# Scaling Of Ferroelectric Properties In Thin Films

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## ABSTRACT

A fundamental issue in ferroic systems (ferromagnetic and ferroelectric) is the scaling of the order parameter (magnetization or polarization) with size. Specifically, in ferroelectric thin films, deviations in the polarization can occur due to: (i) competition between thermal vibrations and the correlation energy (which aligns the dipoles); (ii) damage during fabrication. These deviations will have a profound impact on the performance of the next generation of high-density nonvolatile memories based on the spontaneous polarization. We have combined two novel approaches, namely focused ion beam milling to define sub-micron capacitors and scanning force microscopy to examine the scaling of the fundamental ferroelectric response of these capacitors. We find that the capacitors exhibit ferroelectric properties for lateral dimensions down to at least 100nm, suggesting that memories with densities in the range of 4-16 Gbits can be successfully fabricated.

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Ferroelectric materials continue to draw considerable attention in the international research and development community due to the broad range of physical properties of technological value.[1] The spontaneous polarization in these materials below the Curie temperature is being exploited for nonvolatile information storage. In order to be competitive with other information storage technologies, they have to be implemented at densities of the order of 1 Gbit on a chip, which is typically 1cmx1cm in lateral dimensions. Consequently, this necessitates the reduction in the lateral dimensions of the storage element into the sub-micron range. For example, it is expected that the Gbit chip will have storage capacitor areas of the order of 100nm x100nm, in a planar arrangement. This brings us to the crux of this report: namely, what is the behavior of the spontaneous polarization as a function of the size of the storage capacitor (thickness and lateral dimensions) ?

The effect of free surfaces and size on ferroelectricity has been the focus of several theoretical studies.[2-5] The profound and direct impact of these size effects on the ability to design and engineer the next generation of non-volatile ferroelectric memories forms the technological backdrop and a key driver for many of these studies. In general, they predict: (i) a reduction of the polarization near the surfaces due to the depolarizing fields present therein; (ii) a distinct size effect on the stability of the ferroelectric state, i.e., the ferroelectric state becomes unstable below a certain size, which is estimated to be of the order of 7-10nm along each of the three directions of well known ferroelectrics such as $BaTiO_3$ and $PbTiO_3$. These predictions set the stage for experimental studies that can be aimed at verifying the validity of such models as well as exploring the fundamental aspects of size effects in such systems. Reducing the thickness of the ferroelectric layer to below 10nm has provided one approach to study scaling effects. However, fabricating devices with sub-10nm lateral dimensions can become quite complicated. We have therefore focused on test structures in the size range of 0.1-1.0µm as a starting point to experimentally verify the size scaling effects.

Scanning force microscopy (SFM) has opened up a new vista of research into the microscopic responses of ferroic materials.[6-10] Several groups, including ours, have demonstrated the ability to explore and exploit the piezoelectric response that is available through the interaction of the ferroelectric crystal (or grain) and the ac signal imposed on the AFM tip. The ability to probe the microscopic details and to write sub-100nm "domains" has already been demonstrated in continuous thin films and heterostructures. It is however noteworthy that all these studies have been carried out on continuous films or crystals in which the in-plane dimensions are much larger (essentially infinite) compared to the thickness dimension. For example, Tybell *et al.*[8] and Hidaka *et al.*[7] have demonstrated the feasibility of writing "domains" in such thin film heterostructures that are as small as 30-100nm in diameter. In our study, we clearly observed that individual grains in a polycrystalline matrix behaved as single domains, when their size was smaller than about 100nm.[10] We also observed a strong correlation of the stability of the written "domain" with the immediate electrostatic environment within the grain as well as around it, again suggesting the strong influence of free surfaces, interfaces and electrostatic coupling across the grains on the ability to sustain the written "domain".[11]

