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Hysteretic properties of Mn-doped $Pb(Zr,Ti)O_3$ thin films

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Abstract

$Pb(Zr,Ti)O_3$ (PZT 30/70) and Mn-doped $Pb(Zr,Ti)O_3$ (PMZT 30/70) thin films have been fabricated on $Pt/Ti/SiO_2/Si$ substrates by a chemical solution deposition technique. The experiments found that the addition of Mn in PZT thin films greatly improves the ferroelectric properties of thin films. It is demonstrated that the Mn-doped (1 mol%) PZT showed fatigue-free characteristics at least up to 10^{10} switching bipolar pulse cycles under 10 V and excellent retention properties. The Mn-doped PZT thin films also exhibited well-defined hysteresis loops with a remnant polarization (Pr) of 34 $\mu C/cm^2$ and a coercive field (Ec) of 100 kV/cm for the thickness of 300 nm. Dielectric constant and loss ($\tan\delta$) for Mn doped PZT thin films are 214 and 0.008, respectively. These figures compare well with or exceed the values reported previously. In this paper, the mechanism by which Mn influences on the ferroelectric properties of PZT thin films has also been discussed.

Keywords: Doping; Ferroelectric properties; PZT; Sol-gel processing

1. Introduction

Ferroelectric thin films have attracted a great deal of attention for use in non-volatile semiconductor memories because of their many advantages over Si-based devices.[1–3] Lead zirconate titanate $Pb(Zr, Ti)O_3$ (PZT) thin films have been widely studied and are recognized to be highly promising because of their excellent ferroelectric properties. Megabit-scale stacked memories have been produced using PZT or bismuth layered perovskites.[4] PZT thin films have the advantage that they form at significantly lower temperature than the latter. However, PZT thin films on Pt electrodes for ferroelectric random access memories exhibit degradation problems such as severe polarization fatigue after long bipolar switching pulses. The bismuth layer structure ferroelectric thin films such as $SrBi_2Ta_2O_9$ and $(Bi_{3.25}La_{0.75})Ti_3O_{12}$ (BLT) have been found to exhibit essentially no fatigue and low coercive field with Pt bottom electrodes.[5,6] However, they are generally prepared at relatively high processing temperatures, and show low remnant polarization. There has been some success in finding methods to mitigate fatigue in PZT thin films, mainly through the use of metal oxide electrode materials.

Previous papers[7] have reported a significant improvement in the pyroelectric properties of PZT 30/70 thin films when doped with Mn. In this study, the ferroelectric properties of Mn-doped PZT 30/70 thin films are reported.

2. Experimental

Detailed preparation procedures of PZT 30/70 or PMZT 30/70 sols and thin films are described in an earlier publication.[7] The orientation and phase purity of the films were determined using an θ–2θ X-ray diffraction (XRD) method with CuK_α radiation on a Siemens D5005 diffractometer equiped with a Goebel mirror. A set of Au/Cr electrode dots with area 3.142 mm^2 was sputtered onto the film surface through a metal foil shadow mask to make a AuCr/PZT/Pt electrode. The Pt bottom electrode beneath the film provided the other electrode. Film thickness was measured using a Dektak surface profilometer after acid-etching a corner of the film. All the films discussed were approximately 300 nm thick and poled by applying a dc bias of 5 V onto two electrodes at 90 °C for 10min. Electrical properties including hysteresis loop, fatigue and retention characteristics, dielectric constant, dissipation factor, etc were studied using a Radiant Technologies RT66A ferroelectric test system and a Genrad 1689M RLC Digibridge impedance analyzer.

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3. Results

Fig. 1 shows the XRD patterns for undoped and doped PZT thin films on $Pt/Ti/SiO_2/Si$ substrates annealed at a temperature of 530 °C. All the films were single-phase perovskite and possessed a [111] preferential orientation. A small percentage of [100] orientation was observed in the doped-PZT thin film. The sharp XRD peaks suggested that the films were well crystallized.

