Feature Article

High-resolution Piezoresponse Force Microscopy Imaging of a Few Layered 2D Ferroelectric

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Two-dimensional (2D) ferroelectrics are promising materials for future applications in advanced nanoelectronics. Piezoresponse force microscopy (PFM) is extensively used to investigate nanoscale-electromechanical properties. However, the underlaying small mechanical deformations displayed by 2D ferroelectrics, ion conductivity, and side effects from tip-surface forces, complicate the high-resolution imaging of ferroelectric domains and domain walls in ambient conditions. Here, we demonstrate that the setup versatility of HORIBA AFM together with its scanning method "PFM-Top mode", further improve signal sensitivity and spatial resolution when mapping low-dimensional ferroelectrics. This approach is demonstrated by the PFM imaging with up to 12 nm spatial resolution of ferroelectric domains, and domain walls, from a 16 nm thick $CuInP_2S_6$ flake.

Introduction

Ferroelectrics are crystals which structural lattice polarization can be reversed under an external electric field, and remain polarized even when the field is removed[1]. This quality of ferroelectrics has motivated the scientific interest for their potential application in developing future electronic, optoelectronic, and photovoltaic nanodevices[2,3]. However, the successful integration of classic ferroelectrics like thin-perovskites in nano-sized devices, remains precluded by problems related to material degradation and ferroelectricity loss, when the thickness of the film shrinks to tens of nm[4,5]. In this respect, 2D van der Waals (vdW) ferroelectrics offer a means to overcome these downsides. Mainly, 2D-vdW ferroelectrics are nanometer-to-atomic scale thick, structurally stable, and prone to be controlled or modulated[5].

Up to now, several 2D vdW ferroelectric structures have been theoretically predicted but a few experimentally