Therefore it is imperative to fabricate test structures with the required dimensions in order to study scaling of the polarization properties. In this study, we have used a combination of two novel approaches to create and test capacitor structures that are smaller than 100nm in lateral dimensions. The first is the use of a focused ion beam milling tool[12] to delineate sub-micron test structures, such as those illustrated in Fig. 1. The second is the use of scanning force microscopy (SFM) to obtain piezoelectric hysteresis loops and thereby information on the ferroelectric properties from sub-micron structures. SFM provides at least two types of information that is valuable in enabling the understanding of local ferroelectric properties. First, piezoelectric hysteresis loops can be measured (similar to a conventional ferroelectric hysteresis loop) in capacitor structures with a top electrode.[9,13] Second, spatially resolved images of the polarization direction can be obtained using a capacitor without the top electrode.[10] The key is the combination of the ability to fabricate sub-micron structures using focused ion beam milling (FIB) which can be tested and imaged by SFM. We report here results of experiments to create such structures and explore the impact of scaling on the ferroelectric properties. The absence of a top electrode in all of the imaging studies induces a strong propensity for asymmetry in the stability of the written state. In addition, the field distribution in this type of experiment is quite non-uniform and therefore interpretation of the data becomes more complicated. The use of a conducting top electrode, as described in this study, provides a relatively uniform field distribution under the top electrode and a reasonably symmetric behavior of the polarization state.

Polycrystalline $Pb_{1.0}(Nb_{0.04}Zr_{0.28}Ti_{0.68})O_3$ (PNZT) thin films with thickness of 1200Å and grain size of ~ 1000A were deposited by sol-gel processing onto platinized Si wafers with a bottom electrode of the conducting oxide, La-Sr-Co-O. The details of the thin film processing are outlined elsewhere.[13] Test capacitor structures in the size range of 1µm -0.1µm were fabricated by focused Ga ion beam milling. An accelerating voltage of 50kV, dose of $8x10^{17}$ions/cm$^2$ and a beam size of 6-20nm (MICRION 2500) was used to delineate the structures. The SFM technique has been described elsewhere[10]. Application of a dc voltage to the tip allows "writing" of domain states. The dc voltage was reduced to zero each time the ac signal was applied to "read" the state. Thus, a "hysteresis" loop can be traced out by plotting the tip vibration signal as a function of the write voltage. For our experiments, we used a commercial Digital Instruments Nanoscope IIIA Multimode scanning probe microscope equipped with standard silicon nitride tips coated with gold-cadmium. The typical force constant of these tips was 0.09N/m and the apex radius was 20-40nm. All measurements were done in dry nitrogen ambient at room temperature.

SFM studies of the test structures in the as-fabricated condition showed very little indication of a piezoelectric hysteresis loop. However, in all cases annealing at 600°C enabled a complete recovery, as is illustrated in Fig. 2(a-d) for capacitors in the 1.0µm - 0.1µm size range. The piezoresponse, observed at the highest applied DC voltage as well as at remanence, and the coercive field for these capacitors are commensurate with that of large (20µm x 20µm) capacitors. These measurements were repeated on several independent wafers with identical capacitor sizes and the piezoelectric responses were repeatable. This provides first evidence that the piezoresponse scales reasonably well with the lateral dimensions of the test capacitor down to at least 0.1µm. Since the piezoresponse in the SFM measurement is, to first order, directly proportional to the magnitude and direction of polarization in the capacitor, we believe that the polarization also scales reasonably well with size in such sub-micron structures. We find that the piezoresponse is higher for a sub-micron capacitor where the PNZT layer was milled out by the FIB process, compared to a capacitor of identical size with only the top electrode delineated (i.e., the PNZT layer is continuous), suggesting the possible role of in-plane constraints in the continuous film. After the annealing treatment, ferroelectric hysteresis loops on larger (20µmx20µm) capacitors showed polarization values and coercive fields commensurate with that of test capacitors fabricated without ion beam milling, showing that the damage is fully recoverable. Ion beam induced damage frequently leads to shifted or collapsed hysteresis loops, with the consequent formation of an internal field or loss of ferroelectricity. The primary source of the damage is possibly due to ion beam implantation into the ferroelectric capacitor or ion beam induced transport of chemical species such as oxygen in the ferroelectric layer.

A serious concern is the ability of such sub-micron capacitor structures to retain the polarized state over long periods of time (data retention). Fig. 3(a) shows the results of retention studies carried out on a single 0.5μm x 0.5μm capacitor. In this study the test capacitor was written with a single pulse and the piezoelectric response at zero applied bias was measured with a small ac signal at 6.39kHz after each wait period. There is an initial drop in the piezoresponse within 1 second, subsequent to which the drop in the piezoresponse is quite small. This behavior is consistent with macroscopic retention measurements carried out on a 20μm diameter capacitor, Fig. 3(b), which also shows an initial drop (within 1 second) and then levels out to a slow decrease. The results of the retention study on the single 0.5μm x 0.5μm capacitor are consistent over a number of measurements.

