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Journal
Applied Physics Letters, 99(17)

ISSN
0003-6951

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Publication Date
2011-10-24

DOI
10.1063/1.3652771

Peer reviewed

High-temperature piezoresponse force microscopy

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(Received 12 August 2011; accepted 26 September 2011; published online 24 October 2011)

We report high temperature piezoresponse force microscopy (PFM) on 100 nm thick $PbZr_{0.2}Ti_{0.8}O_3$ films fabricated on a miniature heater stage. The microfabricated resistive heater allows local temperature control up to 1000 °C with minimal electrostatic interactions. The PFM measurements were used to collect piezoelectric hysteresis loops over the temperature range 25–400 °C. The piezoresponse increases with temperature and then decreases rapidly near 400 °C, which is indicative of ferroelectric-paraelectric phase transition. © *2011 American Institute of Physics*. [doi:10.1063/1.3652771]

The extensive use of ferroelectric thin films in sensors, actuators, and non-volatile memory applications[1] requires the understanding of local ferroelectric properties. Ferroelectric phenomena such as switching kinetics and polarization dynamics depend upon temperature,[2] and the temperature-dependence of ferroelectric properties is of particular interest for energy conversion applications.[3] However, there is a lack of high temperature measurements of ferroelectric thin films. This letter describes scanning probe-based measurements of a ferroelectric thin film at high temperature.

Lead zirconate titanate (PZT) is one of the most extensively studied ferroelectric materials due to its excellent ferroelectric, piezoelectric, and pyroelectric properties.[1,4,5] There have been few published measurements of local ferroelectric switching and phase transitions at high temperature. Traditional dielectric and ferroelectric measurements using capacitor structures have been limited by a lack of high-temperature stable electrical contacts and substantial increases in leakage currents at high temperatures. This has lead researchers to focus on non-contact techniques such as second harmonic generation (SHG)[6,7] and x-ray diffraction (XRD),[7,8] to probe the nature of order in such thin film samples. Unfortunately, it is hard to obtain quantitative measurements from such techniques especially at high spatial resolution. Some articles report local measurements of ferroelectric materials using scanning probe-based techniques,[9,10] but only a few have considered ferroelectric response above room temperature.[10–13]

Piezoresponse force microscopy (PFM) is an atomic force microscopy (AFM) based technique in which an electrically biased conductive AFM tip is used to detect the inverse piezoelectric response of the bias-induced tip deflection. It has become the primary tool to study local static and dynamic properties of ferroelectric thin films.[11] There is, however, limited work on the electromechanical response of thin ferroelectric films at elevated temperatures, since high temperature characterization is challenging in conventional AFM. Most AFM-compatible heater stages are not capable of reaching temperatures above about 200 °C, due to thermal drift, noise, and the general inability of the AFM systems to withstand high temperature. Variable temperature PFM has been reported but at relatively low temperatures.[10,12–14]

This letter presents high temperature piezoresponse measurements of $PbZr_{0.2}Ti_{0.8}O_3$ films using a microfabricated heated platform inside a commercial AFM system.

Figure 1 shows the experimental setup, consisting of a PZT thin film synthesized onto a microfabricated heating platform and mounted in our AFM system. The heater was batch-fabricated on a silicon-on-insulator (SOI) wafer. First, the device layer was patterned and etched to form the "hour-glass" shaped heater structure. The 500 μm long and 30 μm wide strip of silicon at the "neck" of the hour-glass shape is the heating line. The heater structure was then doped with phosphorus in two steps[15] to produce a heater line of electrical resistance 1 kΩ and diverging silicon traces of electrical resistance 0.1 kΩ. Device design and doping concentrations were chosen to achieve a uniform temperature in the heater line and negligible heating elsewhere. The silicon dioxide layer reduces heat flow into the substrate and allows high temperature operation. Further details of the fabrication process can be found in the supplementary material.[16] The heater structure temperature was calibrated using Raman spectroscopy.[15] The temperature-dependence of the heater electrical resistance allows the temperature to be controlled over the temperature range 25–400 °C. A 100 nm thick $PbZr_{0.2}Ti_{0.8}O_3$ film was deposited on the device by pulsed laser deposition. The single phase (00l)-oriented PZT film had an RMS roughness <6 nm (see supplementary material[16]).

