Nanoscale control of ferroelectric polarization and domain size in epitaxial $Pb(Zr_{0.2}Ti_{0.8})O_3$ thin films

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We demonstrate that atomic force microscopy can be used to precisely manipulate individual sub-50 nm ferroelectric domains in ultrahigh density arrays on high-quality epitaxial $Pb(Zr_{0.2}Ti_{0.8})O_3$ thin films. Control of domain size was achieved by varying the strength and duration of the voltage pulses used to polarize the material. Domain size was found to depend logarithmically upon the writing time and linearly upon the writing voltage. All domains, including those written with ~100 ns pulses, remained completely stable for the 7 day duration of the experiment. © *2001 American Institute of Physics.* [DOI: 10.1063/1.1388024]

Increasing demand for ultrahigh density (uhd) information storage has fueled significant interest in the use of atomic force microscopy (AFM) for nanoscopic read/write operations. General requirements of nonvolatile uhd memories are fast operating times, small bit size, and long-term data retention. Nonreversible AFM lithography by local oxidation and thermomechanical processes has been extensively researched.[1–3] Solutions incorporating parallel processing have also been explored, increasing the scan range and speed of possible applications.[4,5] A particularly appealing approach, allowing dynamic memory as well as data storage, is to locally modify the reversible and nonvolatile polarization of ferroelectric oxides with an AFM-generated electric field,[6–12] a technique recently extended to ferroelectric/silicon heterostructures.[13] Detailed studies of domain switching behavior in these materials, focusing on domain size and stability in relation to writing time, writing voltage, and the shape of the AFM tip, are therefore important for the development of memory applications. Such studies would also aid in understanding the fundamental physics of domain dynamics in thin films. The perovskite $Pb(Zr_xTi_{1-x})O_3$ (PZT), a stable compound with high remanent polarization, has been widely recognized as an attractive candidate for memory applications. Epitaxially grown monocrystalline films of this material are particularly suitable for domain behavior studies due to the uniformity of their switching properties over the sample surface.[10] Although desirable long-term stability has been found for standard 100 nm sized capacitors in 1000-Å-thick films of related ferroelectric compounds,[11] studies of retention loss in sub-100 nm PZT domains using the AFM approach, with the tip itself serving as a mobile top electrode, present contradictory results. The extrapolation of temperature dependence data for epitaxial PZT films gives polarization retention estimates of decades at RT,[9] while other groups report spontaneous reversal of polarization after a few hours.[8]

In this letter we demonstrate nanoscopic control of read/write operations in uhd arrays, and report on the time dependence of domain switching behavior for domains as small as 40 nm, over eight orders of magnitude in writing time, down to ~100 ns. We also discuss how different applied voltages affect the size of the polarized domains. Finally, we show full retention of polarization for all domains over a period of 7 days (the running time of the experiment), regardless of writing time.

The tetragonal PZT films used in the study, with a Zr:Ti ratio of 1:4, were grown on metallic Nb-doped single crystal (001) $SrTiO_3$ substrates by off-axis radio frequency magnetron sputtering in an argon–oxygen flow ($Ar:O_2 = 58:42$) at 180 mTorr and at a substrate temperature of ~500 °C. X-ray analyses revealed monocrystalline growth of *c*-axis oriented PZT. Multiple orders of finite size effect peaks indicated high quality crystallization and allowed precise measurement of film thickness.[10] AFM measurements of sample topography revealed extremely flat and uniform surfaces over large areas, with a measured root-mean-square roughness of ~3 Å over a 5 μm×5 μm for typical films. High surface uniformity and crystallization quality are advantages for effective writing and imaging of ferroelectric domains at uhd, where perturbation due to topographic defects could deteriorate the interaction between the tip and the nanofeatures written on the sample.

A commercial AFM under ambient conditions was used to polarize the ferroelectric domains. The resulting features were then imaged by exploiting the piezoelectric response of the material.[14] Writing times in the range from 250 ns to 3 s were investigated for writing voltages between 6 and 12 V, after a uniformly polarized background was obtained by repeated scanning of the 10 μm×10 μm designated test area at −10 V.

First, the precise control of individual domains (bits) in a high information density array was investigated. A series of different arrays was written throughout the background area with a 10 V pulse applied for a range of writing times to create each bit. Figure 1 shows a piezoelectric image of an 11×11 array at 4 Gbit cm^{-2} information density with an average domain radius of 47 nm full width at half maximum (FWHM), written with 3 ms voltage pulses. As seen, each bit is clearly defined with respect to the background level, and

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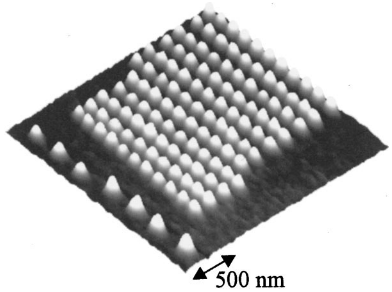

FIG. 1. Piezoelectric image of an 11×11 array, written at 4 Gbit cm^{-2} information density with 10 V pulses applied for 3 ms.

