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Local probing of relaxation time distributions in ferroelectric polymer nanomesas: Time-resolved piezoresponse force spectroscopy and spectroscopic imaging

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Time-resolved piezoresponse force spectroscopy (TR-PFS) and spectroscopic imaging are developed to probe the spatial variability of relaxation behavior in nanoscale ferroelectric materials and structures. TR-PFS was applied to study polarization dynamics in polyvinylidene fluoride and trifluoroethylene nanomesas. We demonstrate that polarization relaxation in ferroelectric polymers is slow even on the ∼10 nm length scale of piezoresponse force microscopy (PFM) signal generation. Furthermore, the relaxation times are found to be nonuniform within the nanomesa, indicative of a complex internal structure. The applicability of TR-PFM for studies of polarization dynamics in ferroelectric polymers and relaxors is discussed. © 2008 American Institute of Physics. [DOI: 10.1063/1.2942390]
signal generation and data acquisition system similar to that described in Ref. 12. To minimize surface damage, PFM measurements were performed using ultrasoft Au–Cr coated Si tips (Micromasch, spring constant $k = 0.03$ N/m). Imaging was performed using a 1.1 MHz, 5 V bias. As the aluminum contact on the back side of the doped Si substrate was used as the back side electrical contact in the PFM measurements, a voltage drop of no more than 1 V is expected to occur across the thin oxidized layer (as estimated for flat geometry; for a localized PFM tip, the field concentration in PVDF should be even larger).\textsuperscript{13}

Topography, PFM amplitude, and PFM phase images of PVDF nanomesas are shown in Figs. 1(a)–1(c), respectively. The images demonstrate strong electromechanical contrast at the nanomesas, as expected for the ferroelectric state of the polymer. The PFM phase image indicates that mesas are in a uniformly polarized state.

To probe the polarization relaxation at a single point, the microscope was configured in the TR-PFS mode, as illustrated in Figs. 2(a) and 2(b). A setting pulse of 10 V is applied to the probe for 20 ms, and then the bias is turned off for the following 200 ms. The evolution of the electromechanical response during this relaxation stage is measured using a 1.1 MHz ac signal. The sequence is repeated five times, and the results are averaged, resulting in a 1.1 pixel/s data acquisition rate. Several relaxation curves (smoothed by adjacent averaging) from the substrate and nanomesas are shown in Figs. 2(c) and 2(d), respectively. The curves are approximated using the exponential decay,

$$PR = A_1 \exp(-t/\tau) + B,$$

where $PR$ is the piezoresponse signal, $A_1$ is the relaxation amplitude (switchable response), $\tau$ is the time constant, and $B$ is the nonrelaxing component (remnant response). In automatic data analysis, the fitting is performed starting from delay time, $t = t_0$. Note that relatively high noise levels corresponding to small ($\sim 10$ pm/V) piezoelectric coefficients of PVDF and limited pixel times do not allow elucidation of the exact relaxation kinetics (e.g., distinguishing exponential and stretched exponential responses). Relaxation behavior in P(VDF-TrFE) nanomesas could also arise from charge on the surface; however, this response is anticipated to appear as a uniform offset on the images and cannot account for the...
sharp variability of relaxation behavior within the nanomesa discussed below.

To probe variability of relaxation behavior on a sample surface, the relaxation measurements are performed over a grid of $N \times N$ points, as illustrated schematically in Fig. 2(b). The resulting three dimensional data array is fitted by Eq. (1) [Figs. 2(e) and 2(f)], and coefficients at each point are plotted as two dimensional maps. Shown in Fig. 3 are the resulting time-resolved spectroscopic maps for PVDF nanomesas ($N=30$). Figure 3(a) clearly shows a large remanent response within the nanomesa region, suggesting that most of the response is either constant or relaxes slowly on the time scale of the experiment. The relaxation amplitude [Fig. 3(b)] is higher within the mesa, as anticipated. However, nonzero switchable contrast was observed on the (nominally) bare SiO$_2$ surface as well. This behavior can be attributed either due to the presence of residual PVDF contaminants on the surface (tip or) or time-dependent phenomena associated with electrostatic and electrocapillary condensation at the tip-surface junction.

The most interesting contrast is observed in the relaxation time constant image [Fig. 3(c)]. Note that the majority of the nanomesa is characterized by much larger relaxation times ($\sim 0.1-1$ s) than the substrate (0.05 s). Furthermore, the TR-PFS measurements demonstrate an inhomogeneous relaxation time distribution within the nanomesa. Note that the orientation and clustering of the regions with different relaxation times are such that they minimize the probability of topographic cross-talk or tip-induced changes on observed contrast.

To summarize, we have developed a spatially resolved imaging approach, time-resolved piezoresponse spectroscopic imaging, to probe the spatial variability of relaxation behavior in nanoscale ferroelectrics. The approach was applied to study polarization dynamics in P(VDF-TrFE) nanomesas. The relaxation times even within a single nanomesa were found to be relatively large, on the scale of 0.1–1 s. The spatially resolved mapping illustrated that relaxation times are inhomogeneous within the nanomesa. While the origins of this behavior are unknown, this behavior can be associated with the presence of an internal grain boundary between two grains in a mesa structure. Overall, we believe that this technique has the potential for nanoscale mapping of relaxation behavior in ferroelectric polymers and relaxors.

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