Switching spectroscopic measurement of surface potentials on ferroelectric surfaces via an open-loop Kelvin probe force microscopy method

Qian Li, Yun Liu, Danyang Wang, Ray L. Withers, Zhenrong Li et al.

Citation: *Appl. Phys. Lett.* **101**, 242906 (2012); doi: 10.1063/1.4772511

View online: <http://dx.doi.org/10.1063/1.4772511>

View Table of Contents: <http://apl.aip.org/resource/1/APPLAB/v101/i24>

Published by the [American Institute of Physics](#).

Related Articles

Friction measurement on free standing plates using atomic force microscopy

Rev. Sci. Instrum. **84**, 013702 (2013)

A correlation force spectrometer for single molecule measurements under tensile load

J. Appl. Phys. **113**, 013503 (2013)

Compact metal probes: A solution for atomic force microscopy based tip-enhanced Raman spectroscopy

Rev. Sci. Instrum. **83**, 123708 (2012)

Note: Radiofrequency scanning probe microscopy using vertically oriented cantilevers

Rev. Sci. Instrum. **83**, 126103 (2012)

Enhanced quality factors and force sensitivity by attaching magnetic beads to cantilevers for atomic force microscopy in liquid

J. Appl. Phys. **112**, 114324 (2012)

Additional information on *Appl. Phys. Lett.*

Journal Homepage: <http://apl.aip.org/>

Journal Information: http://apl.aip.org/about/about_the_journal

Top downloads: http://apl.aip.org/features/most_downloaded

Information for Authors: <http://apl.aip.org/authors>

ADVERTISEMENT

AIP | Applied Physics
Letters

**EXPLORE WHAT'S
NEW IN APL**

SUBMIT YOUR PAPER NOW!

**SURFACES AND
INTERFACES**

Focusing on physical, chemical, biological, structural, optical, magnetic and electrical properties of surfaces and interfaces, and more...

**ENERGY CONVERSION
AND STORAGE**

Focusing on all aspects of static and dynamic energy conversion, energy storage, photovoltaics, solar fuels, batteries, capacitors, thermoelectrics, and more...

Switching spectroscopic measurement of surface potentials on ferroelectric surfaces via an open-loop Kelvin probe force microscopy method

Qian Li,¹ Yun Liu,^{1,a)} Danyang Wang,² Ray L. Withers,¹ Zhenrong Li,³ Haosu Luo,⁴ and Zhuo Xu³

¹Research School of Chemistry, The Australian National University, ACT 0200, Australia

²School of Materials Science and Engineering, The University of New South Wales, NSW 2052, Australia

³Electronic Materials Research Laboratory (EMRL), Xi'an Jiaotong University, Shaanxi 710049, China

⁴Shanghai Institute of Ceramics, Chinese Academy of Sciences, Shanghai 201800, China

(Received 18 November 2012; accepted 29 November 2012; published online 12 December 2012)

We report a method for switching spectroscopy Kelvin probe force microscopy (SS-KPFM). The method is established as a counterpart to switching spectroscopy piezoresponse force microscopy (SS-PFM) in Kelvin probe force microscopy. SS-KPFM yields quantitative information about the surface charge state during a local bias-induced polarization switching process, complementary to the electromechanical coupling properties probed via SS-PFM. Typical ferroelectric samples of a Pb-based relaxor single crystal and a BiFeO₃ thin film were investigated using both methods. We briefly discuss the observed surface charging phenomena and their influence on the associated piezoresponse hysteresis loops. © 2012 American Institute of Physics. [<http://dx.doi.org/10.1063/1.4772511>]

As an atomic force microscopy (AFM)-based technique, Kelvin probe force microscopy (KPFM) has led to numerous applications in many research fields over the past 20 years.^{1,2} KPFM detects not only the spatial distribution of charges with high sensitivity and at nanoscale resolution but also the dynamics of these charges when coupled with various forms of excitations, e.g., applied voltages. These capacities of KPFM are particularly useful for probing electronic materials and devices for which charge plays a central role. In ferroelectric materials, there are permanently bound charges on the surfaces as a result of spontaneous polarization. To achieve an energetically stable state, these bound charges must be compensated or screened to a certain extent via either intrinsic and/or external charge carriers. The interplay between polarization and screening determines many of the properties of ferroelectric materials, and has thus driven intensive studies, including those employing KPFM.^{3–6}

