

# Improved ferroelectric and pyroelectric properties in Mn-doped lead zirconate titanate thin films

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We have investigated the effects of Mn doping on the ferroelectric and pyroelectric properties of Pb(Zr<sub>0.3</sub>Ti<sub>0.7</sub>)O<sub>3</sub> (PZT) thin films on substrates Pt/Ti/SiO<sub>2</sub>/Si. The Mn-doped (1 mol %) PZT (PMZT) showed almost no hysteretic fatigue up to 10<sup>10</sup> switching bipolar pulse cycles, coupled with excellent retention properties. We present evidence that while a low permittivity interfacial layer forms between the Pt electrode and PZT films, this does not occur in PMZT. We propose that Mn dopants are able to reduce oxygen vacancy mobility in PZT films and Mn<sup>2+</sup> ions consume the oxygen vacancies generated during repeated switching, forming Mn<sup>4+</sup> ions. These mechanisms are probably responsible for their low observed fatigue characteristics. Mn doping brings additional benefits to the electrical properties of PZT films. The relevant pyroelectric coefficients ( $p$ ) of a 700 nm thick film are  $3.52 \times 10^{-4} \text{ C m}^{-2} \text{ K}^{-1}$  and detectivity figures of merit  $F_D = 3.85 \times 10^{-5} \text{ Pa}^{-0.5}$  at 33 Hz for Mn-doped PZT, compared with  $p = 2.11 \times 10^{-4} \text{ C m}^{-2} \text{ K}^{-1}$  and  $F_D = 1.07 \times 10^{-5} \text{ Pa}^{-0.5}$  for the undoped PZT films. This means that the Mn-doped PZT thin films are excellent candidates as device materials for both memory and pyroelectric applications. © 2003 American Institute of Physics. [DOI: 10.1063/1.1613370]

## I. INTRODUCTION

Ferroelectric thin films have attracted a great deal of attention for use in nonvolatile semiconductor memories (FeRAM) because of their many advantages over Si-based devices.<sup>1-3</sup> Pb(Zr<sub>0.3</sub>Ti<sub>0.7</sub>)O<sub>3</sub> (PZT)-based perovskites have been extensively studied for this application and are very promising because of their excellent ferroelectric properties and low perovskite phase crystallization formation temperature (<600 °C). However, PZT thin films on Pt electrodes exhibit degradation problems such as severe polarization fatigue after long bipolar switching pulses.<sup>4</sup> Although the use of metal oxide electrodes can reduce this fatigue, they are electrically leaky and make the process more complicated and expensive.<sup>5</sup> One feasible approach for reducing fatigue-related problems is donor doping (e.g., La<sup>3+</sup>) without replacing the commonly used Pt electrodes with metal oxide electrodes. According to the defect dipole model, which is well known for titanate ceramics,<sup>6,7</sup> the introduction of aliovalent dopant ions distorts the electroneutrality condition. Therefore, higher-valence foreign cations (donors), such as La<sup>3+</sup> for A site modification or Nb<sup>5+</sup> for B site modification, are compensated by negatively charged defects, such as Pb vacancies. Lower-valence foreign cations (acceptors), such as Li<sup>+</sup> for A site modification or Fe<sup>3+</sup>, Mn<sup>3+</sup>, Ni<sup>2+</sup> for B site modification, are compensated by positively charged defects, such as oxygen vacancies, to maintain the overall electroneutrality. Hence acceptor doping normally leads to an increase in the oxygen vacancy concentration. According to the defect chemistry model, oxygen vacancies are the only ionic species that are mobile in the lattice at ambient temperatures and

the defect dipoles are the oxygen-vacancy-acceptor-ions associates. Hence an enhancement of any internal bias under an applied field can be expected only in the case of acceptor doping, due to the increase in concentration of alignable defect dipoles. Donor doping, on the other hand, mainly introduces immobile defect dipoles which should result in a decrease of the mobile defect dipole concentration and hence in a reduction of imprint and fatigue.<sup>8</sup>

The pyroelectric properties of PZT thin films have been extensively studied.<sup>9</sup> To develop high performance pyroelectric infrared detectors, efforts have been made to improve the desired properties of PZT thin films. Various figures-of-merit (FOM) are used to assess the suitability of pyroelectric materials for use in uncooled IR sensors.<sup>9</sup> The most useful of these for arrays of small detectors is  $F_D = p/[c'(\epsilon\epsilon_0 \tan \delta)^{1/2}]$ , where  $c'$  is the volume specific heat (for PZT thin films,  $c'$  is  $2.7 \times 10^6 \text{ J m}^{-3} \text{ K}^{-1}$ ),  $\epsilon$  is the relative permittivity,  $\epsilon_0$  the permittivity of free space,  $\tan \delta$  is dielectric loss, and  $p$  is the pyroelectric coefficient. An effective way to improve  $F_D$  is to increase the pyroelectric coefficient and/or to reduce the dielectric constant and loss by controlling the microstructure and/or composition of the PZT thin films. Good control of film nucleation and growth<sup>10,11</sup> means that improving electrical properties through the crystalline state of the thin films has become increasingly difficult. Hence measures have to be taken to improve  $F_D$  through the addition of dopants.