Fatigue, retention and imprint under various conditions are recognized as the most important reliability characteristics for memory applications. The imprint is described simply as the preference of a certain polarization state over the other in ferroelectric bistable states and eventually leads to a failure when retrieving the data stored.[8] The preferred state can be developed intrinsically at fabrication process as well as from capacitor structure. Fig. 2 shows the hysteresis loops of PZT and PMZT thin films before poling and after poling at 5 V. The small shift of the hysteresis loop on the non-poled PZT film toward the direction having $|Ec(+)| > |Ec(-)|$ is caused by either the asymmetric top and bottom electrodes or "self" polarization of the film. The direction of the corresponding "internal bias field" was the same in all measured samples directing from the top to the bottom electrode. This "internal bias field" increased when Mn was doped in PZT film. Its magnitude varied from about 5 to 10 KV/cm for the PZT film and about 25 to 30 KV/cm for the PMZT film.

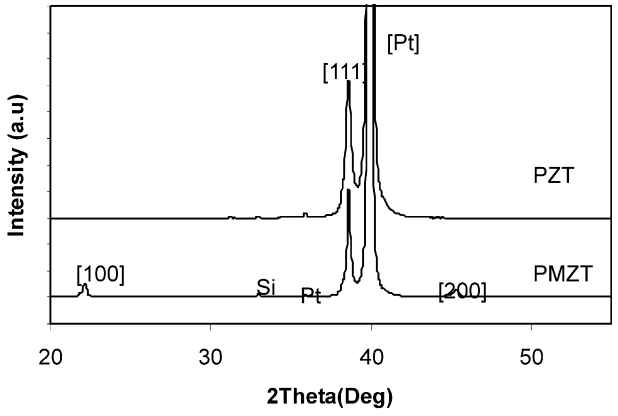

Fig. 1. XRD Patterns of PZT and Mn-doped PZT thin films, thickness = 300 nm.

Table 1 lists the ferroelectric properties of non-poled and poled PZT and PMZT thin films at the applied electric field of 250 kV/cm. The data were taken from Fig. 2. Before poling, both P–E loops of PZT and PMZT thin films showed asymmetry with $|Ec(+)| > |Ec(-)|$. After poling with the positive end of dc bias connecting to top electrode (Au), the P–E loop of PZT film shifted towards the negative electric field having $|Ec(-)| > |Ec(+)|$. This indicated that the poling direction is opposite to the "self

Table 1
Ferroelectric properties of non-poled and poled PZT and PMZT thin films (300 nm thick)

Samples	Ec(+) (kV/cm)	Ec(−) (kV/cm)	Ps (μC/cm²)	Pr (μC/cm²)	(−)Pr (μC/cm²)
Nonpoled PZT	118	−97	41	30	−27
Poled PZT	100	−123	42	34	−31
Nonpoled PMZT	138	−100	38	25	−24
Poled PMZT	103	−160	42	34	−30