Piezoresponse force microscopy (PFM), another established AFM-based technique, can image ferroelectric domains down to the nanoscale using the electromechanical coupling properties of ferroelectrics. In addition to this imaging mode, switching spectroscopy PFM (SS-PFM) enables the measurement of local piezoresponse (PR) hysteresis loops as well as yielding information about the dynamic behavior of ferroelectric domain nucleation and evolution.^{7–9} More recently, SS-PFM has been extended to probe the local ion transport properties for electrochemical materials.¹⁰ An analogous switching spectroscopy method using KPFM, termed switching spectroscopy Kelvin probe force microscopy (SS-KPFM) here, however, has yet to be developed. Instead, the prevailing method adopted to study the effect of applied voltages on surface potentials (SPs) is to pole defined charge patterns in contact mode and then measure them

using KPFM.^{6,11} This method, however, can neither achieve fine spatial resolution and fast tracking of dynamic processes nor reproduce a true local hysteretic process. Thus, it is of some considerable interest to be able to realize SS-KPFM measurements to help elucidate these local charge transport and electromechanical coupling phenomena.

In KPFM, a sinusoidal signal with a dc offset is applied to the AFM tip and sample, i.e., $V_{tip} = V_{dc} + V_{ac}\sin(\omega t)$, ω being an ac frequency usually chosen at the resonances of the cantilevers. As a result, the tip-sample electrostatic force, F_{es} , has the form

$$F_{es} = C'_z(V_{tip} - V_{SP})^2, \quad (1)$$

where C'_z is the tip-surface capacitance gradient and V_{SP} is the surface potential. Expansion of Eq. (1) results in static, linear 1ω , and quadratic 2ω terms. The cantilever response driven by the 1ω component of the electrostatic force, $F_{es}(1\omega)$, can be explicitly written as

$$R(1\omega) = \alpha C'_z V_{ac}(V_{dc} - V_{SP}), \quad (2)$$

where α is a conversion coefficient unrelated to samples.¹² If one keeps zeroing this response by adjusting V_{dc} close to V_{SP} then the SP can thereby be obtained. This is a *closed-loop* feedback method. Alternatively, the SP can also be derived from the data set of $R(1\omega)$ measured at several (in principle, two is adequate) offset voltages. Guo *et al.* have recently demonstrated this so-called *open-loop* (OL) KPFM in conjunction with the band excitation (BE) technique.^{12,13}

The BE technique, originally developed by Jesse *et al.*,¹⁴ has been implemented on our Cypher AFM (Asylum Research). An external BE controller is configured, including NI PXI-5412 arbitrary waveform generator (AWG) and PXIe-5122 digitizer/data acquisition (DAQ) modules. The hardware control and data analysis routines are developed on LABVIEW/IGOR PRO platforms. By using a synthesized signal of

^{a)} Author to whom correspondence should be addressed. Email: yliu@rsc.anu.edu.au.

a predefined band of frequencies to excite the cantilever/sample, the BE technique allows a highly robust resonance tracking and full decoupling of the simple harmonic oscillator (SHO) model from the measured response data. In *amplitude-modulation* KPFM, the shifts in resonant frequency are usually small compared to the PFM case, since KPFM works in non-contact mode. Even so, the BE-based OL KPFM offers the benefits of improved measuring accuracy via the removal of feedback-loop related errors.^{12,13}

