Ferroelectric-like hysteresis loop originated from non-ferroelectric effects

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Abstract

Piezoresponse force microscopy (PFM) has advanced nanoscale understanding and analysis of ferroelectric and piezoelectric properties. In PFM-based studies, electromechanical strain induced by the converse piezoelectric effect is probed and analyzed as a PFM response. However, electromechanical strain can also arise from several non-piezoelectric origins that may lead to a misinterpretation of the observed response. Among them, electrostatic interaction can significantly affect the PFM response. Nonetheless, previous studies explored solely the influence of electrostatic interaction on the PFM response under the situation accompanied with polarization switching. Here, we show the influence of the electrostatic interaction in the absence of polarization switching by using unipolar voltage sweep. The obtained results reveal that the electrical neutralization between polarization and applied voltage plays a crucial role in the observed ferroelectric-like hysteresis loop despite the absence of polarization switching. Thus, our work can provide a basic guideline for the correct interpretation of the hysteresis loop in PFM-based studies.

Piezoresponse force microscopy (PFM) is well established as a useful and versatile tool for exploring ferroelectricity and piezoelectricity of polar materials on the nanoscale.[1–6] To date, the observation of nanoscale ferroelectric and piezoelectric properties using PFM has been primarily demonstrated in ferroelectric and piezoelectric oxides.[7,8] Furthermore, PFM has been recently utilized to investigate the existence of ferroelectricity and piezoelectricity in biological,[9,10] organic,[11] and organic–inorganic hybrid materials,[12] as well as in two-dimensional materials.[13,14] In general, PFM detects the electromechanical strain induced by the converse piezoelectric effect when an ac bias is applied to a conductive tip contacted with the sample surface. However, the electromechanical strain on the surface can stem from several origins, such as electrostatic interaction, electrochemical strain, Joule heating, etc.[15–20] For instance, it was reported that electrochemical strain can also induce electromechanical strain resulting in a ferroelectric-like hysteresis loop.[16,21] In particular, electrostatic interactions can affect the phase contrast of the PFM image and result in the distortion of the hysteresis loop shape.[18] Moreover, the effect of the electrostatic interaction cannot be completely excluded from the PFM response of the hysteresis loop because of the charge injection during the application of the electrical bias.[22,23] Thus, the careful interpretation of the observed results in PFM is very important. Even though electrostatic interaction can be minimized through the use of a stiff cantilever and observation of the off-field response in the hysteresis loop,[18] many exotic contributions to the PFM response cannot be easily eliminated. So far, the influence of the electrostatic interaction on the PFM response under the situation accompanied with polarization switching has been mainly explored, even though the influence of the electrostatic interaction has been known.[18,19] However, the relation between polarization charge and electrostatic interaction has not been systematically understood.

Herein, we demonstrate how electrostatic interaction can affect the PFM response in the absence of polarization switching based on unipolar negative voltage sweep. In order to exclude the potential influence from polarization switching, an epitaxial Pb(Zr,Ti)O_3 (PZT) thin film with upward polarization was chosen as a model sample. We first examined the injection charge according to the magnitude of applied negative voltage using Kelvin probe force microscopy (KPFM). The on- and off-field loops produced by the unipolar negative voltage sweep were then observed to investigate the electrostatic contribution to the hysteresis response. In addition, the change in the current flow was investigated using the *I*–*V* curve.

A 50-nm-thick epitaxial PZT thin film was prepared by pulsed laser deposition on a 0.5% Nb-doped $SrTiO_3$ (001) substrate.[24] All atomic force microscopy (AFM) measurements were performed using a commercial AFM (NX10, Park Systems). We used a commercial lock-in amplifier (SR830, Stanford Research Systems) for performing the PFM measurements. An ac modulation bias of 1.0 V_{rms} at 17 kHz was applied to a Pt/Cr coated conductive probe (Multi75E-G, BudgetSensors). In the KPFM measurements, a 2.0 V_{rms} at 17 kHz ac modulation bias and dc feedback bias were applied to the tip, and a two scan mode (tip-sample distance: 50 nm) with amplitude modulation was employed. To measure the off- and on-field piezoresponse hysteresis loops and *I*–*V* curves through band excitation (BE) method, a function generator (PXIe-1062Q, National Instruments) controlled by home-built LabVIEW/MATLAB software was connected with the above AFM system.[25] The voltage of bipolar and unipolar hysteresis loops range from −12 V to 12 V and 0 V to −10 V, respectively. In both cases, 2 V_{pp} with 290–410 kHz BE modulation bias were applied to the tip.

