ENDURANCE PROPERTIES OF FERROELECTRIC PZT THIN FILMS

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ABSTRACT

The fatigue behavior of sol-gel derived PZT thin films was studied to determine the endurance of nonvolatile ferroelectric memories. The observed capacitance characteristics following polarization cycling are consistent with a domain pinning model. Cycling at low fields improves the endurance significantly. In addition, poling at fields above the cycling field increases the initial remanent polarization and restores the polarization lost from cycling. Both poling and low-field operation may be promising as a means of improving ferroelectric memory endurance.

INTRODUCTION

Nonvolatile memories based on the ferroelectric hysteresis phenomenon combine many of the features of conventional EPROM, NVRAM, and DRAM technologies including high speed read/write operation, long term data retention, and, because of the simplicity of the memory cell (one pass-transistor and one ferroelectric capacitor), the potential for achieving extremely high densities (1). In order to develop a viable nonvolatile ferroelectric memory, several fundamental technology and reliability issues need to be overcome. One such issue is the gradual loss of detectable ferroelectric polarization following repeated polarization switching, commonly referred to as fatigue. Since the one-transistor memory cell has destructive readout, fatigue limits the read cycle endurance in addition to the write cycle endurance of nonvolatile ferroelectric memory. For ferroelectric NVRAM applications, fatigue due to store/recall cycling also reduces the nonswitching polarization essential for volatile DRAM read/write operation (2). This paper discusses the effects of fatigue on the polarization of ferroelectric lead zirconate titanate ($PbZr_xTi_{1-x}O_3$, commonly called PZT) thin films and investigates the possible responsible mechanisms.

POLARIZATION CHARACTERISTICS

Thin films of PZT with equal zirconium and titanium concentration were prepared via a sol gel process (3). Ferroelectric capacitors were fabricated using platinum for both top and bottom electrodes. The polarization characteristics of these films were determined from large-signal quasi-static capacitance-voltage (voltage ramp rate = 1 V/s) and high frequency small-signal capacitance-voltage measurements (1 MHz, 10 mV rms signal). All characteristics were measured at room temperature. Typical unipolar small-signal polarization-voltage curves for 2000Å, 4000Å, and 6000Å films are shown in Figure 1. The polarization calculated from the small-signal capacitance consists primarily of nonferroelectric ionic, electronic, and dipolar polarization. The contribution from domain wall motion is believed to be small since very little frequency dispersion is observed in these films. The polarization calculated from the large-signal capacitance has an additional contribution from the switching of nonremanent domains. A gradual loss of this contribution attributed to space charge accumulation has been observed during both dc bias and unipolar cycling (2). Even if this contribution is completely lost, the small-signal capacitance is still available and is used to determine the lower limit for polarization available for DRAM applications. This limit demonstrates the scaling potential of ferroelectric memory: For DRAM operation, the 2000Å film has a polarization of 90 $fC/\mu m^2$ equivalent to a 10Å silicon dioxide film subjected to a 2.5V voltage swing. The corresponding value for the remanent polarization determined from the quasi-static capacitance characteristics is 200 $fC/\mu m^2$ which at least before fatigue is more than sufficient for nonvolatile memory applications.

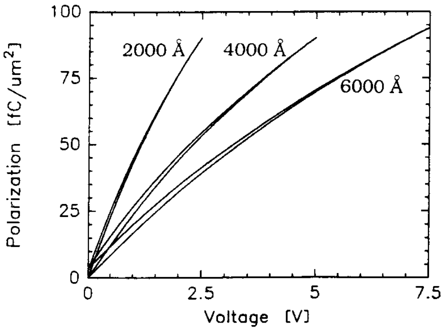

Figure 1. The small-signal polarizability of ferroelectric PZT thin films is found to scale linearly with thickness as expected for nonferroelectric polarizability.

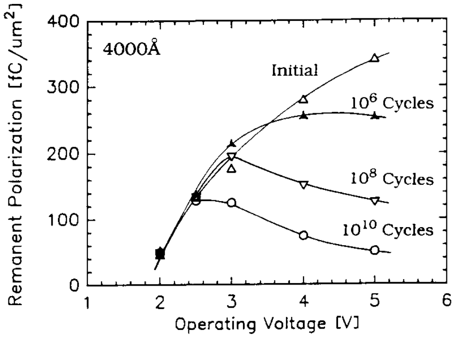

Figure 2. A tradeoff exists between expected storage capacity and endurance. High operating fields increase the initial storage capacity but accelerate fatigue whereas low field operation looks promising for improving endurance but has limited storage capacity. This plot is based on the data presented in Figure 3a.