In Fig. 4 we present results of bipolar fatigue tests carried out on 0.5μmx0.5μm test capacitors at a test frequency of 100kHz and bipolar voltage of ±5V. These test capacitors were delineated in heterostructures with and without the conducting La-Sr-Co-O oxide electrode. As is now well established in large capacitors, we observe virtually no fatigue in the capacitors with LSCO electrodes while those without the conducting oxide contact electrode do show a significant loss of switchable polarization. This data clearly shows that fatigue-free behavior can be obtained in sub-micron capacitors, thus validating this approach to high-density nonvolatile memories.

In summary, we have demonstrated that sub-micron capacitors can be fabricated in lead zirconate titanate thin films by focused ion beam milling. Our studies show that the scaling is reasonably well behaved down to at least 1000Å in lateral dimensions for a capacitor thickness of the same order. We do observe clear differences in the fatigue behavior of these sub-micron capacitors through the introduction of the conducting oxide electrode between the ferroelectric and the Pt electrode, consistent with similar observations on macroscopic capacitors.

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**FIGURES**

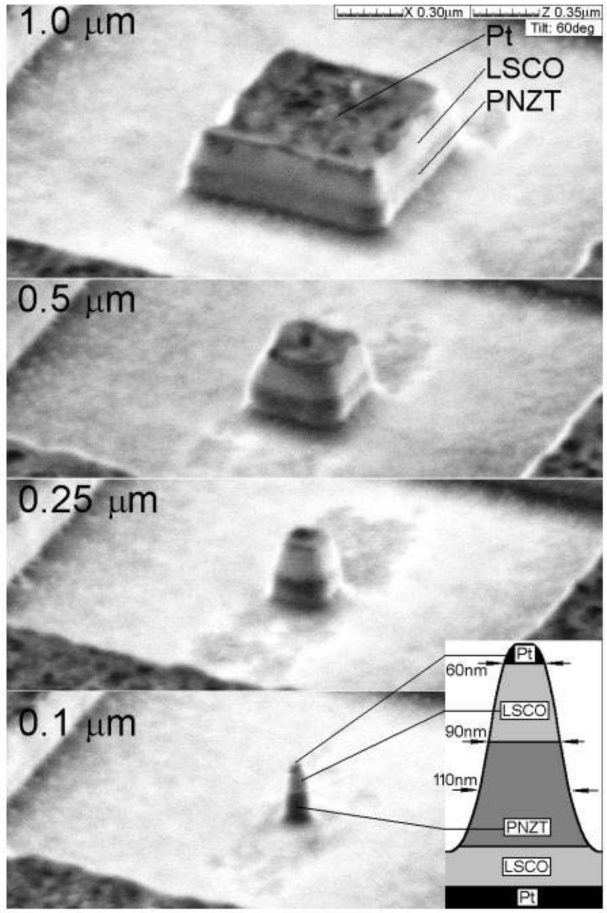


Fig. 1. Scanning ion beam images of the test structures fabricated by focused ion beam milling in the size range from 1µmx1µm to 0.1µmx0.1µm. The contrast from the various layers in the heterostructure is also indicated. The inset is a schematic of the shape and dimensions of the 0.1µm test structure.

