding current map. There are large areas with very small currents on the flatter areas of the topography. The current rather abruptly increases at the slopes of the topography. The 3D view of the surface in Figure 4c, represented in the same way as in Figure 3c, shows clearly that large currents can only be observed at the slopes of the topography as is also the case for bare Au/Si. The flatter areas, however, show very low current values, close to the lower limit of observability. The 3D view also emphasizes the higher roughness of the surface of the DDT SAM on Au/Si compared to the Au/mica substrate.

Additional measurements on SAMs of sulfur-bound oligopeptides (SH-(CH2)2NH-(Ala-Aib)5-COOH) [12] on Au/mica substrates yielded no measurable currents and are therefore omitted in this report.

Our observations show that, when studying the conductive properties of DDT SAMs on Au/Si, the variation in the current is governed by the structure of the substrate, which remains...
qualitatively unchanged by the deposition of the SAM. For the Au/Si substrate, the rough topography yields only small areas on the surface on which comparable conductive properties can be expected. Without information on the surface topography, the conductance obtained from averaging over random points on the surface [12, 21-24] is prone to incorrect averaging. The lateral variation of the conductive properties limits strongly the amount of lateral probe positions over which measurements of such characteristics can be averaged. Using the Au/mica substrate, however, yields large areas of comparable conductive properties, which makes it more suitable for such investigations. Moreover, the strong lateral variation in the current map of Au/Si suggests that it is necessary to choose the points for averaging carefully. A suitable way to do so would be through imaging the surface as presented here.

Conclusion
This report shows that the lateral variation of the conductive properties of molecular SAMs is governed by the choice of the substrate. To achieve comparable, well-measurable currents and conductive properties, flat substrates are favorable. The flatness of the substrate and homogeneity of the current distribution with and without the SAM should be studied in advance to ensure comparability. A rougher substrate surface leads to stronger variations in the conductive properties, limiting the areas over which conductive properties can be sensibly averaged, and should therefore be avoided.

Moreover, the studies presented here show, that a careful study of the correlation between topography and conductive properties of SAMs is strongly advised, especially if CAFM is used to perform the characterization of the conductive properties of the SAM. With such combined investigations, the areas for averaging can be chosen in a sensible way to reproducibly characterize the SAM’s conductivity, for example, by using only the flat areas of the surface and excluding areas with large slopes in the topography.

Supporting Information
Supporting Information File 1
Additional figures.
[https://www.beilstein-journals.org/bjnano/content/supplementary/2190-4286-14-97-S1.pdf]

Acknowledgements
SJ thanks Lukas Gerhard for discussions on the presentation of the data. SJ thanks Norman Blümel for helpful discussions during the stay at Leiden University. Parts of this article are based on the results reported in the doctoral thesis: J. A. Skolaut, "Molecular Motor Based on Single Chiral Tripodal Molecules Studied with STM", Doctoral Dissertation, Karlsruhe Institute of Technology, KIT Scientific Publishing, 2023.

Funding
This work was partly funded by the Netherlands Organisation for Scientific Research (NWO), grant 680.92.18.01. The work was done during the PhD thesis of SJ within Deutsche Forschungsgemeinschaft (DFG) Grant No. GE 2989/2-1. The Karlsruhe House of Young Scientists (KHYS) supplied additional funds for the stay of SJ at Leiden University.

ORCID® iDs
Julian Skolaut - https://orcid.org/0009-0004-2104-6785
Jędrzej Tepper - https://orcid.org/0000-0002-4841-1170
Federica Galli - https://orcid.org/0000-0002-1098-8150
Jürgen Reus - https://orcid.org/0000-0002-2724-874X
Jan M. van Ruitenbeek - https://orcid.org/0000-0003-0381-0132

References
16. Buchholz, S.; Fuchs, H.; Rabe, J. P.
   doi:10.1016/s0039-6028(99)01113-9
   doi:10.1021/cr960074m
   doi:10.1021/jp0219810
   doi:10.1021/acs.jpcc.0c02291
   doi:10.1021/acs.jpcc.7b04194
   Nano Lett. 2016, 16, 4583–4589. doi:10.1021/acs.nanolett.6b01880
   doi:10.1021/jp509974z

License and Terms

This is an open access article licensed under the terms of the Beilstein-Institut Open Access License Agreement (https://www.beilstein-journals.org/bjnano/terms), which is identical to the Creative Commons Attribution 4.0 International License (https://creativecommons.org/licenses/by/4.0). The reuse of material under this license requires that the author(s), source and license are credited. Third-party material in this article could be subject to other licenses (typically indicated in the credit line), and in this case, users are required to obtain permission from the license holder to reuse the material.