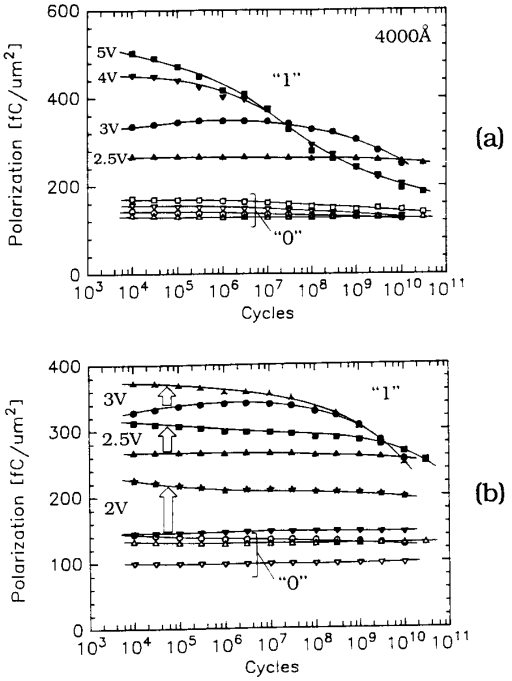

Figure 3. Endurance characteristics of (a) unpoled films and (b) films subjected to an initial -5V to 5V poling cycle (via a quasi-static capacitance measurement) show a loss of remanent polarization (the difference between "1"- and "0"-state polarization) but very little loss of nonremanent polarization. The arrows in (b) illustrate the increase in remanent polarization due to the poling cycle. The polarization values presented here are based on quasi-static capacitance measurements of 20μm×20μm, 4000Å-thick capacitors.

FATIGUE MECHANISMS

The remanent polarization increases as the maximum voltage used to reverse the polarization of the film increases. Therefore, it appears desirable to use the highest read/write voltage allowable to obtain the largest storage capacity. However, there is a tradeoff between storage capacity and endurance (Figure 2): The loss of remanent polarization from fatigue is accelerated considerably when cycling at high voltages as shown in Figure 3. The "0" and "1" values correspond to the polarization available for sensing a "0" and a "1" using a conventional DRAM sensing scheme: the "0" signal corresponds to nonremanent polarization whereas the "1" signal is the sum of the nonremanent and remanent polarization (see Figure 4). Figure 3b illustrates the effect of an initial -5V to 5V cycle (hereafter called a poling step) on the endurance characteristics. This poling step has almost no effect on endurance at high operating fields but causes a dramatic increase in the remanent polarization available for low-field operation (see 2V and 2.5V data). Also note that the nonremanent polarization does not drop significantly during fatigue compared to the detectable remanent polarization. Therefore, it is unlikely that the degradation in remanent polarization is caused by the formation of a lower dielectric constant transition layer near the electrode interfaces (4) since the transition layer should also reduce the detectable nonremanent and nonferroelectric polarization. This is confirmed by comparison of the small-signal and large-signal polarizability during fatigue (Figure 5): The small-signal polarizability shows very little degradation whereas the large-signal hysteresis loops show significant fatigue.

Additional insight into possible mechanisms is provided by the large-signal quasi-static capacitance curves of fatigued samples (Figure 6). At high cycling fields, the capacitance peaks due to domain switching collapse after many polarization reversals. This loss is not recovered even after several cycles at twice the field used during

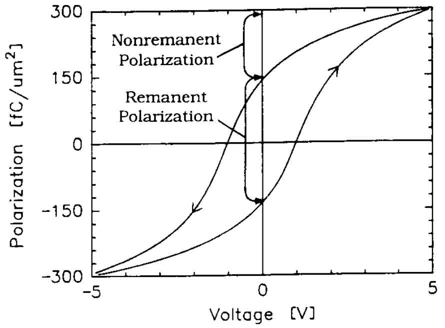

Figure 4. For a DRAM sensing scheme, the polarization for the "0" state corresponds to the nonremanent polarization of the ferroelectric capacitor whereas the polarization for the "1" state corresponds to the sum of the remanent and the nonremanent polarization.