The procedure for SS-KPFM is then straightforward: applying a bias pulse to samples via tips during engagement and subsequently probing SP in lift mode. This, however, is difficult to implement in an automated and deterministic way using the standard KPFM modules available on commercial AFMs. Our approach is to combine the AFM and BE electronics. Figure 1(a) shows a time sequence diagram for the signal channels in SS-KPFM. Two digital-analog converters (DACs) in the AFM are first used to generate two square waveforms synchronously. One of these signals, “TRIG,” is used to trigger the BE controller, while the other, “Z-Mod,” is applied to the Z-axis piezo-scanner after being summed with a dc voltage set for initial engagement. Note that the Z-axis feedback loop of the AFM is disabled here, i.e., the tip-sample separation is *open-loop* modulated by the Z-Mod signals. On the BE controller side, the AWG and DAQ are synchronized with the latter as a slave module. The AWG is triggered at each rising edge of the TRIG signals, generating a dc pulse followed by a segment of BE (in our case, *Chirp*-type) waveforms. Precisely, over the same segment, the output of the AFM photodiode detector is sampled by the DAQ. In general, each SS-KPFM measurement consists of a number of steps in which the same BE excitation signals are used, while dc biases are changed stepwise to match the SS-KPFM procedure. Note that the actual duration, τ_{DC} , of the applied bias pulse is the interval between the rising edge of

the TRIG and the falling edge of the Z-Mod signals, shorter than that supplied by the AWG. Likewise, the other parameters of an SS-KPFM loop, e.g., period, are also regulated by these two waveforms, constructed with proper consideration of the hardware characteristics.

The primary concern with SS-KPFM is the response rate and position repeatability of the scanner during repetitive engagements. Fig. 1(b) illustrates a portion of the actual signals of TRIG and the detector output. Here, the TRIG and Z-Mod waveforms have the same edge positions and are converted at 5 kSa/s, a typical rate used in this work. The measured rising/falling time of the edges agrees with the expected value (0.2 ms). Due to a fast actuation imposed by the Z-axis modulation, the cantilever (Olympus AC240TM) oscillates at its 1st flexural resonant frequency (~ 73.5 kHz) with an exponentially damped amplitude. This transient effect is well-known to be dependent on the mechanical quality factor, Q , of the cantilevers (~ 130 here); a higher Q means a longer settling time. This leads to a region of interference for KPFM detection. The cantilever undergoes another transient when dc biases are switched off due to the attractive, static component of F_{es} . Thus, a 5–10 ms waiting time is generally adopted prior to initiating the BE waveforms. On zeroing the Z-Mod signal, the deflection signal reverts to its initial value instantly, signifying that any drifts are rather small. In practice, the change of deflection values was found to be within 10% of the set-points after performing a 32-step loop.

Fig. 2 presents an example of an SS-KPFM measurement, carried out on a $(\text{Bi}_{0.5}\text{Na}_{0.5})\text{TiO}_3$ single crystal. Based on the OL KPFM method, we used a train of 8 BE waveforms (total length = 8×4 ms), each of which is offset with a dc voltage to excite the cantilever electrically. The digitized time domain vibration signals were Fourier transformed into the frequency response spectra of the cantilever. Figs. 2(a) and 2(b) show the amplitude and phase response, respectively, as a function of dc offset for the first step (bias = 0 V). It is quite clear that $F_{es}(1\omega)$ changes sign between 0 V and 0.5 V offset, where the phase changes by π accompanied by weak amplitudes. By fitting these response spectra with the SHO model,^{12,14} we obtain the parameters: signed driving amplitude A_0 , Q , and resonant frequency, the latter two being of little concern in the present work. The typical spectra and fits shown in Fig. 2(c) illustrate that the measured profiles of the resonance peaks agree very well with the SHO model.