both rows and columns are precisely aligned, as emphasized by the one-column shift in the structure. The domains at the lower edge of the scan were written with 8 ms (3), 28 ms (3), and 53 ms (1) from left to right. (The variation of domain size with writing time is discussed later.) The corresponding topographic image is completely featureless. A second 10×10 array, written with 3 ms pulses at 6 Gbit cm^{-2} density, showed that this process could be repeatably carried out on any part of the uniformly polarized background area. Although single domains had previously been written and erased by an AFM tip,[10,15] this work aimed to demonstrate precision control and full reversibility of the process at information densities comparable to those of uhd memories. We therefore centered the AFM tip sequentially on three chosen dots in the 6 Gbits cm^{-2} array [Fig. 2(a)], and applied a pulse of the opposite voltage (−10 V) to erase the bits [Fig. 2(b)] Subsequently, the bottom left domain was rewritten with the original 10 V pulse [Fig. 2(c)], The center domain was then rewritten in the same fashion and the bottom left domain re-erased by the application of another −10 V pulse [Fig. 2(d)]. The surrounding domains were unaffected by the writing process, indicating the absence of long-range ''crosstalk'' and making each bit individually accessible. The precision control demonstrated at uhd is also interesting in the light of previous studies which have shown that the control of the ferroelectric polarization achievable by an AFM can be extended over ten orders of magnitude in area and is limited only by the size of the sample.[10] These results

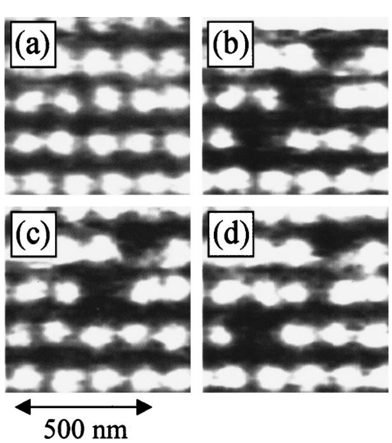

FIG. 2. (a) Close-up of 6 Gbit cm^{-2} array written with 3 ms, 10 V pulses. (b) Three domains were sequentially erased by the application of −10 V pulses. (c) Subsequently, the bottom left domain was rewritten with the original 3 ms, 10 V pulse. (d) The center domain was then rewritten, and the bottom left domain was re-erased.

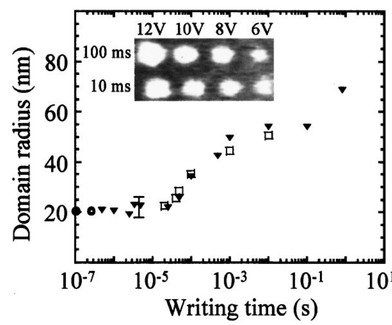

FIG. 3. A plot of domain radius as a function of writing time at 12 V. Measurements taken with two different AFM tips are shown as triangles and squares. Domain radius depends logarithmically on writing times down to 20 μs and saturates at ~20 nm for shorter pulses. Circular points at 100 and 120 ns indicate measured durations for nominal pulses of 250 and 350 ns, respectively. The rms error for the measurement was ~10%. The inset shows two lines of domains written with the times and voltages indicated. Domain radius varies linearly with the applied voltage.

strongly suggest that an AFM approach, combined with parallel processing techniques, will allow the creation of fully functional, dynamic uhd data storage systems in epitaxial ferroelectric thin films.

We next studied the relation between the writing time and the radius of the resulting polarized domain, at a writing voltage of 12 V.[16] As shown in Fig. 3, for experiments conducted with two different AFM tips, the domain size can be controlled by changing the duration of the voltage pulse applied to the tip, with a ~300% change in domain radius in the time range from ~20 μs to ~1 s. With shorter pulses, down to 250 ns, a saturation level is reached at a domain radius of ~20 nm. During such short writing times, the *RC* characteristics of our system played a large role, altering the pulse profile. Subsequent analysis of the measured pulses gave estimated values of 100 and 120 ns, respectively, for the nominal writing times of 250 and 350 ns shown on the graph. We believe that the minimum domain radius observed in these experiments is a limit imposed by the size of the AFM tips themselves, which have a 20–50 nm nominal radius of curvature. Above this saturation limit, the dependence of domain radius on time is logarithmic, possibly linked to domain growth by electrically activated nucleation. We also investigated the effect of varying the size of the voltage pulse between 6 and 12 V, and observed a linear dependence of domain radius on writing voltage. The dependence of domain size on both writing voltage and writing time is shown in the inset of Fig. 3: of the two lines, the first is written at 100 ms, the second at 10 ms, with 12, 10, 8, and 6 V, respectively. We found the domains to be stable at all voltages investigated.

Ultimately, it is this stability of written domains that is crucial for nonvolatile ferroelectric memory applications. For all the different writing times, we found a signal level over one order of magnitude higher than the noise level. Domain retention was investigated with repeated imaging over a 1 week period. During this time, no significant change was observed in the domain size or signal level, even in the domains written with the shortest (~100 ns) pulses. These results confirm and complete our previous studies, which have demonstrated, for comparable PZT thin films, the stability of micrometer sized written domains over ~1 month, and under highly invasive subsequent processing.[17] We have also observed that although the radius of the AFM tip itself probably limits the diameter of the written domains to ~40 nm, during readout much finer features can be resolved, such as 10 nm separations between closely spaced domains, or small intrinsic domains in unwritten parts of the sample. In principle, with a 10 nm separation between 40 nm domains written at the pulse time saturation limit, information densities of up to 40 Gbits cm^{-2} can be achieved. For further increases in information density, a key parameter will be the choice of a finer AFM tip.

In conclusion, we have shown that the combination of AFM techniques and high quality ferroelectric thin films allows manipulation of ferroelectric domains as small as 40 nm with a high degree of precision. Using this control we demonstrated 6 Gbits cm^{-2} uhd arrays, and a 10 nm separation between minimum size domains should allow information storage densities of at least 40 Gbits cm^{-2}. Domain radius was found to depend logarithmically on voltage pulses longer than 20 μs. For shorter pulses, a saturation limit was observed at a domain radius of ~20 nm. Domain radius was also found to depend linearly on writing voltages above the coercive field of the material. For all writing times the polarized domains, including those written at ~100 ns, were completely stable over the 7 day running time of the experiment, fulfilling a crucial requirement for information storage.

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