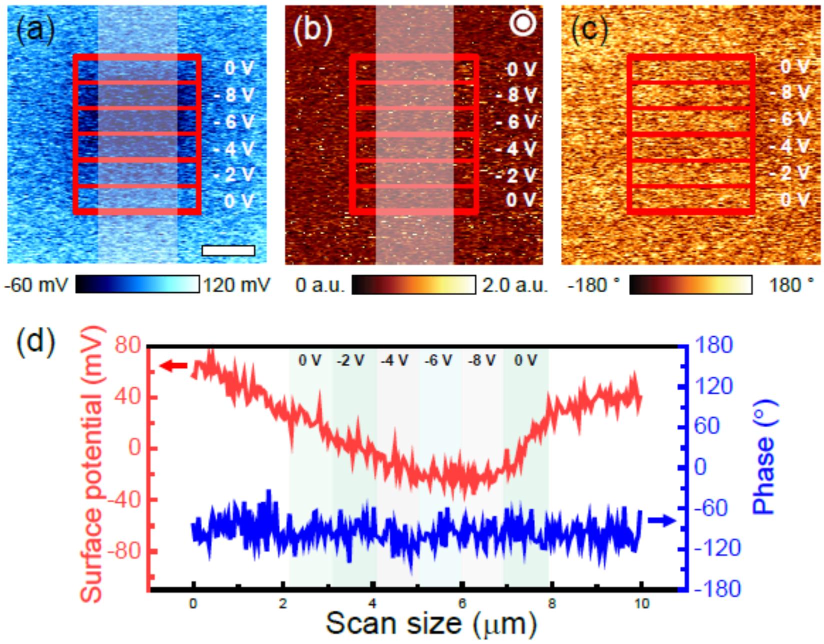

FIG. 1. (a) Surface potential and PFM (b) phase and (c) amplitude images after the application of negative voltages to the AFM tip. Each area indicated as a red rectangle in Figs. (a)–(c) corresponds to 4 × 1 μm^2. The magnitude of the applied voltage is presented in the image and each area was scanned with a scan speed of 0.5 Hz. The dark contrast in the phase image indicates the upward polarization. (d) Area profiles of the (red) surface potential and (blue) phase images. The area profiles were extracted from the gray area as shown in (a) and (b). The voltage was applied to the tip, and the sample was grounded. The scale bar corresponds to 2 μm.

In order to explore the influence of the electrostatic interaction on the PFM response, we have chosen an epitaxial PZT thin film, which has uniform upward polarization, as a model system because it is complicated to interpret observed results if the ferroelectric sample has both upward and downward polarizations. In the present case, while the application of the negative voltage cannot induce ferroelectric switching, it can solely inject negative charges on the ferroelectric surface, which can give rise to electrostatic interaction between an AFM cantilever and the surface. In other words, we are able to control a magnitude of the electrostatic interaction in the absence of ferroelectric switching. After applying negative voltage to the sample surface, we observed surface potential changes dependent on the magnitude of the negative voltage by using KPFM. Figures 1(a) and 1(d) show that the surface potential decreases with the negative charge injection as the magnitude of the negative voltage increases. The change to the surface potential caused by the negative charge injection indicates that the electrostatic interaction can influence the PFM response. However, as can be seen in Figs. 1(b)–(d), the PFM phase and amplitude after the application of the negative voltages do not show any visible change compared with the as-grown regions (outskirts of the red rectangular areas).