The definitive version of this article is the electronic one which can be found at:
https://doi.org/10.3762/bjnano.14.97
Abstract

Scanning probe microscopy (SPM) techniques are widely used to study the structure and properties of surfaces and interfaces across a variety of disciplines in chemistry and physics. One of the major artifacts in SPM is (thermal) drift, an unintended movement between sample and probe, which causes a distortion of the recorded SPM data. Literature holds a multitude of strategies to compensate for drift during the measurement (online drift correction) or afterwards (offline drift correction). With the currently available software tools, however, offline drift correction of SPM data is often a tedious and time-consuming task. This is particularly disadvantageous when analyzing long image series. Here, we present unDrift, an easy-to-use scientific software for fast and reliable drift correction of SPM images. unDrift provides three different algorithms to determine the drift velocity based on two consecutive SPM images. All algorithms can drift-correct the input data without any additional reference. The first semi-automatic drift correction algorithm analyzes the different distortion of periodic structures in two consecutive up and down (down and up) images, which enables unDrift to correct SPM images without stationary features or overlapping scan areas. The other two algorithms determine the drift velocity from the apparent movement of stationary features either by automatic evaluation of the cross-correlation image or based on positions identified manually by the user. We demonstrate the performance and reliability of unDrift using three challenging examples, namely images distorted by a very high drift velocity, only partly usable images, and images exhibiting an overall weak contrast. Moreover, we show that the semi-automatic analysis of periodic images can be applied to a long series containing hundreds of images measured at the calcite–water interface.

Introduction

In science and technology, scanning probe microscopy (SPM) techniques are widely used to study the structure and properties of surfaces and interfaces from the micrometer scale down to the atomic level. The common element of SPM techniques is that surface structure and properties are revealed by moving a probe over the sample covering a given area or volume. During
Drift correction has been carried out based on the apparent movement of stationary features (e.g., fixed defects or adsorbates) traceable in consecutive images [5,29-31] or images with opposing scan directions [12,32]. Instead of analyzing the apparent shift of individual features, the apparent movement of the scan window can also be determined from the maximum of the cross-correlation [26,27,33-36] between consecutive images. Moreover, the different distortion of periodic structures in images with opposing scan directions was used to determine drift and to calculate the undistorted structure [3,37]. Other authors proposed drift correction procedures based on rescanning a small area of an SPM image with the fast and slow scan directions reversed [13,38-40], splitting the scan of an image into several subscreens [41], or periodically rescanning the first scan line [42]. For non-raster SPM, the drift velocity can be extracted without additional scans from the analysis of inherent crossing points in the scanning path [43,44]. Another approach to remove distortions from SPM images is to correct the images with regard to a known reference structure [4,6,18]. While the latter strategy can ensure distortion-free SPM images for known surface structures, it is not suited for investigation of unknown structures.

Here, we present \textit{unDrift}, a free-to-use scientific software for the fast and reliable calibration and drift correction of SPM image data. \textit{unDrift} implements three algorithms to determine the drift velocity based on two consecutive SPM images with or without periodic structures. The first semi-automatic algorithm extracts lattice vectors from two consecutive up and down (down and up) images exhibiting periodic structures. These lattice vectors are, then, used to analyze the distortion of the images and to calculate the drift velocity. This algorithm enables \textit{unDrift} to drift-correct both SPM images without stationary features and SPM images without overlapping scan areas. The second and third drift correction algorithms extract drift velocities from the apparent movement of stationary features as described in [5,12,25-27,29-36,45]. Algorithm II implements the well-known cross-correlation method [26,27,33-36,45] to automatically determine the shift between two SPM images with identical scan directions. From this shift, we calculate the drift velocity. Algorithm III, in contrast, provides the possibility to manually identify stationary features in two SPM images with arbitrary scan direction and use their positions for drift correction [5,12,25,29-32]. Note that all drift correction algorithms applied by \textit{unDrift} rely on information contained within the measurement data solely; thus, \textit{unDrift} allows for the investigation of unknown structures. To demonstrate the performance of \textit{unDrift}, we apply our software to three examples where the drift correction is especially challenging. Namely, we drift-correct SPM images with a very high drift velocity exceeding the slow scan rate, only partly usable images, and
images with an overall weak contrast and high noise level. Moreover, we show that unDrift is suitable for the drift correction and evaluation of measurement sessions spanning several hundred images.

Software

unDrift is scientific software for the fast and accurate drift correction and calibration of SPM image data as necessary for quantitative data analysis. It is written in JavaScript and HTML and runs with all common browsers independent of the operating system. unDrift can be operated either on a local server or as a web-based version. Both versions are available from our website under [46]. All functions of unDrift, such as data import, leveling, calibration, and drift correction of SPM data, are free to use, that is, unDrift is entirely free to use. Analysis results including corrected SPM images as well as extracted lattice vectors and drift velocities are available in standard open data formats.

The full source code of unDrift is also available from our website. JavaScript modules for the import and analysis of SPM data are licensed under the GNU General Public License version 3.0. The visualization of SPM images in unDrift is realized with the proprietary library Kontrast [47], which is available under its own license. This means that all functions of unDrift are free-to-use for non-commercial purposes but the development of new features requires a Kontrast license.