The main purpose of the present study is to develop improved PZT-based thin film materials with Pt electrodes. For this purpose, we prepared a series of Mn-doped PZT films and examined their ferroelectric, dielectric, and pyroelectric properties.

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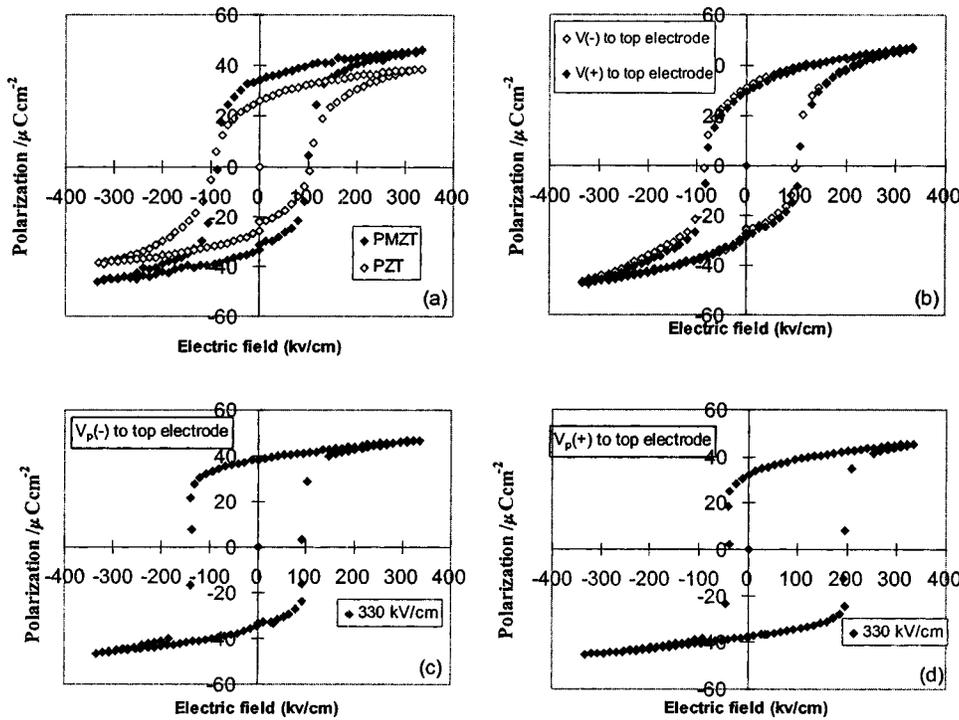


FIG. 1. (a) The  $P-E$  loops of the unpoled Pt/PZT/Pt and unpoled Pt/PMZT/Pt capacitors, measured at 330 kV/cm. (b) The  $P-E$  loops of the Pt/PZT/Pt capacitor poled at different directions, measured at 330 kV/cm. (c) Hysteresis loop of Mn-doped PZT thin films poled with the negative end,  $V_p(-)$ , connected to the top electrode of the film. (d) Positive end,  $V_p(+)$ , connected to the top electrode of the film. The thickness of all the thin films was 300 nm.

**II. EXPERIMENTAL PROCEDURE**

All the PZT and Mn-doped (1 mol %) PZT (PMZT) thin films used in this study were prepared on Pt(100 nm)/Ti(5 nm)/SiO<sub>2</sub>(450 nm)/Si substrates using a sol gel-based process described previously.<sup>12,13</sup> The Pt was highly (111) orientated. The films annealed at 530 or 560 °C, were well crystallized, and showed a single-phase perovskite with [111] preferential orientation by x-ray diffraction (XRD). The Mn doping did not increase the crystallization temperature required to obtain this type of structure. Films were electrically assessed using standard polarization field hysteresis, and dielectric and pyroelectric coefficient measurement methods.<sup>12,13</sup> The polarization fatigue tests were performed using a square wave electric field of 330 kV/cm at 60 kHz. 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 applying two triangular pulses of -10 V (read No. 1) and +10 V (read No. 2). The pulse width for all triangular pulses is 0.5 ms. The time delay between the write pulse and the first read pulse is called the retention time.

