Patterning and switching of nanosize ferroelectric memory cells

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A fundamental limitation on the recent development of nonvolatile ferroelectric memories in 64 Mbit–4 Gbit densities has been the ability to scale ferroelectric capacitor cell sizes below 1 μm^2. In the present work, ferroelectric memory cells with lateral sizes down to 100 nm were fabricated by electron-beam direct writing. Switching of single 100 nm cells was achieved and piezoelectric hysteresis loops were recorded using a scanning probe microscope working in piezoresponse mode.
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The zero-field polarization in ferroelectric crystals has two thermodynamically stable states represented by the remanent polarization $\pm P_r$. Between these two opposite states the polarization can be switched by applying an external electric field larger than a certain value termed coercive field. This is the working principle of nonvolatile ferroelectric random access memories (FeRAM), the binary data ''0'' and ''1'' being in this way encoded by the ferroelectric polarization.[1] Practically, a memory cell contains one ferroelectric capacitor and one access transistor. The information is stored in the ferroelectric capacitor and the transistor addresses the desired cell.[2] High-speed, low-voltage operation and low-power consumption make FeRAMs a competitor not only for other nonvolatile memories but also for the current volatile dynamic random access memory.

Four physics-related issues of ferroelectric memories are currently under discussion, viz: (i) the ultimate switching speed and (ii) the dependence of the coercive field on frequency, which both will limit the access speed of FeRAMs, (iii) the thinnest ferroelectric film that has a stable polarization, which is related to the lowest operation voltage, and finally (iv) how small a ferroelectric capacitor can be and still exhibit ferroelectric switching.[2] The last problem represents a fundamental limitation on the development of high-density ferroelectric memories (64 Mbit–1 Gbit) and is related to the ability to scale down the ferroelectric capacitor sizes to under 1 μm^2. It is worth noting that in a prospective 1 Gbit memory a memory cell should not be larger that $150 \times 150\ nm^2$ and its ferroelectric capacitor will probably have a lateral dimension of about 100 nm. Both patterning and switching of such small structures are unsolved problems, and in the present letter we give an answer to these problems and show the patterning and the ferroelectric switching of ferroelectric cells having lateral dimensions under 100 nm, which corresponds to a density beyond 1 Gbit per chip. $Bi_4Ti_3O_{12}$ structures having lateral dimension of about 150 nm have been pattern by Okamura *et al.*[3] using electron-beam (EB) direct writing. Stanishevsky *et al.*[4] used focused-ion-beam patterning to fabricate individual ferroelectric $Pb(Zr_{0.70}Ti_{0.30})O_3$ (PZT) capacitors down to 130 nm.

We fabricated regular $SrBi_2Ta_2O_9$ (SBT) and PZT structures with lateral sizes under 100 nm using EB direct writing (EBDW). EB lithography is one of the next-generation lithography processes allowing a resolution down to several tens of nanometers and, moreover, the EB direct writing alleviates the etching of ferroelectric thin film, which is known to be an unsolved problem at these dimensions.[5] EBDW is a maskless lithography process widely used for writing metallic and oxide nanostructures using metalorganic precursors.[6] Chemical reactions are locally induced in a metalorganic thin film by irradiation with an EB having sufficient energy and dose and the desired pattern is impressed by scanning the EB over the sample. The pattern is developed by dissolving the unexposed area in a specific solvent and further transformed into metal or oxide by thermal annealing.[3,7]

Test patterns of SBT and PZT cells with lateral dimension between 1 and 0.125 μm (see Fig. 1) were exposed into a corresponding metalorganic film using a commercial EB lithography system (ELPHY Plus) adapted to a JEOL JSM 6400 scanning electron microscope (SEM) working at 40 kV acceleration voltage.[8] After developing, the metalorganic mesas were subsequently transformed into an oxide by annealing in air for 5 min at 300 °C and further crystallized into the ferroelectric phase by annealing at temperatures ranging from 600 to 850 °C.[9] Representative structures consisting of periodic patterns of ferroelectric cells yielding $\sim$1 Gbit/cm^2 density are presented in Fig. 2. The cells are well defined in shape and are polycrystalline with grains of 20 nm or less (smaller for PZT than SBT). During the crystallization process SBT structures lose their rectangular shape while PZT maintains the shape even after a 50% shrinkage.