The samples were measured in our Asylum Cypher AFM. The PFM measurement applied a periodic voltage to the tip, V_{ac}, carried by a steady voltage V_{dc} that steps in magnitude in time.[17] Between each voltage step, V_{dc} was set to 0 V with the AC bias still applied to determine the bias-induced remnant piezoresponse.[18] We used a Pt-coated tip with resonant frequency ~320 kHz and a spring constant ~42 N/m to minimize electrostatic contribution in the PFM signal.[19] A probing signal (V_{ac}) with an amplitude of 1 V and a frequency close to the contact resonance peak (~1.4 MHz) of the tip-sample contact was used to achieve an optimal signal-to-noise ratio.[17] While the operating frequency was close to the contact resonance frequency, the operating frequency was at least 20 kHz away from the peak resonance, to prevent resonance-induced

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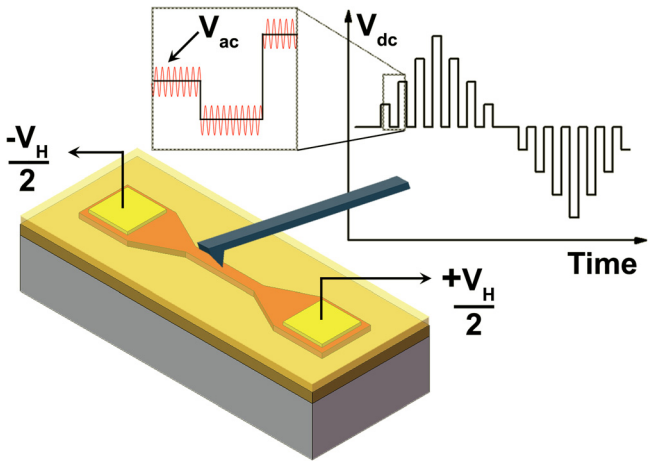

FIG. 1. (Color online) Schematic of the experimental setup. PZT thin film is deposited on the microfabricated heater structure, which can be resistively heated. The voltage waveform applied to the conductive AFM tip for local hysteresis measurements is shown.

phase shift. The AFM feedback loop was enabled to keep the cantilever deflection constant during the hysteresis loops.

To induce heating, the two ends of the heater line were supplied with a DC voltage of $+V_H/2$ and $-V_H/2$. The Pt-coated AFM tip was placed near the middle of the heater line to ensure that the tip was at a point where the voltage on the heater line, directly underneath, was 0 V. Precise positioning of the tip and voltage-controlled-heating minimizes electrostatic interference from the heating setup on the hysteresis measurements (see supplementary material[16]). The cantilever was oriented orthogonal to the narrow heater line to minimize electrostatic and non-local interactions between the tip and sample.[20] In addition to the PZT-coated sample, we performed the same measurements on a SiO_2 sample to establish a baseline response, which was near zero in all cases. At least five measurements were taken on three different samples to verify reproducibility.

Figure 2 shows amplitude and phase measured for the remnant piezoelectric hysteresis loops at 350 °C. Hysteretic behavior is evident from the characteristic "butterfly" amplitude loops and 180° phase switching corresponding to out-of-plane domain switching.

Figure 3(a) shows the measured piezoresponse hysteresis loops for different heater temperatures. The remnant piezoresponse was measured as the deflection of the calibrated AFM tip at the probing bias frequency when the tip DC bias was stepped to zero after each voltage pulse.[17] At a fixed coercive voltage, the overall piezoresponse increased with increasing temperature, up to 400 °C. Figure 3(b) shows the remnant PFM amplitude at zero DC offset at different heater temperatures. The piezoresponse response increases drastically at 350 °C and drops to zero at 400 °C. We propose that this corresponds to the ferroelectric-paraelectric phase transition of the film.

The well-behaved hysteresis loops of Figs. 2 and 3 are consistent with the AFM tip moving with the sample electromechanical response. For the field induced in the 100 nm thick PZT films, we expect the piezoresponse to indicate the inverse piezoelectric coefficient d_{33}.[21] It is thus possible to infer the temperature-dependence of d_{33} from the measured piezoresponse. The solid line of Fig. 3(b) is the qualitative d_{33}, which is proportional to $(T_C–T)^{-1/2}$. This d_{33} temperature-dependence is expected from previous measurements of $LiTaO_3$ crystals[22] and also from phenomenological models.[2] In previous high-temperature PFM measurements on triglycine sulfate single crystals,[9] the piezoresponse followed the temperature-dependence of spontaneous polarization and did not indicate the temperature-dependence of d_{33}. This observation was attributed to electrostatic forces that arose from unscreened polarization-bound charge, which induce cantilever deflections that can be comparable to or larger than the electromechanical response.[13,23] The thin film geometry of the present study allows for a more uniform electrical field to be induced in the sample compared to previous measurements on bulk crystals. Moreover, the experimental setup investigated here allows minimal electrostatic and non-local interactions between the tip and the sample through the use of stiff cantilevers and a configuration that minimizes the cantilever-sample overlap region. A complete set of the corresponding amplitude and phase loops can be found in the supplementary material.[16]