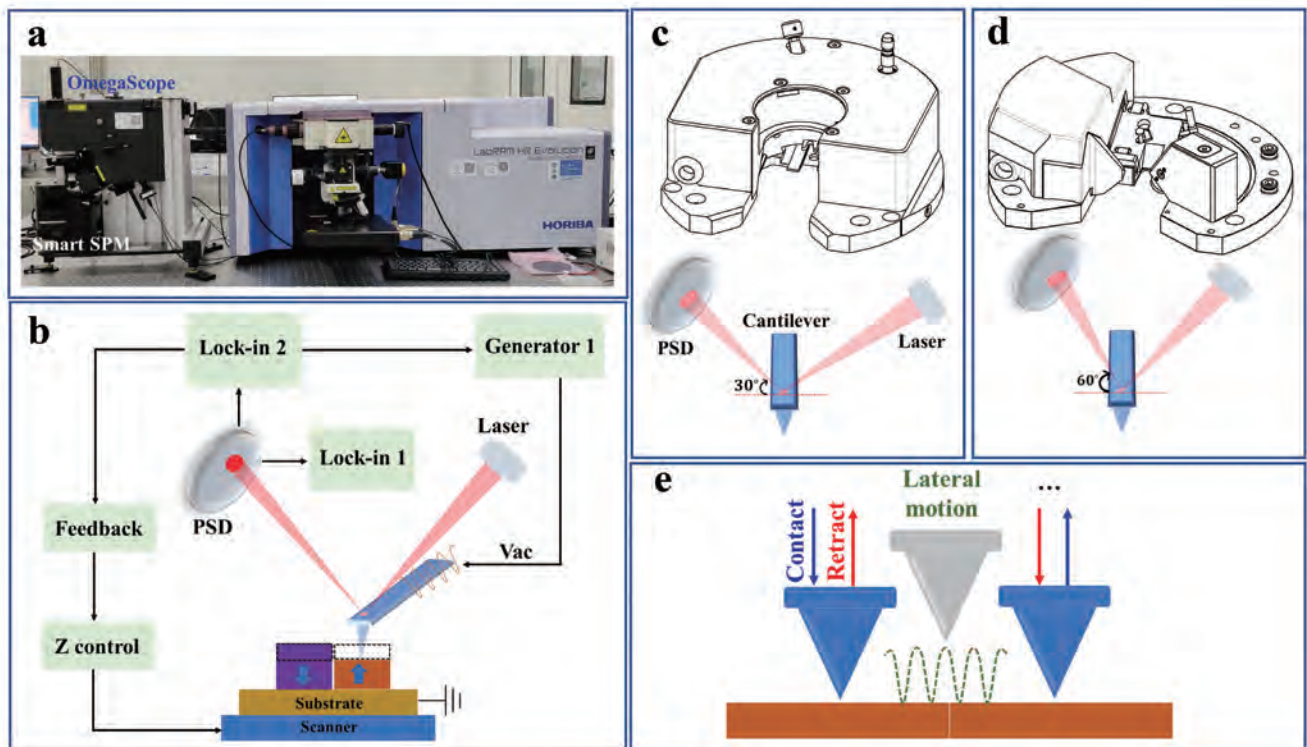

Figure 1 PFM operation principle and experimental set up in (a) HORIBA AFM-Raman. (b) Basics of PFM: a conductive tip is brought into contact with the piezoelectric sample. An alternating voltage (Vac) is applied to the tip at a given amplitude and frequency by the function generator (generator 1), while the sample substrate (or back electrode) is kept grounded. The generated oscillating electric field leads to the localized mechanical deformation of the sample (i.e., either and extension or contraction). In turns, the resulting strain induces the deflection of the tip cantilever. The reflected laser signal is read out by a position sensitive detector (PSD) that is connected to two lock-in amplifiers. The output signals from lock-in 2 are the PFM amplitude and phase, which contain the information about the strength of the vertical electromechanical response, and the direction of the polarization, respectively. In addition, lock-in 2 is the main amplifier of the feedback-controller loop. While, the output readings from lock-in 1 are the lateral PFM amplitude and phase signals. Schematic drawing of AFM heads (c) HE002 and corresponding optical registration system; and (d) HE001 and its optical registration system. (e) Simplified sketch of the point-contact mode operation of PFM-Top mode.

proven[3,6]. To unequivocally verify ferroelectricity, the formation of well-defined ferroelectric domain patterns has to be observed[7]. Ferroelectric domains are nanometer-scale structures with opposite polarization and separated by boundaries known as domain walls. Nevertheless, it is challenging to observe nanoscale domains on materials with intrinsic small-vertical deformations and so, weak ferroelectric responses. This is even more critical when characterizing domain walls. Therefore, to further the experimental discovery, and application of 2D ferroelectrics for advanced nanoelectronics, the electromechanical properties of domain patterns, and domain walls have to be characterized with nanoscale-spatial resolution. PFM is conventionally employed to explore nanoscale electromechanical properties. Since the mechanical deformation (i.e., crystal lattice extension or contraction) induced by the applied electric field is recorded by means of the lock-in technique, strains in the order of picometres can be detected[1] (working principle in Figure 1b). Despite, when imaging piezoelectric responses at high-spatial resolutions, background noises considerably degrade the image signal-to-noise ratio (SNR). In addition, the tip-sample contact nature of PFM makes piezoresponse readings prone to artifacts generated by long-range electrostatic interactions. The use of stiff cantilevers (tens of N/m) helps to circumvent electrostatic-side effects. Yet, at the cost of damaging either the tip or the sample. In this manner, the synergic effect of background noises and electrostatics interactions complicate the PFM imaging at high-spatial resolutions of 2D ferroelectrics.

Fortunately, HORIBA AFM offers practical solutions to these issues thanks to its versatile instrumental setup and scanning method PFM-Top mode (Figure 1). These advantages are explained and demonstrated below in the framework of working with HORIBA AFM-Raman (Figure 1a).

In the standard configuration of HORIBA AFM Raman, the Smart SPM (Figure 1a) is coupled to the AFM HE002 head (Figure 1c), which optical detection system is arranged such as the diode laser beam is reflected by the cantilever (at its rest position) to the PSD at an angle of 30°. The aim of this wide angle is to allow the top and side interface of the Smart SPM to the Omegascope (or Raman laser path, Figure 1a). Conversely, the reflected angle of the laser in the registration system of head HE001 is 60° (Figure 1d). With this narrower angle, the signal-collection efficiency (sensitivity) of the registration system is improved a tend fold compared to the sensitivity achieved with the wide angle: HE001's registration system noise <0.03nm vs HE002's registration system noise