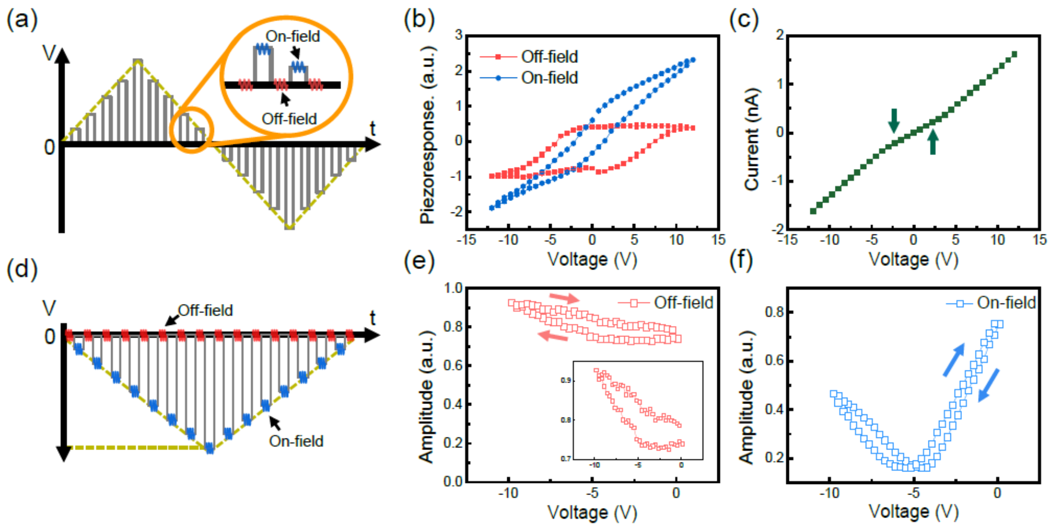

FIG. 2. (a) Schematic of a triangular voltage waveform and corresponding (b) off- and on-field piezoresponse hysteresis loops and (c) *I*–*V* curve. Note that (b) and (c) were simultaneously obtained. (d) Schematic of a unipolar negative voltage waveform and corresponding (e) off- and (f) on-field unipolar hysteresis loops. Inset in (e) shows an enlarged off-field unipolar hysteresis loop. Figures (b,c) and (e,f) were obtained from the average of 25 and 100 measurements, respectively.

In order to further examine the influence of the electrostatic interaction on the PFM response, we employed piezoresponse hysteresis loop measurements and simultaneously monitored the current flow. In general, a pulse-type triangular voltage waveform (see Fig. 2(a)) is used to measure the piezoresponse hysteresis loops, and the response in the off-field state is acquired to identify the piezoresponse because the electrostatic interaction can contribute to the piezoresponse during the application of the dc pulse in the on-field state.[18,19] That is, the shape of the hysteresis loop in the on-field state can be distorted into a slant shape compared with that in the off-field state owing to the electrostatic interaction.[18] Indeed, the on-field hysteresis loop shows a thin lozenge shape and higher response than the off-field loop (see Fig. 2(b)). However, we note that the shape of the hysteresis loop in the on-field state can be affected by several other factors.[15,17,19] For example, the distortion of the hysteresis loop can be also caused by the Joule heating effect from the current flow.[17,19] The current flow during the application of the voltage (Fig. 2(c)) may induce additional surface displacement through the Joule heating effect.[17,19] In addition, it is worth mentioning that the obtained *I–V* curve shows an intriguing shape that includes two inflection points, around ±2.3 V (see green arrows in Fig. 2(c)). It was found that the location of the inflection points is in similar ranges to those of the *x*-intercepts of the on-field hysteresis loop. This implies that the observed inflection points may be correlated with the electrostatic interaction. These inflection points will be discussed in further detail in Fig. 4. Overall, by comparing the shapes of the off- and on-field hysteresis loops, it is concluded that the on-field measurement results in the distortion of the hysteresis loop. However, in this case, the distortion of the hysteresis loop was explored through a triangular voltage waveform that generally accompanies polarization switching. Thus, the influence of the electrostatic interaction on the distortion of the hysteresis loop cannot be clearly accounted for because of the contribution from the polarization switching; hence, a direct observation of the electrostatic interaction in the absence of polarization switching is necessary.

Consequently, in order to investigate the electrostatic interaction on the PFM response in the absence of polarization switching, we employed unipolar negative voltage sweep as presented in Fig. 2(d) because the prepared epitaxial PZT thin films have upward polarization (see Fig. 1) and it are not switched under the negative voltage. Figures 2(e) and 2(f) show off- and on-field unipolar amplitude loops, respectively. Here, the results obtained by unipolar negative voltage sweep are referred to as "unipolar loop". Intriguingly, while the electrostatic interaction was not observed in the PFM images of Fig. 1(a), the off-field unipolar amplitude loop in Fig. 2(e) shows a slightly hysteric behavior as a half butterfly shape under the negative voltage sweep. After the negative voltage sweep, the magnitude of the amplitude at 0 V increases from 0.739 a.u. to 0.786 a.u. (about 6.36%). Since the polarization is already fully aligned in an upward direction and the polarization state has not changed under the negative voltage, the hysteric behavior of the off-field amplitude loop may be solely related with the electrostatic interaction by the charge injection.[19] Nonetheless, we note that there is no significant change in the amplitude up to around 5 V from the initial point. This indicates that the electrostatic effect may not be significant to the PFM response up to around 5 V for this case. Additionally, the shape of the unipolar amplitude loop in the on-field state significantly differs from that in the off-field state, showing a butterfly-like shape even though there is no polarization switching.

