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Dual Harmonic Kelvin Probe Force Microscopy for Surface Potential Measurements of Ferroelectrics

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***Abstract*— In this work, we implemented dual harmonic Kelvin probe force microscopy (DH-KPFM) for surface potential mapping of ferroelectric thin films, namely bismuth ferrite (BFO) and strontium barium niobate (SBN). We applied DH and conventional KPFM to charge-patterned BFO and found agreement between recorded relative surface potential values between domains, demonstrating that DH-KPFM can be used for quantitative mapping of relative surface potentials. We used piezoresponse force microscopy (PFM) to determine whether polarization switching had occurred. From the PFM data, we found that BFO was poled successfully, and that the measured surface potential was consistent with the sign of the bound polarization charge. For SBN, a thin surface layer was evident in the topography after the application of DC bias, suggesting an electrochemical reaction had taken place between the tip and the sample. We used DH-KPFM to simultaneously map the surface potential and changes in the dielectric properties resulting from this surface layer. The results presented herein demonstrate that DH-KPFM can be used for electric characterization of voltage-sensitive materials, and we anticipate that DH-KFPM will become a useful tool for non-intrusive electrical characterization of materials.**

Keywords- Kelvin probe force microscopy; piezoresponse force microscopy; ferroelectric materials; surface potential mapping; capacitance mapping; dual harmonic Kelvin probe force microscopy.

I. INTRODUCTION

Ferroelectrics are materials possessing a spontaneous polarization with a strong electrical depolarisation field near the surface of the polar faces [1-3]. These properties make ferroelectric materials interesting for the development of a broad range of applications and nanoscale devices based on polarization reversal, and have been the motivation for numerous nanoscale characterizations of ferroelectric materials with scanning probe-based microscopies [4]. Kelvin probe force microscopy (KPFM) [5] has become a useful tool for surface potential mapping of these materials at the nanoscale. This intermittent / non-contact technique exploits the high force sensitivity and lateral resolution of the atomic force microscope (AFM) to probe the potential difference between a conductive AFM tip and a sample. KPFM can provide key information about the electronic properties of the ferroelectric surface, such as surface charge and band bending [6]. Application of KPFM is useful in determining the factors governing the stability of the ferroelectric domains and control surface electrochemical reactivity [7].

KPFM does have some disadvantages in that it is prone to intrinsic artefacts such as feedback errors and stray capacitance effects, which can hinder the determination of the absolute surface potential [8, 9]. Also, the requirement for closed loop DC bias regulation can introduce uncertainty arising from feedback errors resulting from incorrect optimization. The phase of the deflection signal must also be adjusted correctly and not drift during the course of the measurement in order to maintain an accurate error signal for the feedback loop [10]. Additionally, the application of a DC bias makes KPFM unsuitable for non-intrusive characterization of some voltage-sensitive materials such as semiconductors, insulators, and organic and inorganic photovoltaics. In some measurements, surface potential has been shown to be dependent on DC bias voltage, and can result in charge transfer or tip-induced band bending in the sample [11, 12]. Furthermore, the necessity for application of DC biases limits this technique to vacuum and ambient conditions due to electrochemical reactions, which can take place at low biases in most liquids. Techniques such as DH-KPFM, which are capable of quantitative surface potential mapping without bias feedback, can circumvent the limitations of conventional KPFM.

In this paper, we demonstrate a quantitative, open loop variant of KPFM called dual harmonic KPFM (DH-KPFM). The term “open loop” refers to a system which does not require feedback control in order to determine the output of the system. KPFM is itself an extension of an open loop method known as electrostatic force microscopy (EFM). EFM does not allow direct measurement of the surface potential, and is generally used to qualitatively map surface charge

density across the sample surface [13]. Some success has been demonstrated quantifying EFM data, but this requires precise tip characterization and mathematical modelling, making quantitative EFM impractical when applied to unknown systems [14]. The DH technique was first proposed by Takeuchi *et al.* to measure the surface potential of semiconducting or insulating materials in vacuum [15]. This method did not require DC bias feedback to determine the contact potential difference, offering significant advantages over conventional KPFM. Recently, a DH technique has shown promise for mapping surface potential of charged nanoparticles in low molarity solutions [16, 17]. Here, we demonstrate quantitative surface potential mapping of ferroelectric thin film samples, which have been charge-patterned using piezoresponse force microscopy (PFM), using DH-KPFM.