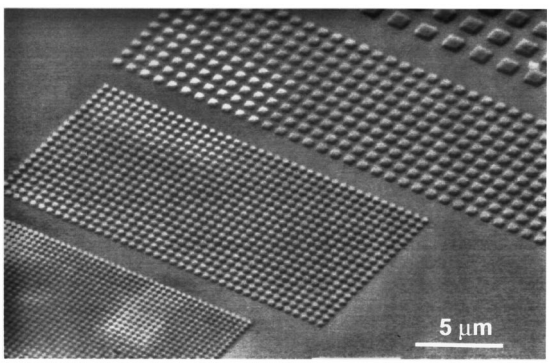

FIG. 1. Metalorganic SBT test structure developed in xylene after *e*-beam exposure with an electron dose of 3 mC/cm^2.

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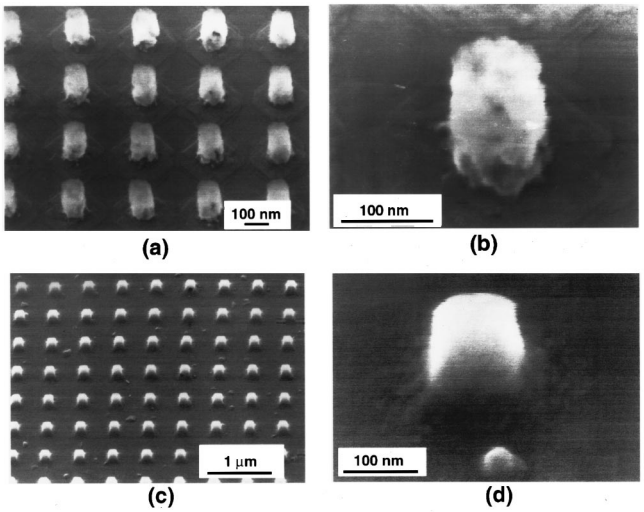

FIG. 2. SEMs showing (a) an SBT cell array on a $SrTiO_3$: Nb substrate after crystallization annealing at 800 °C, (b) one 100 nm SBT cell, (c) a PZT cell array after the crystallization annealing at 650 °C, and (d) a 100 nm PZT cell.

We have obtained ferroelectric switching of 100 nm cells via a scanning probe microscope working in piezoresponse mode.[10,11] Briefly, a conductive tip probes the sample surface, maintaining a constant deflection of the cantilever (constant force mode). Simultaneously, a testing ac signal (2–3 V) with a frequency $f=14.2$ kHz is applied between the tip and the bottom electrode of the sample. Owing to the converse piezoelectric effect, the sample underneath the tip will mechanically oscillate with the same frequency and will induce these oscillations in the cantilever. Using a lock-in technique the piezoelectric signal is extracted from the total deflection signal of the tip. By simultaneously applying a dc voltage, a piezoelectric strain-electric field loop can be acquired. A hysteresis in this strain-field loop is always associated with ferroelectric properties of the sample, the presence of this loop being unequivocal evidence of ferroelectricity.[12] Figure 3 shows the piezoelectric hysteresis

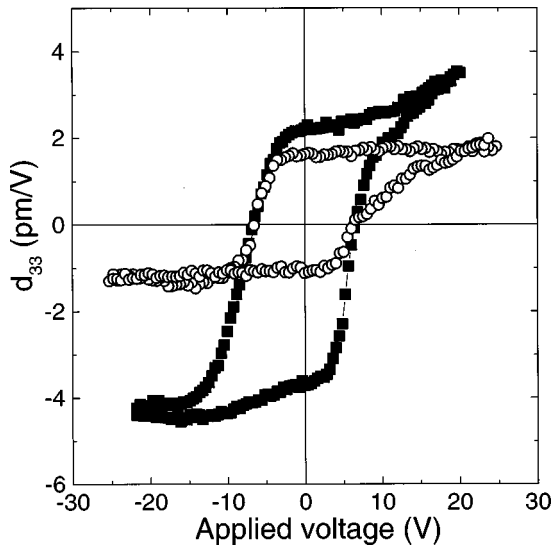

FIG. 3. Piezoelectric hysteresis loops of a 1 μm PZT cell (—■—) and of a 100 nm PZT cell (—○—). Each point of the hysteresis was acquired at zero dc bias after polarizing the sample with a bias pulse (100 ms width) at the desired voltage.