Input data

The import of SPM data into unDrift is designed to read files in the Gwyddion Native Format (gwy format) as created with the open source SPM data analysis software Gwyddion [48]. Gwyddion contains import modules for a wide variety of scanning probe microscopes as well as tools for SPM data processing and analysis. This enables the user to choose between data processing in unDrift and Gwyddion. unDrift supports basic data processing methods such as leveling (mean plane, polynomial) and an automatic color scale adaption; thus, the processing of most standard images can be done directly in unDrift. For more complex processing steps, the user is referred to Gwyddion. Then, the pre-processed SPM data can be calibrated and drift-corrected with unDrift. Moreover, unDrift can export data in the gwy format, which enables a seamless integration between unDrift and Gwyddion.

The gwy format does not contain standardized containers for scan direction, scan angle, and raster time per pixel, which constitute vital information for an accurate drift correction and calibration. unDrift extracts these parameters from the metadata, where they are typically stored with varying names depending on the manufacturer and version of the used microscope. Because of this, it is necessary to specify the matching between scanning parameters and metadata names for each microscope individually. We did this specification for the instruments and file formats listed in Table 1. For all other devices, this easy step needs to be done by the user in the preferences of unDrift.

Drift correction

Next, we will discuss the main feature of unDrift, the offline drift correction of SPM images. Depending on the surface structure and scan directions of the SPM images, unDrift provides different algorithms to determine the drift velocity and to drift-correct the data. In terms of surface structure, we distinguish between images exhibiting a periodic structure and those without periodic structures. For images showing two-dimensional periodic structures, the drift velocity can be calculated from the different distortion of the surface periodicity in two SPM images with opposing slow scan direction (algorithm I). For the drift correction of SPM images without periodic structures, in contrast, unDrift implements two strategies (algorithms II and III) described in literature [5,12,25-27,29-36,45] to extract the drift velocity from the apparent movement of stationary features in consecutive images. Algorithm II uses the cross-correlation function between two images recorded in the same scan direction and evaluation of measurement sessions spanning several hundred images.

### Table 1: Overview of SPM devices and third-party file formats supported by unDrift.

<table>
<thead>
<tr>
<th>Device</th>
<th>Format</th>
<th>Direct import</th>
<th>Import via Gwyddion</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bruker Nanoscope V</td>
<td>.001, .002, ...</td>
<td>no</td>
<td>yes</td>
</tr>
<tr>
<td>Cypher ES AFM</td>
<td>.ibw</td>
<td>yes</td>
<td>yes</td>
</tr>
<tr>
<td>Nanonis controller</td>
<td>.sxm</td>
<td>yes</td>
<td>yes</td>
</tr>
<tr>
<td>other devices supported by Gwyddion others</td>
<td>no</td>
<td>limited(^a)</td>
<td>no</td>
</tr>
</tbody>
</table>

\(^a\)In principle, unDrift can read all SPM data saved with Gwyddion in the gwy format. However, as the gwy format lacks standardized containers for some of the information necessary for drift correction and calibration, the user needs to specify the mapping of meta data headers in the preferences of unDrift before use.
direction to evaluate the drift velocity [26,27,33-36,45], while algorithm III evaluates the position shift of stationary features between two images with arbitrary scan direction [5,12,25,29-32]. Both algorithms II and III also work for images exhibiting periodic structures if they contain stationary features. In the following two sections, we discuss the different algorithms clustered by the surface structures they are suitable for. Regardless of surface structure and scan direction, however, all drift correction algorithms applied by *unDrift* rely on information contained within the measurement data solely; thus, they allow for a quantitative data analysis without any knowledge on the surface geometry. Instead, all of the applied algorithms use the difference between two consecutive images to determine the drift velocity and to correct the SPM data. Hence, *unDrift* is, in contrast to drift correction schemes relying on known surface geometries, suited to investigate substrates with an unknown surface structure.

**Images with periodic structures**

For the drift correction of images exhibiting periodic structures, *unDrift* uses the algorithm shown in Figure 1 (algorithm I). This algorithm takes advantage of the characteristic distortion of periodic structures in SPM images depending on drift velocity and scan direction [3,6,12,37]. For two consecutive SPM images with opposing slow scan directions, we will observe two different apparent surface structures, as drift distorts the real periodic surface structure differently for a different scan direction (see Figure 2a,d). As we know that the real surface structure is, indeed, independent of the scan direction, we can use the difference between distortions to calculate the drift velocity (and the real surface structure) as described in Supporting Information File 1. Algorithm I has the advantage that it relies only on the surface periodicity; thus, the scan areas of the two images used for drift correction do not need to overlap. The only requirements for this algorithm are a constant drift velocity and two SPM images exhibiting periodic structures measured with different slow scan directions. Note that, in principle, this strategy is not limited to images with opposing slow scan directions but should also work for images with different fast scan directions. In real measurements, however, we find that the difference in the distortion of images with different fast scan directions is too small compared to the uncertainty to achieve reliable results for the drift correction. Consequently, *unDrift* implements this algorithm for consecutive images with opposing slow scan directions solely.

As shown in Figure 1, algorithm I consists of five main steps, namely (1) import of input data, (2) extraction of primitive lattice vectors, (3) generation of linear combinations of these lattice vectors, (4) calculation of possible drift velocities, and (5) selection of the true drift velocity. After that, the obtained drift velocity is used to calculate the real lattice vectors and drift-correct the SPM images.