II. Background Theory

In conventional KPFM, a DC voltage, V_{dc}, superimposed on an AC voltage, V_{ac}, is applied between tip and sample. The resulting electrostatic force is given by (1).

$$F_{es} = -\frac{1}{2}\frac{\partial C}{\partial z}(V_{tip})^2 \tag{1}$$

Where, $\partial C/\partial z$ is the capacitance gradient, which is dependent on tip geometry, local dielectric properties, and tip-sample distance, $V_{tip}=[(V_{dc}-\Delta\phi/e) + V_{ac}\sin(\omega t)]$, where $\Delta\phi$ is the contact potential difference between tip and sample and e is the elementary charge. Depending on the material under investigation, this contact potential difference can be related to work function in metals, doping profiles in semiconductors, and surface photo-voltage and surface potential characterisation in polymeric thin films, devices, and ferroelectrics [5]. Expanding equation (1), we find that the electrostatic force can be split into three spectral components, a static DC term, and two oscillatory force components.

$$A_{\omega} = \frac{|F_{es1}|}{k} = \left|\frac{\partial C}{\partial z}(V_{dc} - \frac{\Delta\phi}{e})\right|\frac{V_{ac}}{k} \tag{2}$$

$$A_{2\omega} = \frac{|F_{es2}|}{k} = \left|\frac{\partial C}{\partial z}\right|\frac{V_{ac}^2}{4k} \tag{3}$$

$$\frac{\Delta\phi}{e} = \frac{A_{\omega}\cos(\varphi_{\omega})}{A_{2\omega}}\frac{V_{ac}}{4} \tag{4}$$

Equations (2) and (3) describe the resultant amplitude of vibration at ω_m and $2\omega_m$ (A_{ω} and $A_{2\omega}$, respectively) induced by F_{es}. In conventional KPFM, the first derivative force A_{ω} is detected using a lock in amplifier (LIA), the in-phase component of which is used to determine $\Delta\phi$. This first derivative force cannot directly provide quantitative surface potential measurements. In KPFM, the detected in-phase signal is fed into a bias feedback loop, which adjusts V_{dc} to minimize the error signal, at which point, $V_{dc}=\Delta\phi/e$. This V_{dc} signal is then used to build up a 2D map of local potential difference as the tip is scanned across a sample surface. If, however, no DC bias is applied to the tip (DH-KPFM), then for a given V_{ac}, the A_{ω} component is comprised of both the capacitance gradient and $\Delta\phi$, whilst the $A_{2\omega}$ component is dependant only on the capacitance gradient. Equating these formulae, we find it is possible to determine the magnitude of $\Delta\phi$ *via* knowledge of V_{ac}, A_{ω}, and $A_{2\omega}$. The polarity of $\Delta\phi$ is then determined by the phase (φ_{ω}) of the cantilever vibration at ω_m, as described by equation (4).