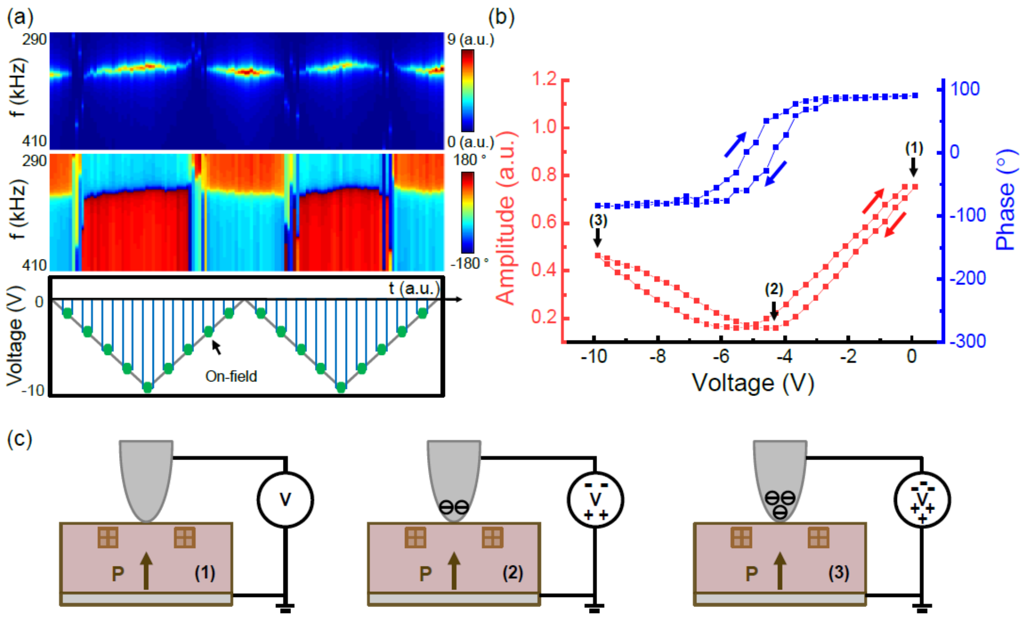

FIG. 3. (a) (bottom) Applied voltage waveform and corresponding (top) PFM amplitude and (middle) phase spectra in the on-field state. (b) On-field unipolar amplitude and phase hysteresis loops. The loops were acquired from the average value of 100 measurements. (c) Schematic representation at each state indicated in (b). The positive polarization charges and negative dc pulse charges are depicted as rectangles and circles, respectively.

In Fig 3(a), we further investigate the unipolar hysteresis behavior in the on-field state, amplitude, and phase spectra. An appreciable switching-like behavior is clearly seen as straight vertical lines where the amplitude becomes very small and the phase changes by 180° in the spectra images.[26] Moreover, butterfly and rectangular shapes of the unipolar amplitude and phase loops are also observed (Fig. 3(b)), respectively. The voltages at the inflection points—which correspond to the coercive voltages for the ferroelectric materials if we consider typical ferroelectric switching—were observed as −4.3 and −5.5 V, and the phase was also switched by 180° in the vicinity of the coercive voltages. Since the above results were observed in the on-field state, this behavior is likely to be strongly correlated with the electrostatic interaction. Even though Joule heating originated from the current flow can contribute to the hysteresis loop, it may be a minor effect because it cannot change the phase. Again, it should be noted that there is no actual polarization switching because we only applied the negative voltage to the sample. The obtained unipolar hysteresis loop may then result from the combination of the positive polarization charges and the application of negative voltage (including injected negative charges on the ferroelectric surface).