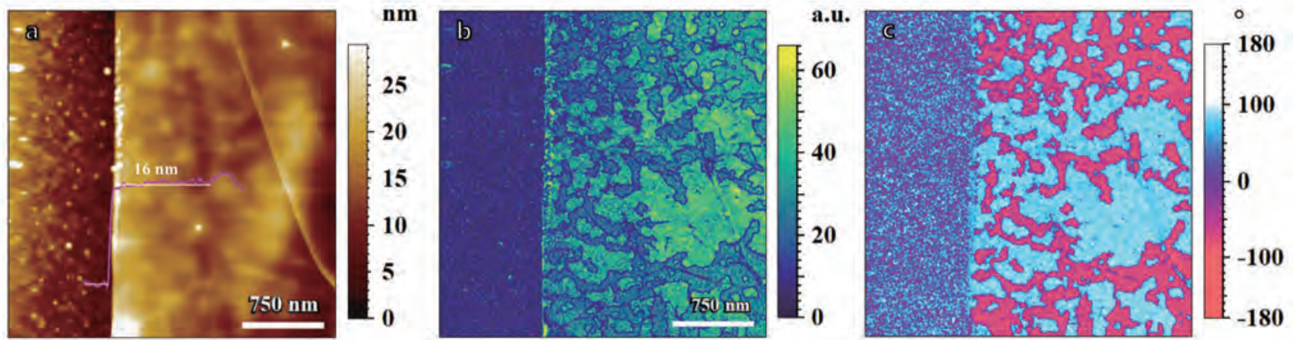

Figure 2 Topography and heigh-line profile (a), amplitude (b) and phase (c) images of a CIPS flake with a thickness of 16 nm. Experimental settings: driving PFM voltage (Vac) = 3 V; driving PFM frequency (f) = 114 KHz (contact resonance); Probe = Pt/Ir coated Si tip, spring constant (k) = 15 N/m; resolution = 256 x 256 pixels; humidity ~ 38%.

<0.1nm. The superior sensitivity performance of HE001 makes this head suitable to conduct AFM and/or NanoRaman experiments in liquid media. Notably, users can take advantage of this detection scheme to achieve ambient experiments in which resolving very short cantilever deflections is a most. This is the case of high-resolution PFM studies of ultra-thin ferroelectric materials. Because unlike to most of the AFM methods in which the lateral resolution depends on the tip radius, in PFM, this merit is strongly influenced by the material's elasticity[1].

On the other hand, when scanning via PFM-top mode, the piezoresponse signal is recorded when the tip is in contact with the sample, while the lateral motion of the tip to the next measuring point is performed in semicontact mode (Figure 1e). This operation is repeated on each pixel of the image. The key advantages of this point-contact operation compared to plane-contact mode are the reduction of the tip-sample contact time (in the order of milliseconds) and lateral forces. In turn, short contact times minimize tip and sample damage, loading force drifts and indirectly, electrostatics side effects because stiff cantilevers can safely be used. On the other hand, abrasive lateral forces are avoided because the lateral motion between measuring points is performed in semicontact mode. The absence of lateral forces allows to resolve more precisely the fine contours of the objects.

Explained the instrumental and scanning advantages, in the following sections we probe the capabilities of HORIBA AFM for the high-resolution PFM imaging on ambient conditions of the 2D ferroelectric $CuInP_2S_6$ (CIPS). CIPS is a vdW ferroelectric with unique properties such as negative piezoelectricity, negative capacitance behavior, and interchange between ferroelectricity and ionic conductivity[8]. Yet, its reliable nanoscale imaging for fundamental research is scarce due to complications from low ferroelectric signals and ion conductivity effect (see below).

Piezoresponse imaging of a few layered CIPS

This section describes the PFM imaging of a 16 nm thick CIPS flake obtained by coupling the HE002 head to Smart SPM, and by the scanning method PFM-Top mode. The ambient topography, amplitude, and phase PFM images acquired simultaneously during scanning are shown in Figure 2a-c. The experimental conditions are described in the image's caption. The amplitude image (Figure 2b) reveals the existence of domain patterns with labyrinthine-like topology and uniform piezoresponse, but enclosed by domain walls exhibiting low signal strength (Figure 2b, dark-blue stripes). The phase image (Figure 2c) unveils a contrast between domains close to 180°, as expected for domains with opposite polarization. The formation of opposite polarized domain structures is direct evidence of material ferroelectricity and reliable PFM imaging. Notice that the PFM images depict clear signal contrast between domains and domain walls. However, a closer inspection of domain walls requires of higher spatially resolved images.