First, two SPM images with opposing slow scan directions (i.e., one up and one down image) are imported as described before (step 1). Next, *unDrift* extracts primitive lattice vectors from both images as shown in Figure 2 (step 2). *unDrift* determines the lattice vectors either based on the Fourier transforms (Figure 2b,e) or autocorrelations (Figure 2c,f). In both cases, our software searches for local maxima in the transformed image first (red dots in Figure 2). Then, it extracts guesses for the lattice vectors based on the maxima with the highest intensity, the maxima closest to the origin, or based on user selection. After that, these guessed lattice parameters and the spots belonging to the lattice are optimized with a least squares algorithm to obtain optimal lattice parameters. In Figure 2 the optimized lattice parameters are shown as a lattice drawn with red lines. For the Fourier transform, this fit yields lattice vectors of the inverse lattice, which are then transformed into real-space lattice vectors. For the autocorrelation, the optimization yields
Figure 2: Extraction of lattice vectors from images exhibiting periodic structures. (a, d) High-resolution AFM images showing atomic resolution at the calcite (10.4)–water interface. (b, e) Fourier transform images of the real-space images shown in (a) and (d). The maxima in the Fourier transforms are marked by red circles, and the optimized lattice as found by unDrift is shown as red lines. Only the centers of the Fourier transformations are shown. (c, f) Autocorrelation images of the real-space images shown in (a) and (d). The maxima in the autocorrelation images are marked by red circles, and the optimized lattices as found by unDrift are shown as red lines. Only the centers of the autocorrelations are shown.

the real-space lattice vectors directly. To finish step 2, unDrift applies simple geometry to calculate the shortest possible lattice vectors for the lattice extracted in the optimization step.

This extraction of lattice vectors is a semi-automatic step, as the user needs to specify parameters for the peak finding. While these parameters need to be chosen manually, it can be easily determined from the fit quality whether these parameters are chosen correctly. We find that the optimal parameters for this step depend on the image size and contrast; thus, it can be necessary to change these parameters after a contrast change. Moreover, the user needs to choose whether the algorithm operates based on Fourier transform or autocorrelation. This choice mostly depends on the size of the image relative to the size of the observed periodic structure. For images showing many unit cells, we find that the Fourier transform yields better results, while the autocorrelation is superior for images containing very few unit cells. In between these extremes, there is a range where both methods work well as shown in our examples in Figure 2. The dependence of the optimal transformation for peak extraction on the image size is caused by the finite resolution of the measured SPM images. For images containing many unit cells, each unit cell only consists of few pixels; thus, the maxima in the autocorrelation are difficult to separate, as they also consist of few pixels. The Fourier transform, in contrast, works in the inverse space, which is why the maxima are very nicely separated by many pixels and easy to find by the algorithm. For images containing few unit cells, it is the other way around. The autocorrelation maxima are nicely separated, while the maxima in the Fourier transform sometimes even merge together.

After the extraction of lattice vectors, unDrift applies steps 3 to 5 to determine the drift velocity from these lattice vectors. It is important to note that the calculation of drift velocities requires a set of two differently distorted versions of the same vector (see Supporting Information File 1). The identification of a matching pair of lattice vectors, however, becomes increasingly difficult with increasing drift velocity and, thus, increasing image distortion. To solve this problem and to ensure that unDrift also works reliably for high drift velocities, we apply steps 3 to 5 of algorithm I. The idea behind this part of the algorithm is the following: Each pair of lattice vectors \((\vec{a}_x, \vec{a}_y)\) and
Next, we can use this criterion to find matching pairs of lattice vectors and, thus, calculate the true drift velocity. We can start by choosing a set of lattice vectors for the first image, as this initial choice is arbitrary. For the second image, however, we need to find the matching lattice vectors. To realize this, we take the lattice vectors extracted from the image and generate a set of linear combinations for both vectors \( \mathbf{a} \) and \( \mathbf{b} \) (see Figure 1, step 3). These sets \( \{\mathbf{a}_1\} \) and \( \{\mathbf{b}_1\} \) then contain the matching vectors as well as several other vectors. In the next steps, the program subsequently calculates the corresponding sets of drift velocities \( \{\mathbf{v}_d,\mathbf{v}_b\} \) and \( \{\mathbf{v}_d',\mathbf{v}_b'\} \) (step 4) and selects the pair of drift velocities with the smallest difference between \( \mathbf{v}_d,\mathbf{v}_b' \) and \( \mathbf{v}_d',\mathbf{v}_b \) (step 5). Note that we cannot search for identical drift velocities, as the individual drift velocities are always slightly different because of experimental noise and a small non-linearity in the drift. Instead, we use the two drift velocities with the smallest difference. Finally, the true drift velocity \( \mathbf{v}_d \) is calculated by averaging over the individual drift velocities.