III. Methods

All measurements were implemented on a commercial AFM (MFP-3D, Asylum Research, USA), with the aid of an external LIA (HF2LI, Zurich Instruments, Switzerland). Measurements were performed using Pt–Ir coated (DPE18, MikroMasch, Spain) cantilevers with a nominal resonant frequency and spring constant of 75 kHz and 2.8 N/m, respectively. DH-KPFM was performed with amplitude modulation AFM in lift mode at lift heights of 50 nm, unless otherwise stated. The LIA was used to control the V_{ac} applied to the tip and to demodulate the deflection signal. For all measurements, a $2V_{ac}$ tip bias at a frequency of 12.5 kHz was applied to the tip. All electrical pathways were carefully characterized prior to measurements. Corrections for influence of the electrical pathways and the frequency dependent gain of the cantilever transfer function between ω_m and $2\omega_m$ were applied. This procedure is described in detail elsewhere [18]. All samples were mounted using silver paint on a conductive disc, which was then grounded. Epitaxial bismuth ferrite (BFO) films (200 nm thickness) were deposited by pulsed laser deposition on $SrRuO_3$-coated (50 nm thickness) (001)-oriented $SrTiO_3$ substrates [19]. Lattice guiding and RF magnetron sputtering were used to synthesize single domain strontium barium niobate (SBN) films [20]. Poling of the ferroelectric films was performed by scanning an area of the sample with a DC biased conductive tip in contact with the surface. PFM was then used to verify polarization switching had taken place [21].

IV. Results and discussion

The polarization of a ferroelectric material can be switched using a biased conductive tip in contact with the surface providing a mechanism to pattern the BFO film. Reversing the polarization of the sample also results in a redistribution of charges at the surface. This technique provides a convenient and reproducible method of decoupling the surface charge from topography. Figures 1(a) and (b) show the topography and PFM phase image of the BFO sample after switching had taken place. The phase image shows a 180° shift in the phase signal between areas patterned with +15 and -15 V. Figures 1(c) and (d) show the first (A_{ω}) and second ($A_{2\omega}$) harmonic amplitude of the long range electrostatic force collected by DH-KPFM at a lift height of 50 nm. A_{ω} shows contrast corresponding to the charge-patterned surface, whereas $A_{2\omega}$ is constant, with a few features corresponding to debris or rough features evident in the topography. Figure 1(e) shows the DH phase (φ_{ω}), showing 180° shifts, indicating a reversal in the

polarity of the net charge between patterned regions. The DH surface potential (Figure 1(f)) was then calculated from the data contained in Figure 1(c-e). Surface potential images were calculated offline using IGOR Pro (WaveMetrics, USA). The measured surface potential of a polarized region is a sum of the contribution of the internal and external screening charges and the bound polarization charge. PFM and DH-KPFM phase images (Figure 1(b) and (e), respectively) reveal that the net surface potential of poled regions are determined by the remnant polarization charge and not the trapped surface charge *i.e.*, domains with an out-of-plane polarization pointing towards the sample surface have a positive net charge.

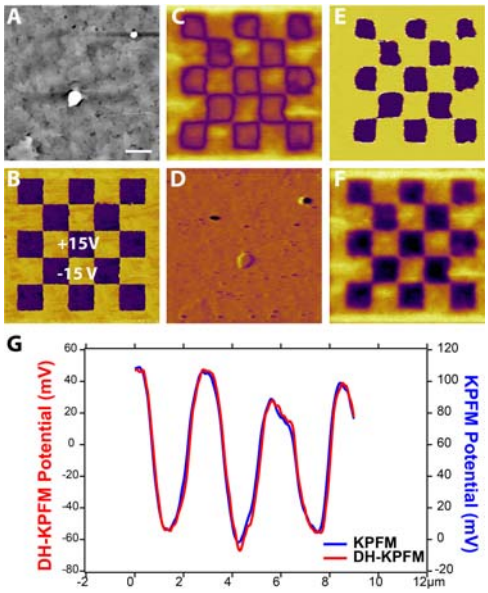

Figure 1. (a) Topography (*z*-range = 8.8 nm) and (b) PFM phase images of a patterned BFO thin film where bright colour represents domains with out-of-plane polarization pointing towards the sample surface. Images of (c) first and (d) second harmonic amplitudes, (e) first harmonic phase, and (f) recorded DH surface potential. (g) Line profile cross section of the same area, recorded using conventional KPFM and DH-KPFM and plotted on different axis scales. Scale bar represents 2 µm.