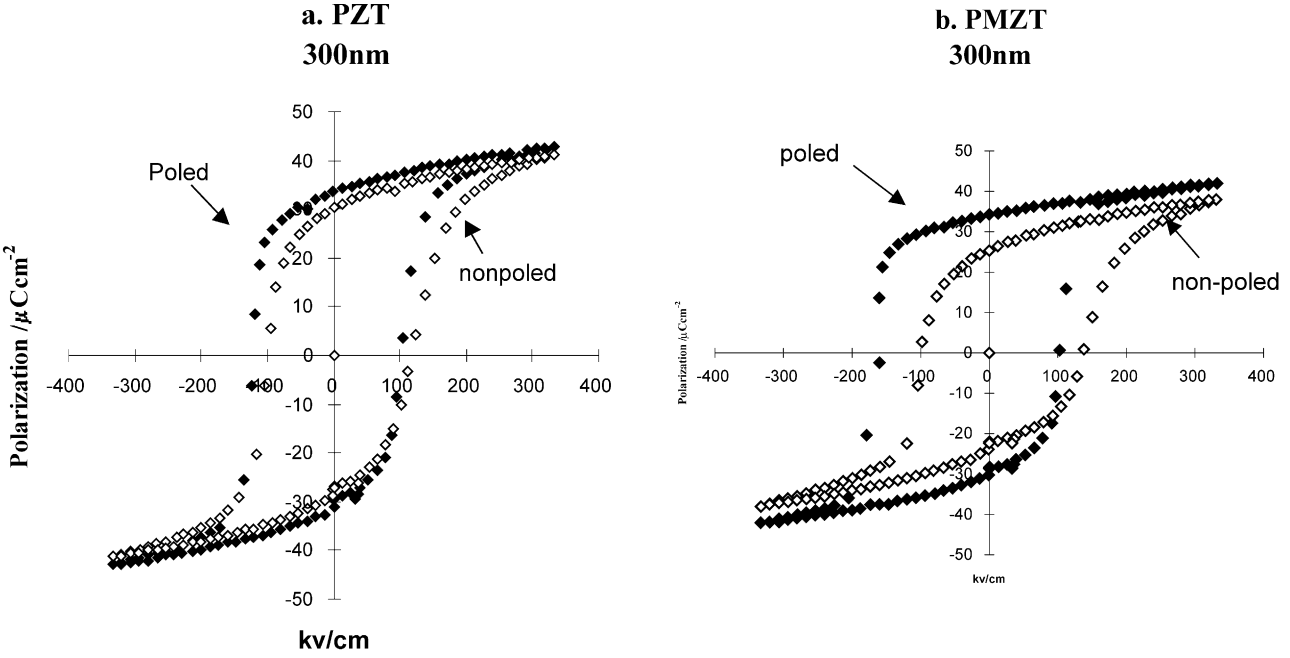

Fig. 2. Hysteresis loops of non-poled and poled (a) PZT and (b) PMZT thin films, film thickness = 300 nm. A dc bias was applied to the films for poling with positive voltage linked to the top electrodes.

polarization'' of the films. The self-polarization direction was pointing to the Pt bottom electrode.[9] This shift of the P–E loop was even more obvious in the case of poled PMZT film. The shape of the hysteresis loop becomes more "square". The total coercive field ($|Ec(+)|+|Ec(-)|$) increased. Its magnitude, ($|Ec(+)|+|Ec(-)|$), is about 223 and 263 kV/cm for PZT and PMZT thin films, respectively. The increase of the coercive field in PMZT films is most likely to be due to the large crystal strain in the tetragonal phase and small grain size as the tetragonality increases with Mn addition. It was observed that if repeated polarization reversals were given the P–E loop of PMZT films would shift towards a symmetric position though a completely symmetric P–E loop could not ultimately be reached. Similar effects are known from bulk ceramics.[10] Yet, in bulk ceramics, an internal bias develops only during aging, after poling of the ceramic. Currently, there are two explanations for the appearance of the internal bias: (a) dipole orientation in the bulk of the domains;[11] (b) space-charge layers inside each domain.[12,13] Explanation (a) seems to be able to explain the case of bulk ceramics, while explanation (b) is in favour of the case of thin films. The space charges, such as lattice vacancies or impurity atoms, are collected at grain boundaries or domain walls and shift under internal or external fields. The space charge layers partially lock in ferroelectric polarization. In contrast to bulk ceramics, in thin films, the space-charge field develops during the film growth prior to any poling treatment. This is in accordance with results of our virgin films.

Ferroelectric fatigue is the loss of switchable polarization with repeated polarization reversals, which is due to pinning of domain walls, inhibiting switching of the domains. Polarization fatigue tests were performed using a square wave electric field of 300 kV/cm at 60 kHz. Fig. 3 shows the normalized polarization as a function of polarization switching cycles, where P^* and $P^\wedge$ represent the switching polarization between two opposite polarity pulses and non-switching polarization between the two same polarization pulses, respectively. The values of P^*–$P^\wedge$ denote the switchable polarization. The switching cycles in terms of logarithm on the x-axis are generally used to evaluate the fatigue characteristics. For Au/PZT/Pt capacitor, three stages are found in the cumulative switching cycles which is in consistent with those reported previously.[14] (1) Slow fatigue state: this stage corresponds to the cumulative switching cycles ranging from 1 to 1×10^4 cycles. No obvious polarization degradation was observed at this stage. (2) Logarithmic fatigue stage: this stage ranges from 1×10^4 to 1×10^8 cycles and was commonly recognized by many researchers.[14–16] $P^* - P^\wedge$ decreases continuously with the increase of cycle number. (3) Saturated stage: this stage corresponds to at switching cycles above 10^8. The P^*–$P^\wedge$ tends toward a saturated value which is about 67% of the original value. For Au/PMZT/Pt capacitor, no fatigue behaviours were observed at least up to 10^8 cycles as shown in Fig. 3. The PMZT thin films almost shows a fatigue-free behaviours at the cycles of 10^{10} at which cycles the P^*–$P^\wedge$ value only had a reduction of 7% of the original value. Fig. 4 shows the hysteresis measurements of a PMZT thin film capacitor before and after fatigue test. There is no obvious reduction of switchable polarization at 10^{10} cycles. This indicates that Mn can greatly improve