For the selection of the drift velocity in step 5, unDrift provides an alternative selection procedure based on the lattice vectors. Not only the drift velocity needs to be identical for both pairs of lattice vectors, but also the primitive unit cell with the shortest lattice vectors has to be identical in both images after drift correction. The second selection procedure, thus, operates based on the difference between drift-corrected lattice vectors in both images. Again, we search for the minimum difference and select the corresponding drift velocity as the real drift velocity. The selection procedure used in step 5 can be chosen by the user under lattice matching. We find that this second selection procedure tends to work better for images with low signal-to-noise ratio.

Images without periodic structures
As discussed before, unDrift features two algorithms to drift-correct SPM images without periodic structures based on the apparent movement of stationary features in consecutive images. In this section, we will describe these two algorithms, referred to as algorithm II and III, and discuss their applicability to different situations in terms of scan directions and experimental systems.

Algorithm II uses the cross-correlation between two consecutive images recorded in the same scan direction to evaluate the shift between the images and to calculate the drift velocity. The distortion of SPM images by drift only depends on drift velocity and scan direction (see Supporting Information File 1). Hence, two images measured with the same scan direction and a constant drift velocity are distorted in the same way. The only difference between these two images is that they are measured at a slightly different position on the surface, because drift moved the scanner and surface relative to each other. In SPM images, this effect manifests itself in an apparent movement of stationary surface features whose positions are actually constant, such as defects and step edges. This is illustrated in Figure 3, where the stationary surface features marked with colored crosses seem to move between Figure 3a and Figure 3b. Here, it is important to note that all stationary features “moved” by the same vector.

To evaluate this shift between images, we can apply the cross-correlation function between both images as described in

![Figure 3](https://example.com/figure3.jpg)

**Figure 3**: (a, b) Two consecutive up images recorded with high-resolution AFM on calcite(10.4) in ultrahigh vacuum. The images show several defects, whose positions are marked with colored crosses in both images. It is apparent that the defect positions are shifted in the second image compared to the first one. (c) Image of the cross-correlation function \( R_{XX}[\Delta \nu_{exc}] \) between the images shown in (a) and (b). The center of the image and the position of the maximum are marked with red dots and connected with a red line. This line corresponds to the shift between images (a) and (b).
In the cross-correlation image, the global maximum corresponds to the shift necessary to achieve maximum similarity between both images [33,34], where a maximum in the image center means that both images are identical without any shift. We show the cross-correlation of our two example images (Figure 3a,b) in Figure 3c. We marked the center of the image and the global maximum with red dots connected by a red line to illustrate the shift between images. When we compare the shift derived from the cross-correlation image, it is evident that this shift is identical to the shift of the stationary features between the images in Figure 3a and Figure 3b.

In the next step, unDrift uses the shift derived from the cross-correlation function to calculate the drift velocity as described in Supporting Information File 1 and to drift-correct the input data. This algorithm is fully automatic and does not require any additional input from the user.

In addition to the global maximum, the cross-correlation image in our example in Figure 3c also exhibits a periodic structure. This periodicity stems from the periodic structure observed in the input images, and it can be evaluated by unDrift to obtain lattice parameters. For the drift correction with algorithm II, however, the stationary features in the input images are decisive and not the surface periodicity. This algorithm does not work reliably for perfectly periodic surfaces without any stationary features as all maxima would have the same intensity; thus, the algorithm cannot decide which maximum corresponds to the shift between the images [30]. For images exhibiting a periodic structure and stationary features, however, we find that algorithm II works with remarkable reliability.

In contrast to algorithm II, algorithm III does not evaluate the mean shift between images but the apparent shift of single stationary features as described by Rahe and co-workers [5]. It is necessary to subsequently identify stationary features in the SPM images and to determine their positions. For the determination of a feature position, unDrift provides the possibility to refine the manually selected positions to the closest maximum or minimum. The drift velocity is calculated for each feature individually; then, the mean drift velocity can be calculated by averaging over the individual drift velocities. The deviation between these yields information about the non-linearity of the drift. With algorithm III, unDrift provides the possibility to use positions of stationary features identified manually by the user. The software displays both images used for drift correction and a variable number of markers in different colors as shown in Figure 3a,b. The user can, then, move these markers to match the positions of stationary features and start the drift correction by clicking a button. As this positioning of markers on identical positions of the stationary features is never perfect, we recommend to use as many stationary features as possible for the drift correction.

Algorithm III is arguably the slowest algorithm in unDrift in terms of evaluation time per image, and the selection of feature positions is, at least, partly subjective. However, algorithm III has the important advantage that it works for all images with stationary features regardless of scan direction and image quality. As long as the user can identify features in the SPM images, this algorithm will work for the drift correction. Moreover, algorithm III offers the possibility to easily assess and quantify the effect of non-linear drift in the drift-corrected SPM data, which is not available from the other algorithms.