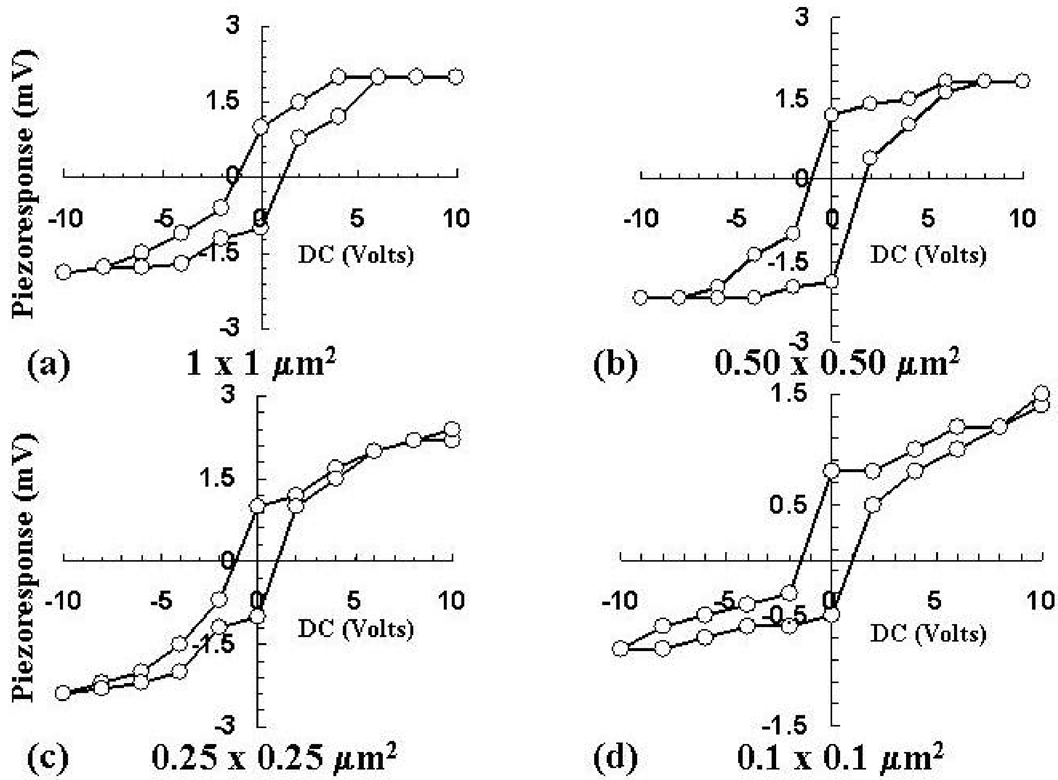


Fig. 2. SFM obtained piezoresponse hysteresis loops for the 1μm, 0.5μm, 0.25μm and the 0.1μm test structures, showing that the piezoelectric response and thereby the ferroelectric polarization properties scale with size. Also note that the coercive voltage for all these test structures are similar (about 1V) which is commensurate with that obtained from a conventional ferroelectric hysteresis loop measured from a macroscopic capacitor.

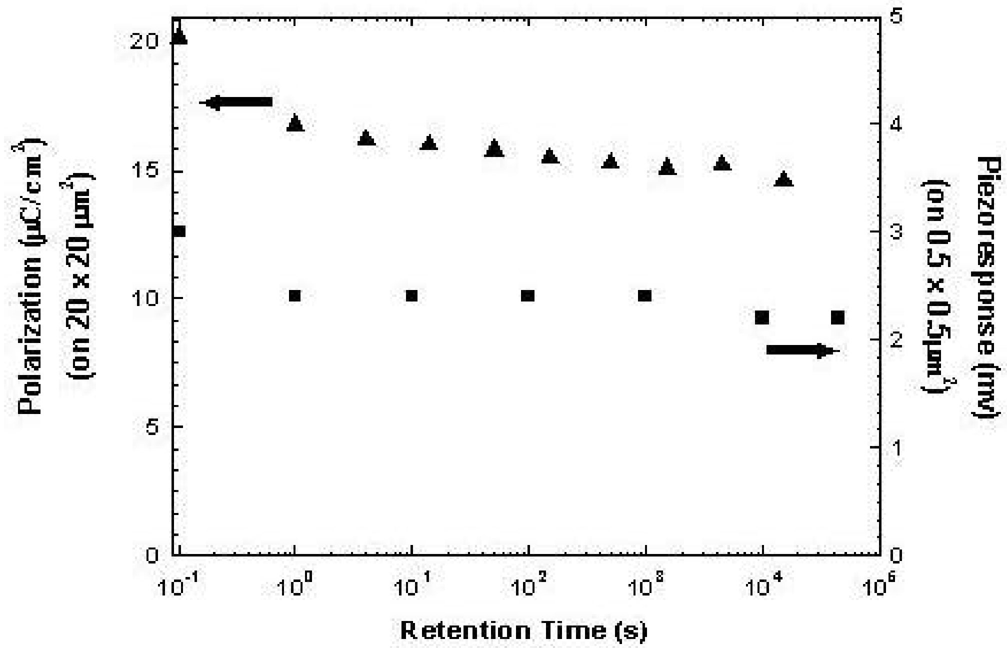


Fig. 3. Stability of the poled state (polarization retention) in a 0.5μm x 0.5μm capacitor as a function of retention time and polarization retention for a macroscopic 20μm x 20μm capacitor showing a similar trend in the decay of the poled state.