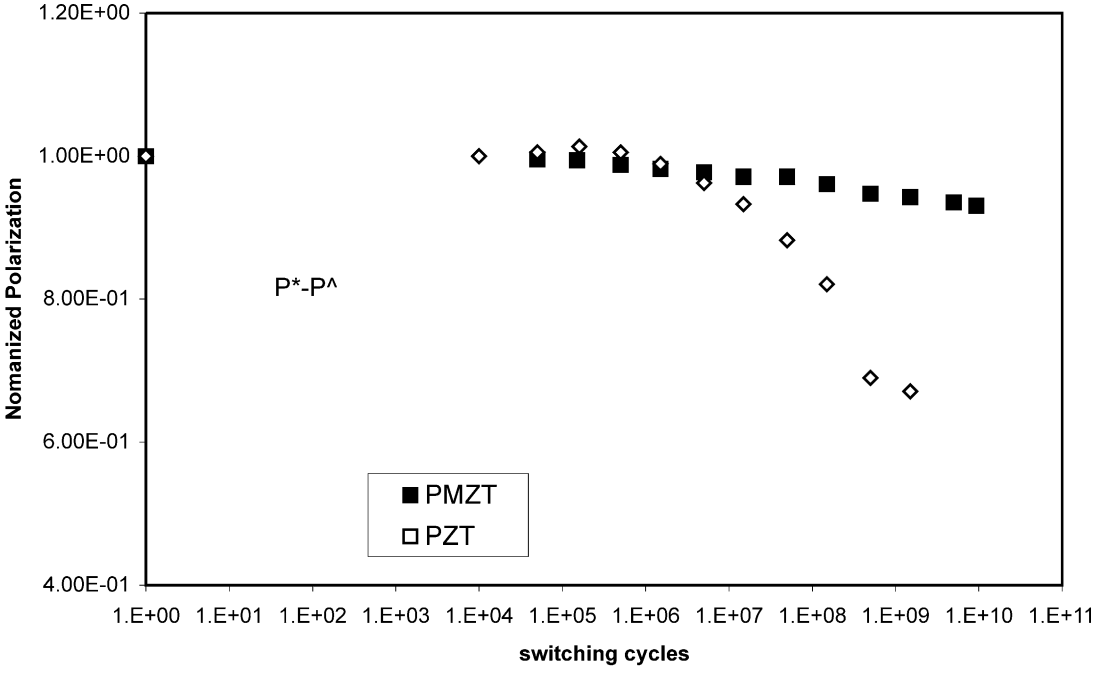

Fig. 3. Fatigue characteristics of the ferroelectric capacitors of (a) PMZT (30/70) thin film and (b) PZT (30/70) thin film, thickness = 300 nm.

the fatigue behaviours of ferroelectric PZT thin films. It is worth noting that after the cycles of 10^{10}, the P–E loop shifted to a relatively symmetrical position and toward the self-polarization direction.

Ferroelectric retention properties were measured at room temperature. The test pulse sequence used for retention measurement was as follows: at first, a triangular pulse of −10 V was applied to write a known logic state; then, after a predetermined time, the logic state was sequentially read by applied two triangular pulses of +10 V (read#1) and −10 V (read#2). The pulse width for all triangular pulse is 0.5 ms. The time delay between the write pulse and the first read pulse is called the retention time. Fig. 5 shows the polarization dacay of capacitor Au/PMZT/Pt measured at the above conditions over a range of retention time 1–30 000 s. As can be seen, the polarization of this capacitor almost remained constant, indicating that the written logic states kept well after 3×10^4 s. A retention test has also been performed using the write voltage of +10 and a read voltage −10 V and +10 V as a function of retention time and similar retention properties were obtained.