The above analysis procedure is performed for the data acquired at each pulse step. The resultant A_0 data set in dimensions of dc offset and bias pulse is shown in Fig. 2(d). An apparent fluctuation in A_0 suggests that the SP of the sample is altered by the pulses. According to Eq. (2), SP and C'_z can be obtained by linearly fitting to A_0 about the dc offset, with SP corresponding to the x intercept and C'_z to the slope of the fitted line, respectively. Fig. 2(e) shows the A_0 data for selected steps along with the corresponding fits. Notably, the slope of A_0 (i.e., C'_z) changes very little and averages to 8.67(7) for all steps. Such a small deviation verifies that a stable lift height (~ 200 nm) was maintained over the loop.¹² The applicability of linear fitting in this case also reveals that the SP after biasing does not change significantly

FIG. 1. (a) Schematic time sequence diagram for the signal channels in SS-KPFM. Dashed lines denote the triggering occurring at the corresponding edges. (b) Signals of TRIG and AFM deflection output, recorded with an oscilloscope (sampling rate: 250 kSa/s).

FIG. 2. (a) Amplitude and (b) phase of the cantilever response as a function of dc offset. (c) Typical amplitude spectra and their SHO fits. (d) dc offset and pulse bias dependence of the signed driving amplitude A_0 . (e) A_0 vs dc offset at selected steps and their linear fits. (f) The derived SP hysteresis loop (first loop) and the second loop measured in a reversed sequence of bias. $\tau_{DC} = 20$ ms; lift height ~ 200 nm.

over the probing timescale approximately tens of ms, otherwise the fitting model would be coupled with the charge dynamics involved. Finally, the derived SP loop is shown in Fig. 2(f), with a subsequent loop measured at the same location after a short tip-grounding. These loops are hysteretic. Their openness indicates that a net charging effect occurred to the sample dependent on the pulse sequence. We defer the further interpretation of this result here.

As expected, a combined SS-KPFM and SS-PFM analysis provides fresh insights into the formation mechanisms of

their respective hysteresis loops. Fig. 3 shows a set of results measured on a [111]-oriented 0.29Pb ($\text{In}_{1/2}\text{Nb}_{1/2}$) $\text{O}_{3-0.44}\text{Pb}$ ($\text{Mg}_{1/3}\text{Nb}_{2/3}$) $\text{O}_{3-0.27}\text{PbTiO}_3$ (PIMNT) single crystal and a 200 nm BiFeO_3 (BFO) thin film.¹⁵ In these measurements, we used two fresh AC240TM tips, and acquired dynamic PR loops⁹ and SP loops in sequence at the same location for each sample. We emphasize that the loops obtained at many other random locations show similar features and seem to be uncorrelated to the pristine domain directions. As regards the results obtained

FIG. 3. (a)-(d) Dynamic PR loops and (e)-(h) SP loops for the [111]-PIMNT single crystal and the BFO thin film. The PR loops in black line are the first loops of the second cycles. The PR and SP loops were acquired at the same location for each sample using two AC240TM probes: tip-A [the results in (a), (c), (e), and (g)] and tip-B [(b), (d), (f), and (h)]. $\tau_{DC} = 20$ ms; lift height ~ 200 nm.