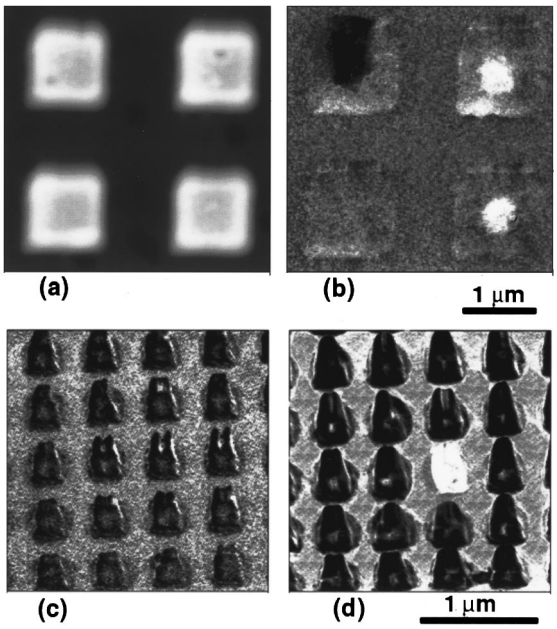

FIG. 4. Topographic (a) and piezoelectric (b) images of four 1 μm PZT cells. The piezoelectric image was acquired after the conductive tip probed each cell in the middle and polarized the cell. The lower left cell is not polarized. The upper left cell was polarized with a −20 V dc bias pulse while the right cells were polarized with a +20 V bias pulse. Piezoelectric images of a 250 nm PZT cell array are shown before (c) and after (d) switching a cell with a +20 V pulse. Note the full switching of the 250 nm cell and the presence of only one switched domain within the 1 μm cell.

loop of a 1 μm and a 100 nm PZT cell, respectively. Both cell sizes exhibit well-defined hysteresis loops having exactly the same coercive voltages, which indicates that shrinking the cell down to 100 nm does not modify the coercive field. The piezoelectric coefficient at zero field decreases as the size decreases, the value for the 1 μm cell being about two times larger than that of the 100 nm cell. As the interaction between the tip and the sample is extremely complex[13] and at the present time poorly known, neither the absolute polarization nor the true coercive field can be extracted from these measurements. Nevertheless, the main achievement is the switching of a three-dimensional structure having a lateral size of 100 nm and an aspect ratio of 1:1. Theoretical studies on size effects[14] estimated the minimum volume at which the polarization and the ferroelectric properties vanish (critical volume) to be about 1000 nm^3. The actual critical volume could be even higher if one considers the influence of fringing fields, which are important at aspect ratios lower than 5:1, and of surface states on the side walls, which can drastically affect the ferroelectric switching by domain pinning or can lead to an excessive leakage current.[15] The piezoelectricity and its hysteresis of a 100 nm PZT cell demonstrated by Fig. 3 show that the actual critical volume of ferroelectrics is less than 10^6 nm^3, and that a further decrease in the cell volume appears to be possible.

An image of the piezoelectric signal can be acquired by scanning the tip over a certain area. White and dark contrasts are associated with the two remnant polarization states $\pm P_r$ and a gray contrast, indicating the absence of piezoelectric activity is associated with zero polarization. Figures 4(a) and 4(b) show topographic and piezoelectric images, respectively, for four 1 μm PZT cell. Figures 4(c) and 4(d) show

switching of a single cell with 250 nm lateral dimension.[16] The asymmetry in the hysteresis loop is confirmed by the equivalent piezoelectric image [Fig. 4(b)] where the negative domain (black contrast) is larger than the positive domain (white contrast). The asymmetry in the switching behavior is presently not understood. It could be an intrinsic effect, an effect of the asymmetry in the electrodes (the substrate and the tip), or an artifact from the measurement setup. The minimum diameter of the switched area under the tip is the range of 300 nm, one cell of 250 nm or less being fully switched by applying a single voltage pulse in the middle of the cell [see Figs. 4(c) and 4(d)]. From Fig. 4(b) it can be seen that the switched domain (dark) exactly ends at the cell side wall. We attribute this to a good surface quality of the side walls, which allows ferroelectric switching in close proximity of side walls.

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[8] Exposure was performed at electron doses varying from 1500 to 6000 μC/cm^2 for PZT and 600 to 1200 μC/cm^2 for SBT. The structures were developed by immersing the exposed sample 1 min in toluene and were dried by blowing with nitrogen.
[9] During the pyrolysis the lateral dimensions of one mesa decrease and this shrinkage process continues during the crystallization anneal. For PZT 30% shrinkage is observed after the pyrolysis and a total shrinkage of about 45% after crystallization.
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[16] Due to the tip shape (triangular with an apex radius ~50 nm) piezoelectric images of structures under 250 nm lateral size are highly distorted, but still show a piezoelectric contrast revealing switching process.