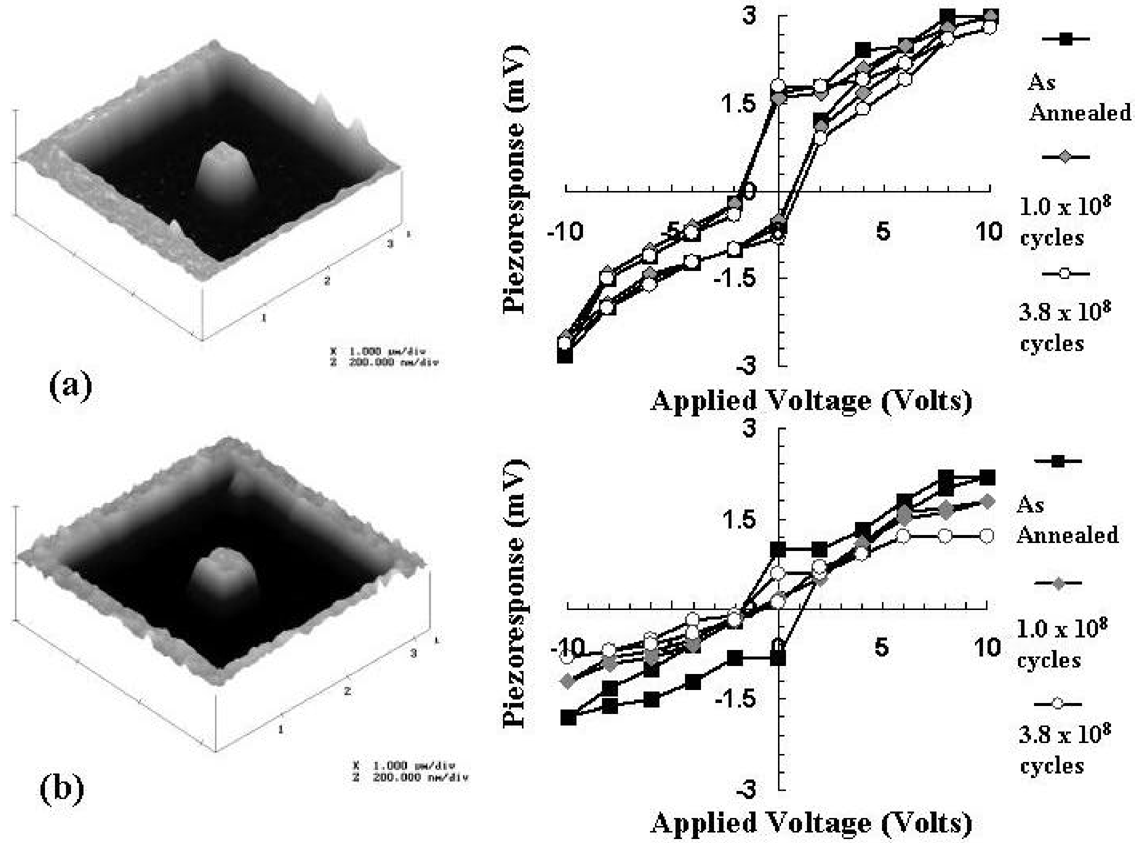


Fig. 4. SFM obtained images of test structures and piezoresponse loops measured before and after bipolar fatigue in: (a) test structures with conducting oxide electrode contact to the ferroelectric PNZT layer; (b) Pt electrode contact to the PNZT layer. Note that the LSCO/PNZT/LSCO capacitors do not show any fatigue even at these dimensions, while the Pt/PNZT/Pt capacitors show a significant loss of polarization due to fatigue.