fatigue, in contrast to the observations for low-field cycling presented below. Cycling at lower voltages reduces the fatigue rate and allows changes in the capacitance characteristics to be monitored closely. In this case, there is a shift in capacitance to higher fields (Figure 7). This shift may be explained by domain "pinning", i.e. a reduction in the mobility of domain walls because of, for example, interaction with charged defects or fragmentation of the original domains and changes in the domain structure (such as an increase in the population of 90° domains) during cycling. In either case, it is expected that a sufficiently high field can enhance domain wall motion and assist domain growth causing at least some recovery in remanent polarization. This is indeed observed as shown in Figure 8: A -5V to 5V poling cycle following 10^9 cycles at 2.5V causes complete recovery of the capacitance characteristics. Recovery from fatigue using high voltage poling has been reported in both PZT and KNO_3 films (5),(6) confirming the observation that at least under certain conditions (e.g., fields below saturation), fatigue is an electrically reversible phenomenon. However, if a sample has been subjected to considerable cycling, the fields required to recover the lost polarization, i.e. unpin domains, may be so large that irreversible damage due to charge trapping and dielectric breakdown may occur (7).

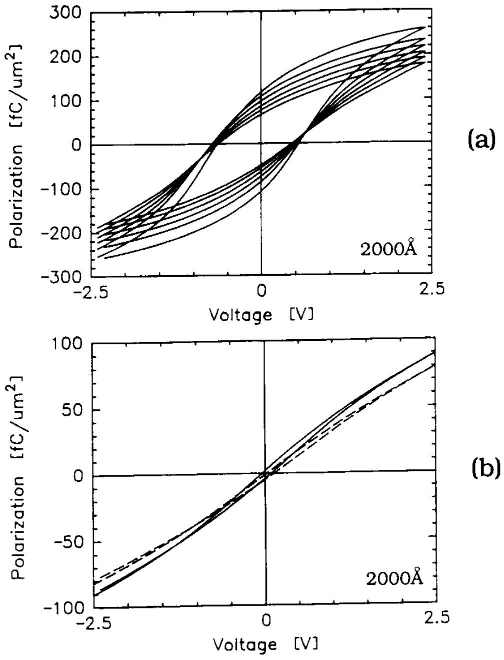

Figure 5. (a) Degradation of the hysteresis loop (determined from the quasi-static capacitance) of a 2000Å film after 1 to 10^{10} polarization reversals. (b) Little degradation is observed in the small-signal polarization after fatigue (dashed line) indicating that the fatigue mechanism most likely does not involve the formation of lower dielectric constant interfacial layers.

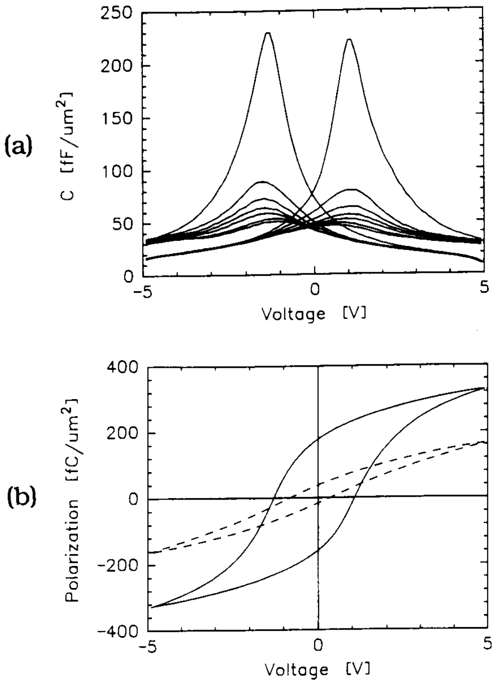

Figure 6. (a) Large-signal quasi-static capacitance characteristics of a 4000Å film demonstrate the rapid collapse of capacitance peaks observed when cycling at high fields (5V, 1MHz). (b) The hysteresis loop has deteriorated dramatically after 10^{10} cycles (dashed line).