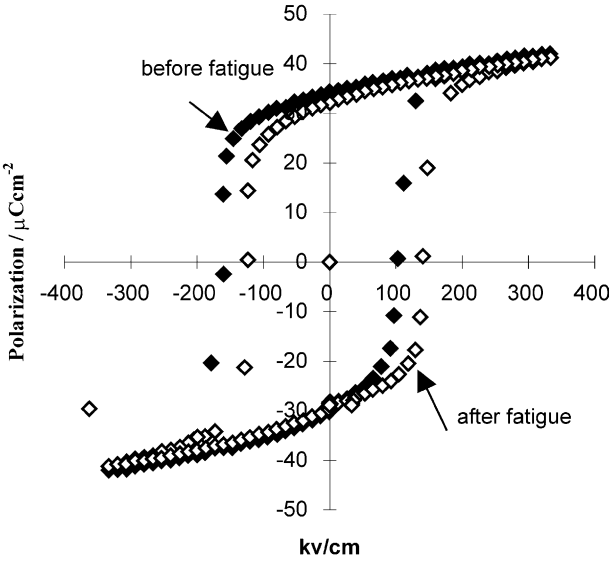

Fig. 4. Hysteresis loops of a PMZT thin film capacitor before and after fatigue test with a bipolar pulse switching up to 10^{10} cycles.

Fig. 6 shows the hysteresis loops of the Au/PMZT/Pt capacitor before and after retention time of 3×10^4 s with 10 V write/read voltage. The hysteresis loop obtained after retention test was essentially identical to that observed before the retention test, indicating that the switchable polarization has no loss.

Dielectric properties were measured as a function of frequency in the range from 100 Hz to 100 kHz. Dielectric constant and loss for PZT thin films at 100 kHz are 375 and 0.016, respectively. Correspondingly, the dielectric constant and loss for Mn-doped PZT thin films are 214 and 0.008, respectively. This indicates that Mn doping reduced the dielectric constant and loss of PZT thin films.

4. Discussion

There are a few types of mechanisms that can cause fatigue in a PZT thin film with Pt electrodes. These mechanisms include 90° domains and resultant strains, electromigration of oxygen vacancies to form extended defects capable of pinning domains, charge injection of electrons from the cathode, formation of interfacial layers between metal electrode and ferroelectric, and conversion of Ti^{4+} to Ti^{3+}.[17] The two popular mechanisms are summed up here. First, internal fields due to space charge segregation at both electrode interfaces can reduce the