- (1) The observed surface charging is mainly due to a bulk injection of electronic charge. For a given negative/positive tip bias, the number of injected electrons/holes is dependent on the Schottky barrier height $\Delta\Phi_B$. This current density is usually so high that the bias-induced polarization can be screened within a sub-ms timescale, as evidenced by the work of Son *et al.*¹⁶ Our results in general show that the bias-induced surface state is over-screened as the change of SP relative to the null bias states, ΔSP , is positive for positive biases and vice versa (Figs. 3(e)–3(h)). Notably, the ΔSP for BFO is much smaller than that for PIMNT measured under the same bias. This is attributed to a large bulk conductance of the BFO film. BFO compounds are well-known for having a small bandgap (2.8 eV) as well as shallow impurity energy levels.¹⁷ The injected carriers can thus easily drift and/or diffuse towards the back electrode. By contrast, in the highly insulating PIMNT crystal, many more carriers are localized at near-surface trap centers leading to a higher SP. Other charging mechanisms via dissimilar charge species, e.g., surface adsorbates, appear less dominant here because typically they are a *sluggish* process,^{4,5} and may not cause any difference in charging behavior for the two studied samples.
- (2) Figs. 3(a) and 3(c) present the normal PR loops obtained using “tip-A.” For PIMNT, a strong relaxation of the PR loops can be observed when the bias window is larger than ~ 10 V; i.e., the PR signal decays with time (in a near-exponential way) after the bias pulses. Interestingly, the associated SP loop shows a similar shape with inflections seen near the same biases. This resemblance may imply a subtle correlation between them. Nevertheless, a direct electrostatic contribution to the observed PR relaxation can be excluded by comparing the phase of the two signals.^{3,8} For instance, after application of a 45 V pulse, the induced SP is ~ 2.6 V, higher than the tip potential ($V_{dc} = 0$). In this case, the pure PR and parasite electrostatic signals are in-phase and 180° out-of-phase with the excitation signals, respectively. Note that for measuring the PR signal, the tip is kept in contact mode. The potential difference, ΔV , between the tip and the surface drives a charge transfer between them and a gradual reduction of ΔV can be expected (see Fig. 2(f)).⁶ Then, the resultant signal should be increasing with time, opposite to the observed trend of relaxation. On the other hand, the intrinsic relaxor character of PIMNT seems a plausible reason here, as no relaxation of the PR signal is observed for the normal ferroelectric BFO (Fig. 3(c)). It has been conjectured that the merging and slowing-down followed by the recovery of polar nano-regions in relaxors are responsible for such a PR relaxation under tip bias stimuli.¹⁸ However, a recent report on dynamic PR loops for non-polar TiO_2 , resembling those in Fig. 3(a), suggests that there might be a universal relaxation mechanism mediated by the dynamics of oxygen vacancies in oxides,¹¹ which by nature is charge-coupled.
- (3) The PR loops obtained with “tip-B” (Figs. 3(b) and 3(d)) are highly irregular and even fully inverted (after

the initial cycles) for PIMNT. Similar phenomena have been reported before by authors including ourselves, and attributed to the domain back-switching effect caused by charge injection.^{19–22} The SP loop for PIMNT (Fig. 3(f)) shows a marked asymmetry (the relatively large uncertainty for negative biases is due to a fast decay of the SP signal therein), reminiscent of the rectifying current-voltage behavior of Schottky junctions. This high rate of charge buildup for negative biases may well explain the steep transition and fast saturation seen on the corresponding part of the PR loops. As for BFO, the SP (Fig. 3(h)) shows rather small variations but the loop shape is well correlated with the PR loops (Fig. 3(d)). Comparing two very different PR loops for the same sample, e.g., PIMNT, leads us to believe that the tip has exerted a significant effect on the character of the PR loops. One possible factor is a variation of $\Delta\Phi_B$ for the two tips, due to different work functions thereof or tip-sample interface states. This is supported by the relative changes of ΔSP ; from Figs. 3(e) and 3(f), the ΔSP at -30 V increases by a factor of ~ 4 , coinciding with a commensurate decrease in the ΔSP at -30 V, indicating a $\Delta\Phi_B$ shift of only 0.036 eV. However, we point out that a quantitative modeling with realistic material parameters may better correlate the measured PR and SP loops, and more credibly delineate the extrinsic role played here by the tips.^{11,23}

In summary, we have developed SS-KPFM via the BE-based OL KPFM approach. SS-KPFM allows one to obtain local SP hysteresis loops closely analogous to the PR hysteresis loops obtained in SS-PFM. SS-KPFM measurement on ferroelectric surfaces provides detailed information about the surface charge state, which is the result of a balance between bias-induced polarization evolution and charge transport processes near the tip-sample junction. Our preliminary results demonstrate the complementarity of SS-KPFM and SS-PFM for analyzing the measured SP and PR loops in relation to the properties of the ferroelectric samples investigated. We expect that SS-KPFM can be further extended to local investigations of non-ferroelectric phenomena, e.g., electrochemical properties.