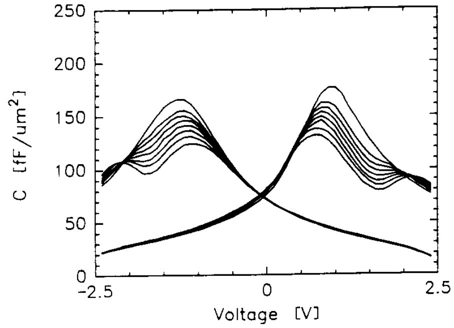

Figure 7. Low-field (2.5V, 4000Å) cycling causes a shift in capacitance to higher fields and the formation of new capacitance peaks. This phenomenon may be attributed to the reduced mobility of domain walls or to changes in the domain structure after cycling. Although this sample was subjected to an initial 5V poling cycle to reduce the asymmetry present in virgin films, the same qualitative behavior is observed in unpoled capacitors.

Since recovery from fatigue is possible with high-field poling (even on nanosecond time scales), it appears unlikely that fatigue is caused by the formation and propagation of conductive, oxygen-deficient dendrites (6). In addition, because of the propagation of dendrites, one would expect that the effect of fatigue on thin films should be even more detrimental than thick films. The opposite effect is in fact observed by comparing the hysteresis loops of 2000Å and 4000Å films subjected to 10^{10} cycles at the same peak field (Figures 5a and 6b).

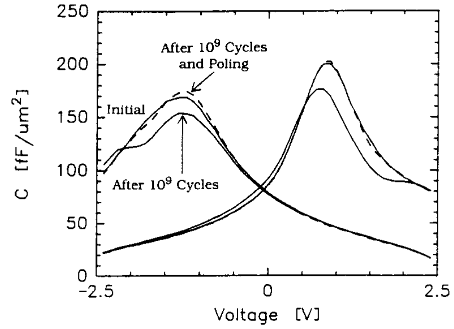

Figure 8. Recovery from fatigue is possible using a high-field poling cycle. This example demonstrates the complete recovery of the polarization of a 4000Å film subjected to 10^9 cycles at 2.5V after the application of a -5V to 5V poling cycle performed by a quasi-static capacitance measurement.

FATIGUE RECOVERY

In order to determine the effectiveness of poling in memory applications, the polarization and endurance of capacitors subjected to periodic poling steps (-5V to 5V voltage ramp at 1V/s) are compared to those of capacitors only subjected to initial poling (Figure 9). At low voltages, a capacitor which has not been subjected to any poling exhibits very little fatigue but has limited polarization. The initial poling step applied before any cycling causes a significant increase in remanent polarization (see Figure 3b). This effect is attributed to the lowering of the built-in field observed in virgin films and an increase in the population of switchable domains. After the initial poling step, the remanent polarization drops gradually with cycling and approaches the polarization of the unpoled capacitor as shown in Figure 3b. If this capacitor is subjected to periodic poling sequences (in this case, every 10^9 cycles), the remanent polarization recovers to almost its original value as shown in Figure 9. Experiments using 500ns, 5V poling pulses every 10^9 cycles demonstrate that there is virtually no loss in remanent polarization even after 10^{11} cycles at 2.5V. In this case, fluctuations in polarization between the value after a poling step and the value immediately before the next poling step are less than 10%.

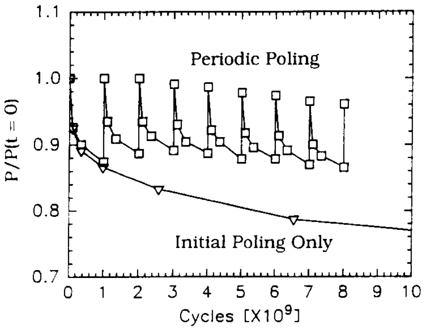

Figure 9. Periodic high voltage poling may improve endurance characteristics as demonstrated here for a 4000Å film subjected to a 5V poling cycles every 10^9 polarization reversals at 2.5V. Note that in this example, poling is preformed using a 1V/s voltage ramp (quasi-static capacitance measurement). However, high-speed poling (500ns pulses) has also been observed to restore polarization loss from fatigue.

SUMMARY AND CONCLUSIONS

The loss of remanent polarization due to fatigue limits ferroelectric memory endurance. Low-field operation reduces the available polarization but improves the endurance considerably. High-field poling steps increase the remanent polarization available at low fields and restore polarization loss from fatigue. This behavior as well as the changes in capacitance characteristics of fatigued films are consistent with a domain pinning model. These results demonstrate the potential for extremely high read/write cycle endurance.

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