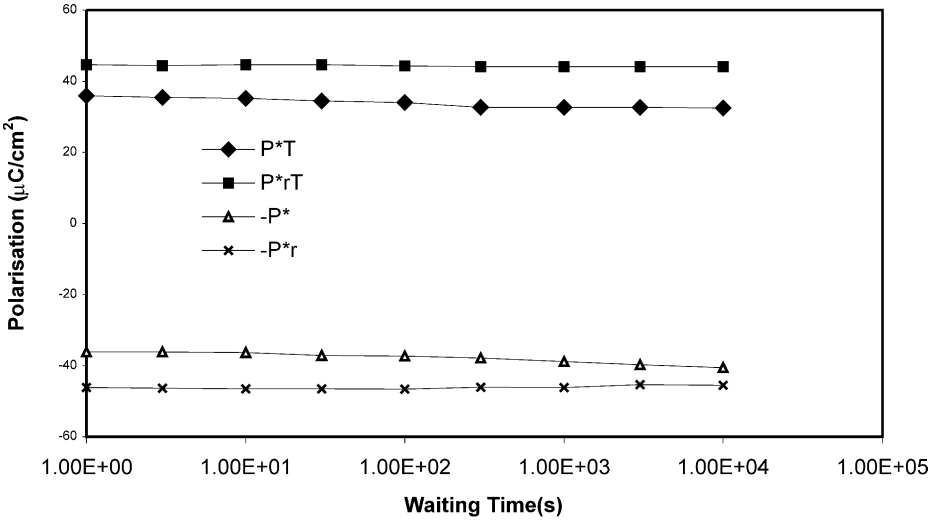

Fig. 5. Retention characteristics of the ferroelectric capacitor of Au/PMZT/Pt. P*T is polarization transferred out of the capacitor from 0 to 10 V (read voltage) at the end of a retention period; P^*_rT is remanent polarization in the capacitor from 10V (read voltage) to 0 during the first read pulse after a retention period; −P* is polarization transferred out of the capacitor from 0 to −10 V (read voltage) during the second read pulse; and −P*r is remanent polarization from −10 V (read voltage) to 0 V during the second read pulse.

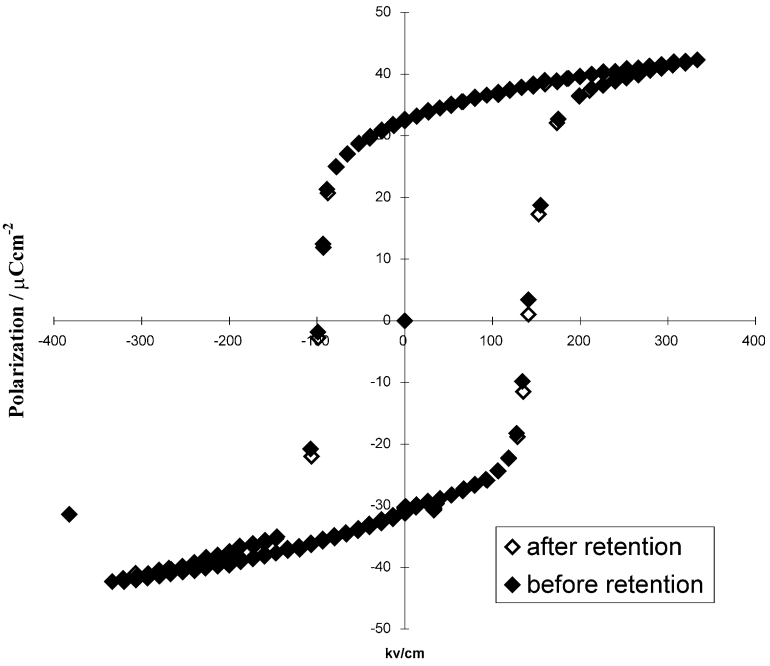

Fig. 6. Hysteresis loops of the Au/PMZT/Pt capacitor before and after a retention time of 3×10^4 s with 10 V write/read voltage.

electric field in the ferroelectric. Therefore, if the space charge segregation builds up during cycling, then polarization will decrease and fatigue will result. During repeated switching, however, oxygen vacancies appear and may be transported toward the electrode interface to set up a space charge layer that has the same characteristic of a Schottky barrier. The use of conducting oxide electrodes is thought advantageous in that it can provide oxygen to compensate for oxygen vacancies. This then alleviates the internal field and thus prevents fatigue. The second mechanism envisions the pinning of the domain walls by electronic carriers or, more likely, by oxygen vacancies. If defects such as oxygen vacancies segregate to the domain wall, it will reduce the domain wall movement, resulting in eventual pinning and degradation of switching ability. Unlike the first mechanism, this pinning effect is a bulk mechanism not limited to the electrode interface.

It appears that most of the suppressed polarization in PZT films is due to the trapping of electronic charge carriers at domain boundaries, either by electrons and/or holes.[18] While several models have been proposed to explain polarization fatigue in PZT,[18–23] none has been proposed to explain the fatigue-free behaviour of doped PZT.