**Lateral calibration**

In addition to the correction of drift, it is crucial for a quantitative analysis of SPM data that the scanner position is calibrated properly. While the drift correction will remove the effect of additional movement between scanner and sample surface, the obtained positions, distances, and angles will still be incorrect as long as the instrument is not properly calibrated. This situation is well known in literature, and there are several different strategies documented to determine the calibration parameters for a scanning probe microscope [1-3,7-9,12,18,19,21,22]. With these calibration parameters, the microscope can either be calibrated before the measurement, or the measured SPM data can be corrected afterwards. The calibration parameters can change over time because of, for example, piezo aging or measurements at different temperatures [3,20]. Thus, it is necessary to validate the calibration parameters regularly. unDrift provides features to (1) correct SPM data with a given set of lateral calibration parameters and (2) determine lateral calibration parameters based on a reference surface geometry.

The lateral calibration of SPM data in unDrift is based on the assumption of a linear relationship [3,7-9,19] between recorded and actual scanner movement as described in Supporting Information File 1. In this case, the calibration only depends on three parameters, namely the correction factors in the x and y directions, κx and κy, respectively, and the angle between both directions, β. These parameters can be provided by the user for a lateral calibration of the drift-corrected SPM data. Alternatively, the default values can be used, which correspond to no additional calibration.

For SPM images exhibiting a periodic structure, unDrift can also calculate the expected lateral calibration parameters based on a reference. In order to do so, the user needs to provide the lattice parameters of the investigated periodic structure, that is, the edge lengths and opening angle of the surface unit cell.
unDrift then compares these reference data to the measured lattice parameters and calculates the lateral calibration parameters necessary to match the measured periodicity with the reference. Thus, unDrift makes it very easy to calibrate a previously not calibrated device or to check whether an existing calibration is still valid. Detailed information on the determination of calibration parameters are given in Supporting Information File 1.

Output data
After calibration and drift correction, unDrift provides a variety of different methods to export the obtained data as shown in Table 2. Corrected SPM images including Fourier transforms and autocorrelations are available for export in the Gwyddion Simple Field and Gwyddion Native formats for further data evaluation or processing in Gwyddion. Moreover, images and image cutouts can be exported into the standard image formats png and svg. The svg exporter also includes the possibility to export ready-to-use figures with annotations and scale bars.

Table 2: Overview of output data and export types available from unDrift.

<table>
<thead>
<tr>
<th>Data type</th>
<th>Image type</th>
<th>Output formats</th>
</tr>
</thead>
<tbody>
<tr>
<td>corrected SPM data</td>
<td>all</td>
<td>.gwy, .gsf</td>
</tr>
<tr>
<td>corrected images</td>
<td>all</td>
<td>.png, .svg</td>
</tr>
<tr>
<td>drift velocity</td>
<td>all</td>
<td>.csv</td>
</tr>
<tr>
<td>corrected lattice parameters</td>
<td>periodic</td>
<td>.csv</td>
</tr>
<tr>
<td>calibration parameters*</td>
<td>periodic</td>
<td>.csv</td>
</tr>
<tr>
<td>user input parameters</td>
<td>all</td>
<td>.csv</td>
</tr>
</tbody>
</table>

*aRequires the user to input reference data for the expected surface geometry.

In addition to the corrected SPM data, drift velocities and lattice parameters (only for images with periodic structures) calculated during drift correction are available as a session report in csv format. Calibration parameters are also available for images with periodic structures in the same session report file if the user specified a reference surface. User input parameters specified during the evaluation are recorded by unDrift and can be downloaded in a separate csv file.

Results and Discussion
To demonstrate the performance of unDrift, we will now apply the software to experimental situations where the drift correction is either especially challenging or time-consuming.

Challenging experimental conditions
For the above presentation of the working principle of our software, we used AFM images with good atomic contrast and reasonable drift velocities. In experiments, however, it is not always possible to reach these desirable conditions, which is why we want to show that our software can also deal with challenging experimental conditions. We will demonstrate that unDrift can handle (1) drift velocities exceeding the slow scan rate, (2) images with only small usable parts, and (3) images exhibiting a weak contrast or low signal-to-noise ratio.

First, we discuss a scenario with very high drift velocity. In Figure 4a,b, we show two consecutive AFM images of a calcium fluoride (111) surface recorded under ultrahigh vacuum conditions. The periodic structures observed in these two raw-data images (see red unit cells in Figure 4a,b) show a striking difference compared to each other and compared to the expected hexagonal structure. This obvious difference in appearance is caused by the strong image distortion associated with an exceptionally high drift velocity. High drift velocities can be challenging for drift correction, because the strong image distortion makes it difficult to identify pairs of features or corresponding lattice points. With unDrift, however, the images in Figure 4a,b can be drift-corrected easily, as algorithm I works reliably even for very high drift velocities.