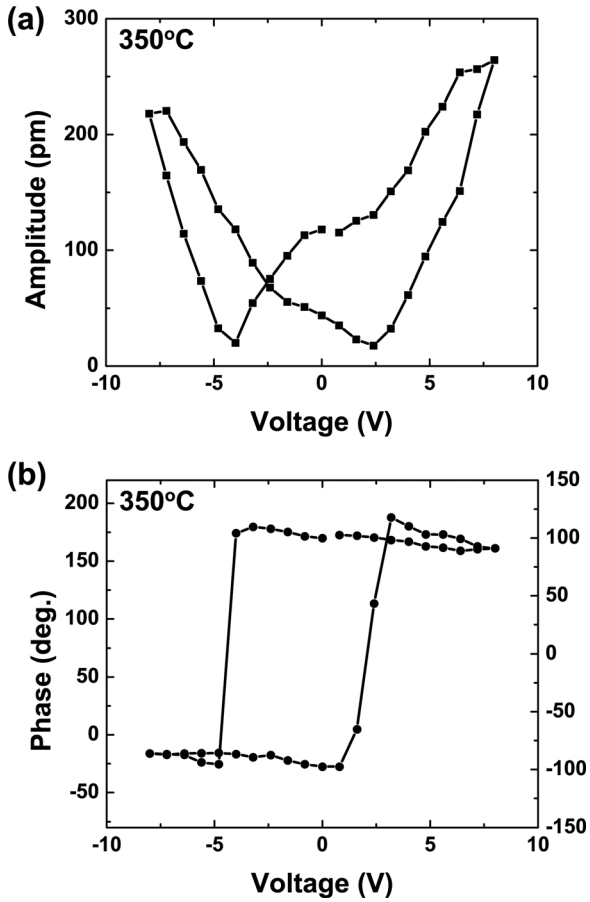

FIG. 2. High temperature remnant hysteresis loops. (a) Amplitude and (b) phase for the local hysteresis loop at high temperature (350 °C).

The vertical shift of the hysteresis loops along the response axis can be explained by the asymmetric electrode structure and the widely observed process of imprint.[24,25] Such shifts of the piezoelectric hysteresis loop can be associated with non-switched or relaxed regions and the presence of the preferred polarization state. Domain pinning at free lateral surfaces and the ferroelectric-electrode interface can also result in such shifts.[26] Some of the measured hysteresis

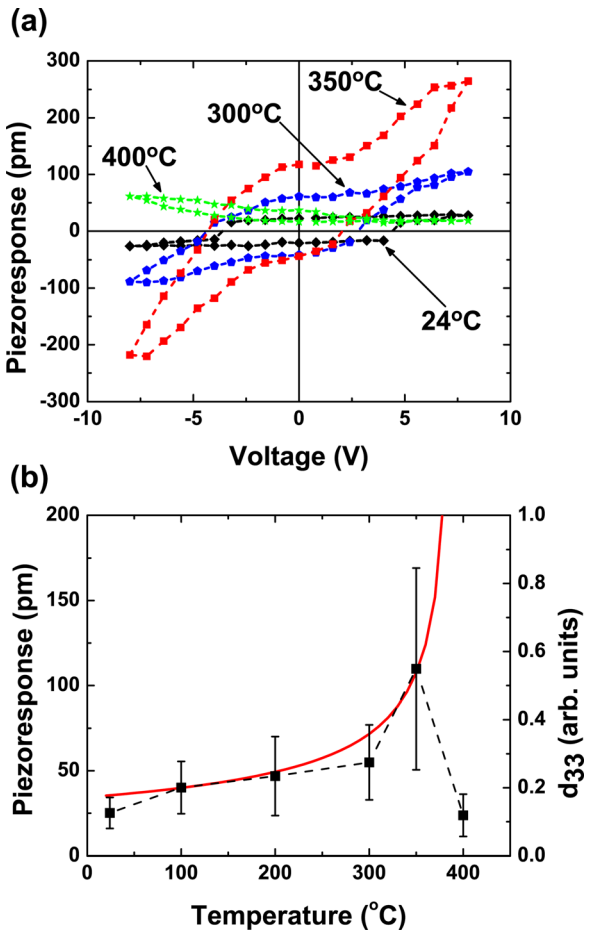

FIG. 3. (Color online) Piezoresponse as a function of temperature. (a) Local hysteresis loops are shown for different heater temperatures. (b) PFM amplitude at 0 V tip DC offset is plotted as a function of the heater temperature. The temperature dependence of piezo-coefficient d_{33} is also shown (solid line). Piezoresponse increases with temperature, as expected from the PFM electromechanical response, until it diminishes at 400 °C indicating a ferroelectric-paraelectric transition.

loops show a small deviation from an ideal loop shape. The measured hysteresis loops were repeatable over many experiments and samples. Similar deviations from ideal loop shapes have been reported by others[17,26] and have been attributed to the interaction of the forming domain with the ferroelectric film topography and microstructure.[27,28]

In summary, we have performed piezoresponse force microscopy on a 100 nm film of PZT over the temperature range 25–400 °C. The piezoresponse increases with temperature but decreases at about 400 °C, which we believe corresponds to the PZT Curie temperature. This work opens possibilities for nanoelectromechanical measurements at temperature well above the heating temperature of commercial AFM heater stages.

The authors acknowledge support from the Office of Naval Research under Grant Number N00014-10-10525. Some work was performed in the Seitz Materials Research Laboratory, which is partially supported by the U.S. Department of Energy under grants DE-FG02-07ER46453 and DE-FG02-07ER46471.

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