There are several possible reasons for the fatigue-free behaviour in Mn doped PZT thin films: (i) an increase in the coercive field is always observed when Mn is doped in PZT thin films compared with pure PZT thin films. The reason for this is unknown at this time and requires further study. The domain locking, due to the trapping of the injected and/or created carries, will occur primarily near the switching threshold field. Fatigue is typically induced by cyclic reversals of the saturating field; fatigue with fields smaller than saturation typically results in less degradation.[24] PMZT has a higher coercive field (Ec) than PZT. Hence, if the same switching electric field (~300 kV/cm) is applied to both, this field to Ec will be smaller for PMZT than PZT. This could result in less fatigue in PMZT thin films. (ii) The substitution of Mn atoms onto Zr and/or Ti sites may result in the generation of more oxygen atoms that compensate for oxygen vacancies, therefore eventually alleviating the internal field and thus preventing fatigue. However, conventional wisdom would suggest that lower valence B-site dopants such as Fe^{3+}, Ni^{2+} or Mn^{3+} should generate more oxygen vacancies, which would make the fatigue worse, not better. We conclude, therefore, that in this case Mn could be going into the lattice at a higher valence state than 4+, perhaps as Mn^{6+}. This needs further study to verify. (iii) Although we observed a 7% reduction of switchable polarization for PMZT thin films after 10^{10} times reversal switching at 10 V bipolar field, we found that applying a slightly higher electric field to cycle the PMZT thin films could rejuvenate this small amount of electrical fatigue. This indicates that the domain boundaries are weakly pinned in PMZT when compared to PZT, where high field cycling of an electrically fatigued film results in further suppression of the switchable polarization. The relatively weak domain wall pinning exhibited by PMZT may be due to (1) a lower concentration of trapped charge at domain boundaries, (2) the lower trap depth for the charge. The addition of Mn in B-sites in PZT films may be reducing the concentration of oxygen vacancies and therefore the possibility of them being

trapped in domain boundaries. The trap depth for the charge is expected to depend on the depth of electrostatic well at the domain boundaries, which is determined by the magnitude of the ferroelectric polarization. The ferroelectric polarization increases with the increase of applied field. Hence, a slightly higher applied field is sufficient to detrap carriers from shallow depth of the charge at domain boundaries.

5. Conclusions

An increase in the coercive field is always observed when Mn is doped in PZT thin film compared to pure PZT thin films. The reason for this is unknown at this time and requires further study. A larger shift of hysteresis loop in PMZT films was found compared with that of pure PZT films and this shift was getting larger after the films were poled. This shift, however, can be restored to a relatively symmetric state by repeatedly measuring the hysteresis loops under the same conditions. We have shown the significant improvement in PZT fatigue characteristics when Mn atoms were doped in PZT thin films. Mn-doped PZT shows an almost fatigue free characteristics up to 10^{10} switching bipolar pulses under 10 V although a 7% reduction of switchable polarization was found. Applying a slightly higher cyclic field can rejuvenate this switchable polarization. The reasons that lead to fatigue-free effect, we think, are as follows:

1. An increase of coercive field in Mn-doped PZT films means the reduction of saturation field used for cyclic reversal compared with pure PZT films.
2. B-site substitution of Mn atoms probably enriches the oxygen concentration that reduces the oxygen vacancies.
3. A relatively weak domain pinning situation exists in Mn-doped PZT films, which makes the domain unpinning easier.

A good retention property was observed in PMZT films. Mn doping in PZT thin films greatly reduces the relative dielectric constant and dielectric loss of PZT thin films. Finally, fatigue free and good retention properties of Mn-doped PZT thin films make these films be very promising candidates as device materials and their simple capacitor structure makes their integration into device more realistic.