We present the drift-corrected images corresponding to the images in Figure 4a,b in Figure 4c,d, respectively. Note that we cut the drift-corrected images to fit the form factor of this figure, while still being able to see the atomic structure. Figure 4c,d shows that the unit cell dimensions in both up and down image are now almost identical, and the surface now appears to be hexagonal. We find lattice parameters of $3.8 \times 10^{-10}$ m and $3.9 \times 10^{-10}$ m with an angle of 114°, which is very close to a hexagonal surface structure. The lattice parameters also agree well with lattice parameters documented in literature ($a = 3.86 \times 10^{-10}$ m and $y = 120°$; [49]). We ascribe the slight deviation from the reference values to the experimental error, which we expect to be higher because of the exceptionally high drift velocity. We want to highlight that this is an extreme example where the absolute drift velocity ($3.8 \times 10^{-11}$ m s$^{-1}$) exceeds the scan velocity in the slow scan direction ($3.7 \times 10^{-11}$ m s$^{-1}$). For most experiments, the drift velocity will be much lower, as SPM experiments are typically optimized for stable conditions with low drift velocity. Nevertheless, this example shows that unDrift is not limited to low-drift environments but is also capable to correct SPM data recorded with (very) high drift velocities.

Second, we turn to images where only parts of the input images can be used for drift correction. During SPM experiments, sudden tip changes or collisions with the surface can significantly worsen or even destroy the observed contrast. Hence, it is quite common that only parts of an image can be used for evalu-
Figure 4: Example images demonstrating the applicability of unDrift to SPM experiments with high drift velocities (a–d), only partly usable images (e–h), and bad image quality (j–m). Raw-data images are shown on the left side of the figure, and the corresponding drift-corrected images are shown on the right side. In all images, the unit cell used for drift correction is shown as a red quadrangle. Images (a–d) show the atomic structure of calcium fluoride (111) recorded with high-resolution AFM in ultrahigh vacuum. Images (e–h) and (j–m) were recorded with high-resolution AFM at the calcite (10.4)–water interface.

To demonstrate that unDrift can drift-correct these images by only considering (small) parts of an image, we show example images recorded at the calcite–water interface in Figure 4e,f. In our example, the sample drifted out of the scanner’s z range after the first third of the second image (Figure 4f), and the image contrast was completely lost. For drift correction, we used algorithm I based on the autocorrelation image and selected the usable part in Figure 4f manually, while the image in Figure 4e was used in its entirety. We show the drift-corrected results for both input images in Figure 4g,h, respectively. Comparison between the raw-data images (Figure 4e,f) and drift-corrected images (Figure 4g,h) shows that the unit cells of both images agree much better after drift correction. We conclude that the drift correction was successful, even though we could only use a small part of the second image for drift correction. This conclusion is confirmed by the derived unit cell dimensions of $5.1 \times 10^{-10}$ m $\times 8.2 \times 10^{-10}$ m with an angle of 89.8°, which fit the expected values ($4.99 \times 10^{-10}$ m $\times 8.10 \times 10^{-10}$ m, 90.0°; [50]) within the experimental accuracy of our AFM instrument (distance accuracy: ±0.3 $\times 10^{-10}$ m, angle accuracy: ±2°; see below).

Third, we discuss the arguably most challenging situation for drift correction, images with an overall weak contrast and low signal-to-noise ratio. The periodic structures of the calcite–water interface in Figure 4j,k are very faint and, thus, hard to recognize by eye. Based on the autocorrelation function, however, unDrift can extract unit cell dimensions even from images with such weak contrast. The different dimensions of the unit cells extracted here (see red quadrangles in Figure 4j,k) reveal that these raw-data images are distorted by drift. We drift-corrected the raw-data images with algorithm I based on the autocorrelation image to obtain the drift-corrected images shown in Figure 4l,m. In the drift-corrected images, the peri-
Figure 5: Application of \textit{un}Drift to the analysis of a measurement session containing 530 AFM images recorded at the calcite–water interface.

(a–c) Typical drift-corrected images from beginning, middle, and end of the evaluated AFM session. (d, e) Calculated drift velocities in polar coordinates as function of the measurement time $t$. The absolute values of $v_d$ and the corresponding angle $\theta_d$ are shown in (d) and (e), respectively. Results from trace and retrace images are shown as black and red circles, respectively, and the smoothed averages for both cases are shown as lines.

Long image series

After discussing the performance of \textit{un}Drift under different experimental conditions, we now demonstrate the applicability to long image series spanning several hundred SPM images with an example shown in Figure 5. The presented series comprises 530 high-resolution AFM images recorded at the calcite–water interface over a measurement time of approximately 4 h. We evaluated these images with the semi-automatic periodic analysis of \textit{un}Drift (algorithm I) in approximately 1 h 40 min, which corresponds to a drift correction rate of 318 images per hour. In this series, the image contrast is rather stable over the full measurement time (see Figure 5a–c), facilitating drift correction. Thus, the given correction rate is likely to be the upper limit. We find that the number of drift-corrected images per hour and,
consequently, the performance of unDrift strongly depend on
the image quality and contrast stability. Moreover, it is typically
faster to evaluate longer image series than several series with
few images. We find that the average drift correction rate with
unDrift for typical AFM images is between 100 images per hour
for short series and 200 images per hour for long series. Note
that the analysis times discussed here are limited by the manual
steps of the analysis (i.e., adjusting the analysis parameters and
checking the results) rather than the computation time on
all tested common desktop computers (e.g., Windows 10, Intel
Core i5-9500, 6 cores @ 3.00 GHz, 8.00 GB RAM).