The polarization fully contributes to the measured PFM response at the initial point, *i.e.*, 0 V, indicated as (1) in Fig. 3(b) (see the left hand side of Fig. 3(c)). However, even though the piezoresponse contributed by the upward polarization is constant, the measured PFM amplitude is gradually decreased with increasing the negative voltage. The decremental amplitude may be correlated with the electrical neutralization on the ferroelectric surface. By increasing the negative voltage, the influence of the electrostatic interaction from the dc negative voltage and injected negative charges becomes more significant on the measured PFM response, resulting in the decremental amplitude. Interestingly, the voltage of the first inflection point, at around −4.3 V, is similar to the inversion voltage of the surface potential from the positive to the negative state as can be seen in Fig. 1(a). Thus, this value could be a critical voltage for the electrical neutralization on the ferroelectric surface (see the middle of Fig. 3(c)). After the first inflection point indicated as (2) in Fig. 3(b), the measured PFM amplitude is gradually increased while increasing the negative voltage. Since the voltage also exceeds the critical value for the electrical neutralization, the amplitude can show opposite behavior (see the right hand side of Fig. 3(c)). Thus, there can be a switching-like behavior according to the mentioned mechanism in the on-field state of unipolar negative voltage sweep. When the negative voltage decreased to zero after the maximum negative voltage indicated as (3) in Fig. 3(b), similar behavior was observed. However, there is a slight hysteric behavior that can be readily identified through a clear loop opening in the unipolar phase hysteresis loop. This may stem from the different amounts of the injected charges between forward and reverse sweep directions.[19] The observed phenomena confirmed that the ferroelectric-like on-field hysteresis loop can be correlated with the electrostatic interaction.

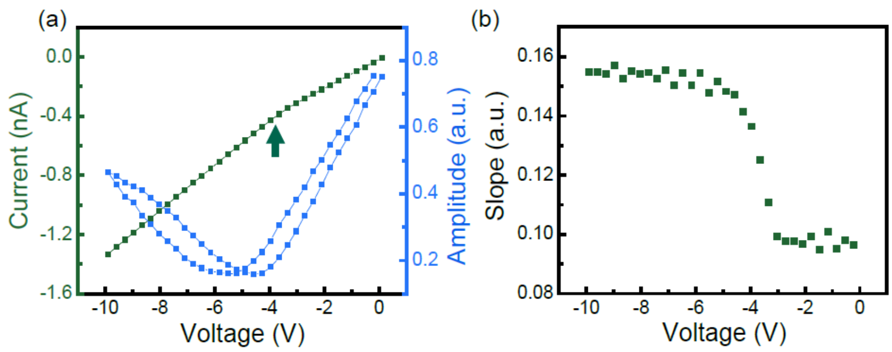

FIG. 4. (a) (green) Unipolar I-V curve and (blue) on-field unipolar amplitude hysteresis loop. Note that the on-field unipolar amplitude loop is the same result as that in Fig. 3(b), and the *I*–*V* curve was simultaneously obtained with the hysteresis loops in Fig. 3. (b) Slope extracted from the *I*–*V* curve. The slope was calculated through the differential between two adjacent points. Note that the *x*-axis in Fig. (b) is presented as in voltage units to readily display the inflection point.

Finally, we investigated the *I*–*V* curve simultaneously obtained with the hysteresis loops in Fig. 3 to verify its leakage current level. Figure 4(a) shows the unipolar *I*–*V* curve and amplitude hysteresis loop in the on-field state. It was found that the slope of *I*–*V* curve becomes higher in the vicinity of the first inflection point in the unipolar amplitude hysteresis loop (see green arrow). This is more clearly visible in Fig. 4(b), which shows the differential of the *I*–*V* curve between two adjacent steps. As described before, the electrical neutralization may be achieved at the first inflection point, around −4.3 V. Hence, the modulated electrical feature can change the tip-sample junction properties, such as the Schottky barrier, which may result in a slope change in the current flow.[27] Thus, these results imply that the observed PFM response as well as *I*–*V* characteristic can be also affected by the electrostatic interaction. Therefore, it can be concluded that the electrostatic interaction has to be taken into consideration for the careful interpretation of the observed material properties in *I*–*V* as well as PFM measurements.

In conclusion, by using an epitaxial PZT thin film with upward polarization as a model sample, we have examined how electrostatic interaction can affect the PFM response in the absence of polarization switching. Under unipolar negative voltage sweep, a switching-like response in the hysteresis loop is found to originate from the electrical neutralization between the upward polarization and applied negative voltage. Interestingly, this behavior changes the amount of current flow between the tip and sample. This result implies that the electrostatic interaction must be considered for accurate interpretation of PFM responses. Therefore, the information on the influence of the electrostatic interaction obtained in this study can be utilized as a basic guideline for carefully interpreting hysteresis loops in PFM-based studies.

Acknowledgements

This research was supported by Basic Science Research Program through the National Research Foundation of Korea (NRF) funded by the Ministry of Science, ICT & Future Planning (NRF-2014R1A1A1008061). The synthesis work at ORNL was supported by the U.S. Department of Energy, Office of Science, Basic Energy Sciences, Materials Sciences and Engineering Division.

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