In order to confirm the viability of surface potential mapping using DH-KPFM, the same area was evaluated using conventional KPFM (image not shown). From the cross section in Figure 1(g), it is evident that both methods record a 100 mV relative potential difference between positive and negative domains, confirming the viability of DH-KPFM for quantitative mapping of relative surface potential.

Figure 2 shows DH-KPFM results for a SBN thin film, which was patterned using a conducting cantilever scanned in contact with the sample while a ±10 DC bias (below the switching bias of the material) was applied to the tip. Charging of the sample is evident in the surface potential image (Figure 2(c)) and an electrochemical reaction between the biased tip and sample has resulted in the observed topography changes (Figure 2(a)). This change of surface chemistry is also reflected in the second harmonic image (Figure 2(b)), which is a function of the capacitance gradient between the tip and sample, suggesting the surface layer has a different dielectric constant than the SBN film. Thus, changes in the dielectric properties of the material under test, or growth of modifying layers can be detected in the second harmonic signal. Using calibrated values for the inverse optical lever sensitivity (63.5 nm/V) and spring constant (2.8 N/m), it was possible to quantify the capacitance measured at a fixed distance above the sample surface. Figure 2(d) shows cross-sectional data on topography changes across the sample surface, in addition to surface potential and capacitance measurements calculated from DH-KPFM. It has been demonstrated that the quantification of the second harmonic signal enables the extraction of the local dielectric constant and may therefore permit DH-KPFM to perform parallel surface potential and dielectric constant measurements [22, 23].

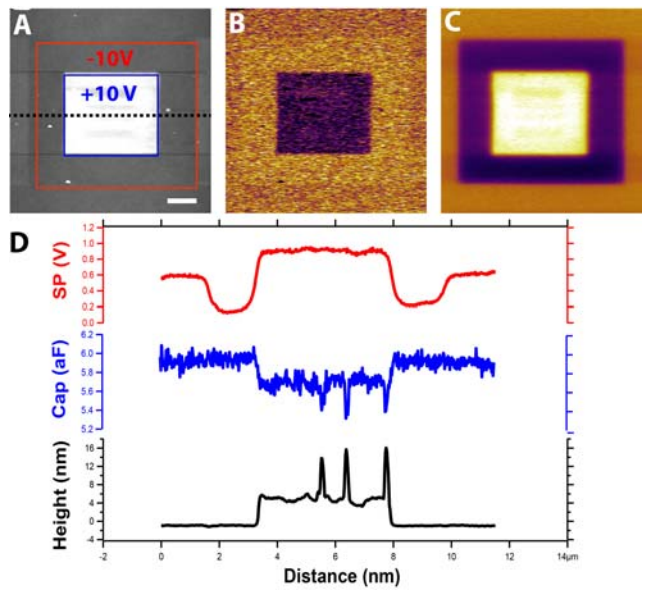

Figure 2. (a) Topography (*z*-range = 17.7 nm) of the SBN film after being scanned in contact mode with a DC biased tip. (b) Second harmonic amplitude depicting changes in the dielectric constant of the material and (c) surface potential recorded with DH-KPFM. (d) Line profile cross sectional data of the surface potential, capacitance, and height taken from the area marked with a dashed black line in (a). Scale bar represents 2 µm.

V. SUMMARY

We have presented DH-KPFM as method of surface potential mapping of ferroelectric thin films. The results show that DH and conventional KPFM can be used to accurately map relative surface potentials for non-voltage sensitive materials. We believe the ability of DH-KPFM to operate without the need to apply a DC bias represents great potential for the study of voltage-sensitive materials whilst mitigating the possibility of charge transfer and/or band bending. In addition, we have demonstrated the ability to perform simultaneous surface potential and capacitance mapping. DH-KPFM is a promising technique for simultaneous measurements of surface potential

and dielectric properties, making it an attractive technique for electrical characterization in materials research.

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