Next, we discuss the drift velocities measured during this image
series and what they tell us about our AFM instrument. In
Figure 5d,e, we show the absolute values of \( \nu_3 \) and polar angle
\( \theta_3 \) of the drift velocity \( \dot{v}_3 \) as functions of the time. We observe a
steep decrease of the drift velocity during the first 800 s
(15 min) of our experiment. Then, the drift velocity decreases
further, but with a lower change rate, until it reaches stable
conditions approximately 8000 s (2 h 15 min) after starting the
experiment. The polar angle \( \theta_3 \) (see Figure 5e) follows the same
trend for the first 6000 s. After that, the change in the scan
angle increases again. Compared to the change at the beginning
of the experiment (before 800 s), however, the change in scan
angle after 6000 s is much more random and looks more like
noise. We explain this observation with the decreasing absolute
value of the drift velocity. At the beginning of the experiment,
the drift is caused by equilibration processes between sample
surface, liquid, and AFM instrument, so the absolute drift
velocity is high and has a stable direction. Then, with increasing
measurement time, the system gets closer to equilibrium,
which causes the drift velocity to decrease. Hence, the relative
contribution of thermal fluctuations to the drift velocity in-
creases and the direction of the drift velocity becomes less
stable. The trends observed in Figure 5d,e show us that our
AFM instrument needs to equilibrate for about 800 s (15 min)
to reach a moderate drift velocity. Stable measurement condi-
tions, however, are only reached after approximately 8000 s
(2 h 15 min) of equilibration time.

In addition to the drift velocities, we want to discuss the lattice
parameters derived by unDrift. Figure 6 shows histograms for
all three lattice parameters derived from all 530 images in the
session shown in Figure 5. Because of the applied drift correc-
tion scheme, we get two sets of lattice parameters for each
image. One dataset originates from drift correction with the
previous image, and the other dataset originates from
drift correction with the next image. Here, we show the
histograms of the average values calculated for each image.
Figure 6 reveals that all three experimental lattice parameters
\( (5.0 \times 10^{-10} \text{ m} \times 8.1 \times 10^{-10} \text{ m}, 90.0^\circ; [50]) \)
within an interval of the standard deviation \( (\sigma_a = 0.06 \times 10^{-10} \text{ m},
\sigma_b = 0.12 \times 10^{-10} \text{ m}, \text{and } \sigma_y = 1.0^\circ) \) from the average value.
Moreover, these histograms give us detailed insight into the ex-
perimental accuracy of our AFM measurements. Figure 6a,b
demonstrates the performance of unDrift in terms of angles
to decrease with decreasing image quality. Hence, we expect the accuracy of distances and
angles to decrease with decreasing image quality.

**Conclusion**

We present unDrift, a versatile and powerful software for
calibration and drift correction of SPM images. unDrift
provides three different drift correction algorithms enabling the
drift correction of SPM images, regardless of their scan direc-
tion and whether they exhibit periodic structures or not. We
demonstrate the performance of unDrift in terms of image
quality and experimental conditions with three examples,
named one image set with exceptionally high drift velocity, one with only a small usable part of an image, and one with an overall low image contrast and low signal-to-noise ratio. unDrift handles these three situations reliably. Moreover, we show that unDrift can be used for the fast evaluation of drift velocities and lattice parameters in long measurement sessions spanning several hundred images. We, thus, conclude that unDrift can be a valuable tool in the evaluation of SPM image data.

Supporting Information

Supporting Information features derivations of the mathematical expressions used for the calibration and drift correction, a description of the procedure used to derive correction parameters as well as other technical aspects. Moreover, the gwy files for all shown AFM images and used analysis parameters are included in Supporting Information Files 2–5.

Supporting Information File 1

Calibration and drift correction procedures
[https://www.beilstein-journals.org/bjnano/content/supplementary/2190-4286-14-101-S1.pdf]

Supporting Information File 2

Experimental data shown in Figure 2.
[https://www.beilstein-journals.org/bjnano/content/supplementary/2190-4286-14-101-S2.zip]

Supporting Information File 3

Experimental data shown in Figure 3.
[https://www.beilstein-journals.org/bjnano/content/supplementary/2190-4286-14-101-S3.zip]

Supporting Information File 4

Experimental data shown in Figure 4.
[https://www.beilstein-journals.org/bjnano/content/supplementary/2190-4286-14-101-S4.zip]

Supporting Information File 5

Experimental data shown in Figure 5.
[https://www.beilstein-journals.org/bjnano/content/supplementary/2190-4286-14-101-S5.zip]

Acknowledgements

We acknowledge fruitful discussions with Philipp Rahe. We thank Adam Sweetman and Dylan Barker for kindly providing us with measurement data from a Nanonis controller, which enabled us to implement the import of Nanonis files.

Funding

We acknowledge financial support from the DFG through grant INST 215/635-1 FUGG and KU 1980/11-1.

ORCID® iDs

Tobias Dickbreder - https://orcid.org/0000-0002-7269-7236
Franziska Sabath - https://orcid.org/0000-0002-1562-7303

References