The PFM amplitude images obtained at different scanning areas are illustrated in Figure 3. At 3 μm^2 image size, the amplitude map depicts good SNR (Figure 3a) and consistent signal. At 2 μm^2 scan area (Figure 3b), the domain walls are well discerned, but the SNR is relatively lower compared to the amplitude map in Figure 3a. A further zoom of the scan area (Figure 3c) lead to the overwhelming of the piezorespose signal by background noises. Such a poor PFM contrast precludes a robust evaluation of the lateral resolution, since background noises may broaden the width of the domain walls[1]. A tentative solution to improve the SNR is to increase the driving voltage (Vac > 3V). But this strategy is not recommended for CIPS since the polar structure and ferroelectricity can be severely damaged due to its high ionic conductivity[9,10]. Besides, high voltages can damage the thin structure of the flake. Thus, to avoid sample damage and the alteration of the ferroelectric properties, we concluded that the sensitivity

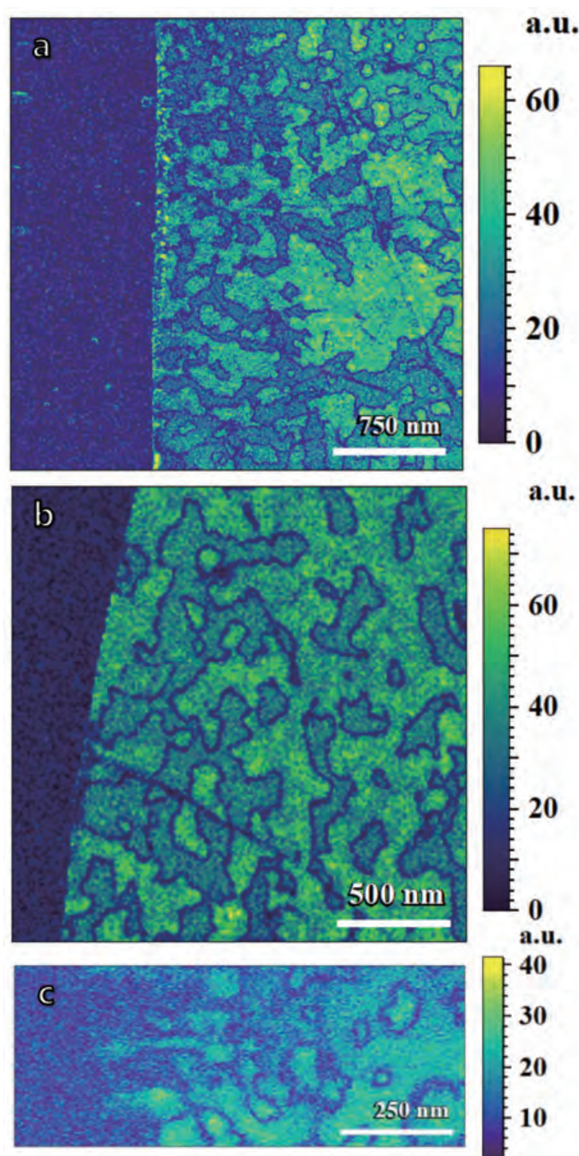

Figure 3 PFM amplitude images taken at 3x3 μm (a); 2x2 μm (b); and 1x0.4 μm (c) scan areas from a 16 nm-thick CIPS flake. Experimental settings: Vac = 3 V; f = 114 KHz (contact resonance); Probe= Pt/Ir coated Si tip, k = 15 N/m; resolution = 256 x 256 pixels; humidity ~ 38%.

of the present approach was not well-suited for the high-resolution imaging of the sample.

Characterization of domain walls

To improve the image SNR and provide a most robust estimation of the achieved lateral resolution, the Smart SPM was coupled to the HE001 head. PFM Top mode was kept as the scanning method. Figure 4 shows the topography, amplitude, and phase high-resolved images (0.5x0.5 μm) acquired from the same 16-nm thick CIPS flake. Notice that the PFM maps (Figure 4b, c) exhibit greater SNR compared to those recorded with the HE002 configuration, although a lower driving voltage (Vac = 2 V) was applied. Similarly, the domain patters present clear 180° polarization contrast.

It is customary to estimate the PFM-lateral resolution by mathematically modelling the amplitude signal of a 180° domain boundary (Figure 4c, d). The resulting full width at half maximum (FWHM) is indicative of lateral spatial resolution[1]. Here, domain wall amplitude profiles from different locations were fit to the Lorentz function (Figure 4e). According to the estimations, the highest lateral resolution is about 12 nm, which corresponds to the measure of the domain wall profile 2 (Figure 4e). It is important to clarify that the estimated lateral resolutions calculated from the domain wall profiles are not their actual width.