Acknowledgements

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References

1. Scott, J. F. and Paz de Araujo, C. A., Ferroelectric memories. *Science*, 1989, **246**, 1400.
2. Tuttle, B. A., Electric ceramic thin films: trends in research and development. *MRS Bull*, 1987, **12**, 40.
3. Shepard, L. M., Advances in processing of ferroelectric thin films. *Am. Ceram. Soc. Bull*., 1992, **71**, 85.
4. Uhlmann, D. R., Dawley, J. T., Poisl, W. H., Zelinski, B. J. J. and Teowee, G., Ferroelectric films. *J. Sol-Gel Sci. Technol*, 2000, **19**, 53.
5. Paz de Araujo, C. A., Cuchiaro, J. D., McMillan, L. D., Scott, M. C. and Scott, J. F., Fatigue-free ferroelectric capacitors with platinum electrodes. *Nature*, 1995, **374**, 627.
6. Park, B. H., Kang, B. S., Bu, S. D., Noh, T. W., Lee, J. and Jo, W., Lanthanum-substituted bismuth titanate for use in non-volatile memories. *Nature*, 1999, **401**, 682.
7. Zhang, Q. and Whatmore, R. W., Sol-gel PZT and Mn-doped PZT thin films for pyroelectric applications. *J. Phys. D: Appl. Phys*., 2001, **34**, 2296.
8. Lee, J. and Ramesh, R., Imprint of (Pb, La)(Zr, Ti)O_3 thin films with various crystalline qualities. *Appl. Phys. Lett*., 1996, **68**(4), 484.
9. Hvizdoš, P., Reece, M. J., Bushby, A. J., Whatmore, R. W., Zhang, Q. and Alguero, M., Localized Electromechnical Properties of PZT Thin Films Measured By Nanoindentation. *Integr. Ferroelectrics*, 2002, **50**, 199–207.
10. Takahashi, M., *Jpn. J. Appl. Phys*, 1970, **9**, 1236.
11. Arlt, G. and Neumann, H., Intenal bias in ferroelectric ceramics: origin and time dependence. *Ferroelectrics*, 1988, **87**, 109.
12. Takayama, R. and Tomita, Y., Preparation of epitaxial Pb(Zr_xTi_{1-x})O_3 thin films and their crystallographic, pyroelectric, and ferroelectric properties. *J. Appl. Phys*, 1989, **65**, 1666.
13. Chen, S. Y. and Sun, C. L., Ferroelectric characteristics of oriented Pb($Zr_{1-x}Ti_x$)O_3 films. *J. Appl. Phys*., 2001, **90**, 2970.
14. Mihara, T., Watanabe, H. and Paz De Araujo, C. A., *Jpn. J. Appl. Phys., Part 1*, 1994, **33**, 5281.
15. Yoo, I. K. and Desu, S. B., Electrochemical models of failure in oxide perovskites. *Integr. Ferroelectr*., 1993, **3**, 365.
16. Duiker, H. M., Batra, P. D., Scott, J., Paz De Araujo, C. A., Melnick, B. M., Cuchiaro, J. D. and McMillam, L. D., Fatigue and switching in ferroelectric memories: theory and experiment. *J. Appl. Phys*, 1990, **68**, 5783.
17. Du, X. F. and Chen, I. W., Fatigue of Pb($Zr_{0.53}Ti_{0.47}$)O_3 ferroelectric thin films. *J. Appl. Phys*., 1998, **83**, 7789.
18. Warren, W. L., Dimos, D., Tuttle, B. A., Nasby, R. D. and Pike, G. E., Electronic domain pinning in Pb(Zr, Ti)O_3 thin films and its role in fatigue. *Appl. Phys. Lett*., 1994, **65**(8), 1018.
19. Warren, W. L., Dimos, D., Al-shareef, H. N., Raymond, M. V., Tuttle, B. A. and Gordon, E. P., Links between electrical and optical fatigue in Pb(Zr, Ti)O_3 thin films. *J. Am. Ceram. Soc*., 1996, **79**(6), 1714.
20. Scott, J. F., Paz de Araujo, C. A., Melnick, B. M., McMillan, L. D. and Zuleeg, R., Quantitative measurement of space charge effects in PZT memories. *J. Appl. Phys*., 1991, **70**, 382.
21. Yoo, I. K. and Desu, S. B., Mechanism of fatigue in ferroelectric thin films. *Phys. Status Solidi A*, 1992, **133**, 565.
22. Al-Shareef, H. N., Tuttle, B. A., Warren, W. L., Headley, T. J., Dimos, D., Voight, J. A. and Nasby, R. D., Effect of *B*-site cation stoichiometry on electrical fatigue of RuO_2/Pb(Zr_xTi_{1-x})O_3//RuO_2 capacitors. *J. Appl. Phys*., 1996, **79**, 1013.
23. Warren, W. L., Tuttle, B. A. and Dimos, D., Polarization suppression in PZT thin films. *Appl. Phys. Lett*., 1995, **67**, 1426.
24. Shepard, W. H., *MRS Symp. Proc*., 1990, **200**, 277.