Q.L., Y.L., D.W., and R.L.W. acknowledge the support of the Australian Research Council (ARC) in the form of ARC Discovery Grants. Y.L. also acknowledges support from the ARC Future Fellowships Program. The authors are grateful to Dr. Sergei Kalinin for his advice on implementing the BE technique.

¹M. Nonnenmacher, M. P. O’boyle, and H. K. Wickramasinghe, *Appl. Phys. Lett.* **58**, 2921 (1991).

²*Kelvin Probe Force Microscopy*, edited by S. Sadewasser and T. Glatzel (Springer, New York, 2011).

³S. Hong, J. Woo, H. Shin, J. U. Jeon, Y. E. Park, E. L. Colla, N. Setter, E. Kim, and K. No, *J. Appl. Phys.* **89**, 1377 (2001).

⁴S. V. Kalinin and D. A. Bonnell, *Phys. Rev. B* **63**, 125411 (2001).

⁵X. Y. Liu, K. Kitamura, and K. Terabe, *Appl. Phys. Lett.* **89**, 132905 (2006).

⁶Y. Kim, C. Bae, K. Ryu, H. Ko, Y. K. Kim, S. Hong, and H. Shin, *Appl. Phys. Lett.* **94**, 032907 (2009).

- ⁷S. Jesse, H. N. Lee, and S. V. Kalinin, *Rev. Sci. Instrum.* **77**, 073702 (2006).
- ⁸S. Jesse, A. P. Baddorf, and S. V. Kalinin, *Nanotechnology* **17**, 1615 (2006).
- ⁹A. Kumar, Y. Ehara, A. Wada, H. Funakubo, F. Griggio, S. Trollet-Mckinstry, S. Jesse, and S. V. Kalinin, *J. Appl. Phys.* **112**, 052021 (2012).
- ¹⁰A. Kumar, F. Ciucci, A. N. Morozovska, S. V. Kalinin, and S. Jesse, *Nat. Chem.* **3**, 707 (2011).
- ¹¹Y. Kim, A. N. Morozovska, A. Kumar, S. Jesse, E. A. Eliseev, F. Alibart, D. Strukov, and S. V. Kalinin, *ACS Nano* **6**, 7026 (2012).
- ¹²S. Guo, S. V. Kalinin, and S. Jesse, *Nanotechnology* **23**, 125704 (2012).
- ¹³S. Guo, S. V. Kalinin, and S. Jesse, *Appl. Phys. Lett.* **100**, 063118 (2012).
- ¹⁴S. Jesse, S. V. Kalinin, R. Proksch, A. P. Baddorf, and B. J. Rodriguez, *Nanotechnology* **18**, 435503 (2007).
- ¹⁵See supplementary material at <http://dx.doi.org/10.1063/1.4772511> for information about the BFO sample, and raw spectrogram data of the dynamic PR loops presented in Fig. 3.
- ¹⁶J. Y. Son, G. Lee, and Y.-H. Shin, *Appl. Phys. Lett.* **94**, 162902 (2009).
- ¹⁷S. J. Clark and J. Robertson, *Appl. Phys. Lett.* **90**, 132903 (2007).
- ¹⁸V. V. Shvartsman and A. L. Kholkin, *Appl. Phys. Lett.* **86**, 222907 (2005).
- ¹⁹S. Bühlmann, E. Colla, and P. Muralt, *Phys. Rev. B* **72**, 214120 (2005).
- ²⁰A. L. Kholkin, I. K. Bdikin, V. V. Shvartsman, and N. A. Pertsev, *Nanotechnology* **18**, 095502 (2007).
- ²¹Q. Li, Y. Liu, J. Schiemer, P. Smith, Z. Li, R. L. Withers, and Z. Xu, *Appl. Phys. Lett.* **98**, 092908 (2011).
- ²²M. Lilienblum and E. Soergel, *J. Appl. Phys.* **110**, 052012 (2011).
- ²³A. N. Morozovska, S. V. Svechnikov, E. A. Eliseev, S. Jesse, B. J. Rodriguez, and S. V. Kalinin, *J. Appl. Phys.* **102**, 114108 (2007).