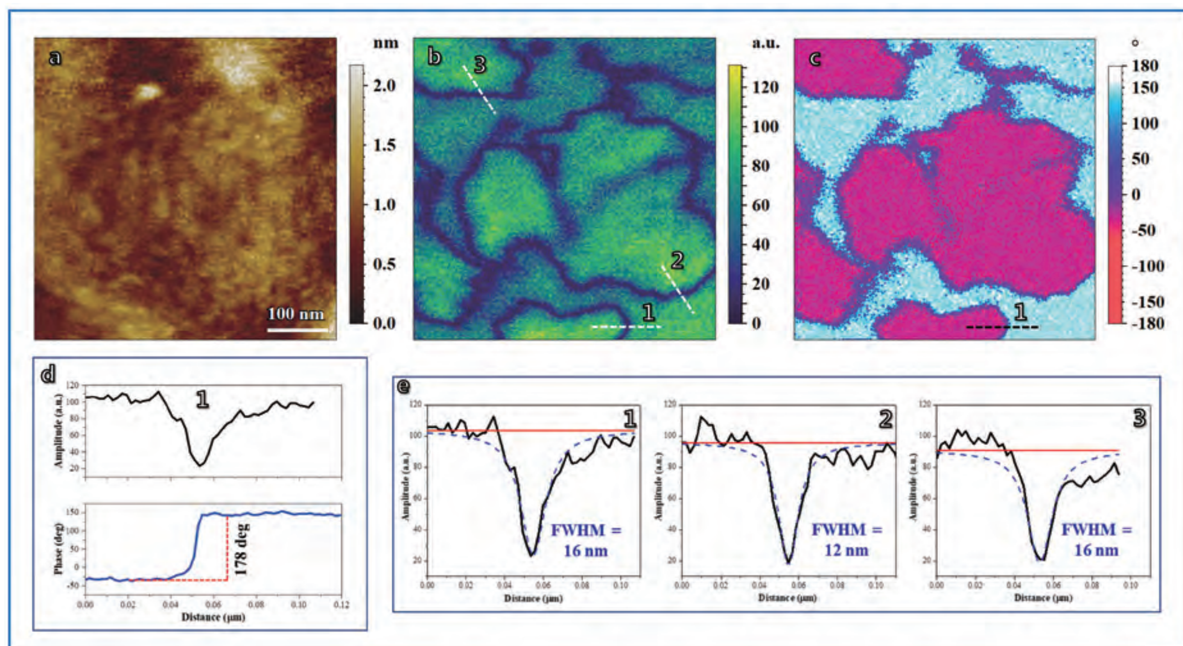

Figure 4 High-resolution AFM topography (a), amplitude (b), and phase (c) images of a 16 nm thick CIPS flake. Amplitude and phase profiles of a nearly 180° domain wall (d, black and blue dashed lines, respectively); domain walls amplitude profiles (e, black line) modeled by Lorentz function (e, blue dashed line). Experimental settings: Vac = 2 V; f = 114 KHz (contact resonance); Probe = Pt/Ir coated Si tip, k = 15 N/m; resolution = 256 x 256 pixels; image size = 0.5 x 0.5 μm; humidity ~ 38%.

Conclusion

In this work we demonstrated the setup versatility of HORIBA AFM together with its scanning method "PFM-Top mode".

The combined use of the HE001 head and PFM-Top scanning mode permitted the high-resolution piezoresponse imaging in ambient conditions and low driving voltages of a few layered CIPS flake at 12 nm spatial resolution. The reliability of the measurements is supported by phase contrast values between domains close to 180°, and the topography integrity of the sample, even though cantilevers with several N/m were used. Hence, confirming non-destructive operation of PFM-Top mode.

Perspectives

Besides the characterization of ultrathin films and domain walls, the present strategy could be implemented to the investigation, in either ambient or liquid environments, of delicate and weakly piezoelectric materials like polymers and biological systems. Certainly, PFM imaging and fundamental studies will be greatly enriched when colocalized with optical techniques like normal and polarized Raman Microscopy, Second-Harmonic Generation (SHG), and NanoRaman. Definitely, correlative analysis will be ideal approaches to fully exploit the capabilities of HORIBA AFM Raman.

* Editorial note: This content in based on HORIBA's investigation at the year of issue unless otherwise stated.

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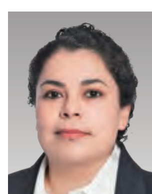

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