**III. RESULTS AND DISCUSSION**

Figure 1(a) shows the polarization–electric field ( $P-E$ ) curves of the unpoled Pt/PZT/Pt and unpoled Pt/PMZT/Pt capacitors, measured at 330 kV/cm. The spontaneous ( $2P_s$ ) and remnant ( $2P_r$ ) polarizations for PZT are 78 and 56  $\mu\text{C}/\text{cm}^2$ , respectively, while they are 92 and 67  $\mu\text{C}/\text{cm}^2$ , respectively, for PMZT. The coercive fields ( $2E_c$ ) for both PZT and PMZT are similar. They are 190 kV/cm with  $E_c(+)$  = 100 kV/cm and  $E_c(-)$  = 90 kV/cm. A slight offset (10 kV/cm) was observed in the coercive voltage. Figure 1(b) shows the  $P-E$  loops of a poled Pt/PZT/Pt capacitor. The

$2P_s$  and  $2P_r$  increased after poling to 94 and 62  $\mu\text{C}/\text{cm}^2$ , respectively, values very similar to the unpoled PMZT. The slight offset (10 kV/cm) in the coercive voltage was still observed and was independent of the poling direction.

Figure 1(c) shows a  $P-E$  hysteresis loop of the Pt/PMZT/Pt capacitor poled with  $V_p(-)$  connected to the top Pt electrode while Fig. 1(d) shows a hysteresis loop of the same capacitor poled with  $V_p(+)$  connected to the top Pt electrode. Both  $P-E$  loops were measured at 330 kV/cm. When poling with  $V_p(-)$ , a 200 kV/cm electric field is required to drive the hysteresis loop to its saturation while a 267 kV/cm electric field is required when poling with  $V_p(+)$ . As shown in both Figs. 1(c) and 1(d), the capacitors are characterized by well-saturated, square  $P-E$  loops if the field strength exceeds a threshold field strength (220 kV/cm). The  $2P_r$  value is unchanged relative to the unpoled capacitors at 67  $\mu\text{C}/\text{cm}^2$ . The  $2E_c$  value is 220 kV/cm in both cases, slightly higher than that of the PZT and unpoled PMZT thin films (190 kV/cm) [Figs. 1(a) and 1(b)]. Unlike the poled PZT thin film, the poled PMZT thin films show a voltage offset. This offset is dependent upon the poling direction. When poling with  $V_p(+)$ , a larger offset was generated ( $|E_c(+)|$  = 190 kV/cm and  $|E_c(-)|$  = 30 kV/cm). The offset was smaller ( $|E_c(+)|$  = 85 kV/cm and  $|E_c(-)|$  = 135 kV/cm) when poling with  $V_p(-)$ . Because the voltage offset does not obviously appear in the cases of the PZT and nonpoled PMZT thin films, this indicates that voltage offsets in PMZT thin films are mainly caused by (1) Mn doping and (2) poling. The shift of hysteresis loop in the poled PMZT thin films is due to the generation of an “internal bias” or dipole moment. For Ti-rich PZT, this has been reported as about 13–15 kV/cm with its direction pointing towards the top electrode.<sup>14,15</sup> This agrees with the observations reported above (10 kV/cm) for the unpoled and poled

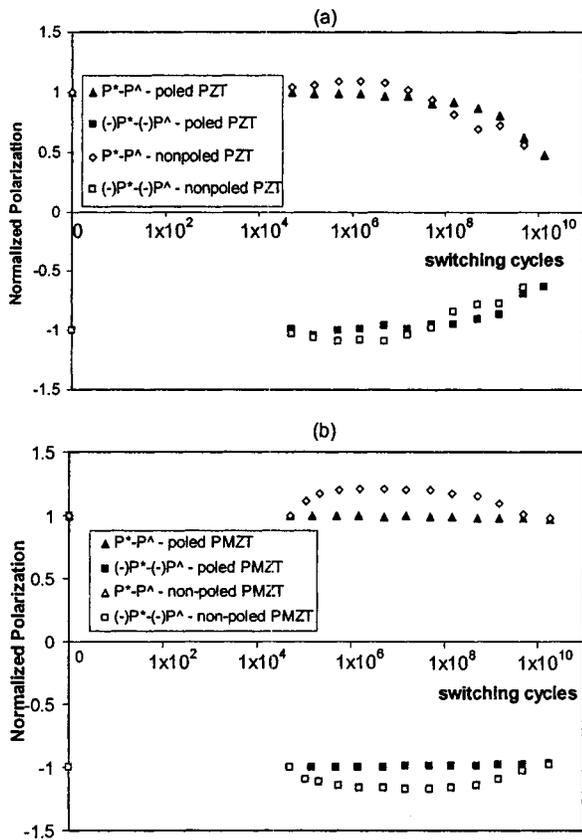


FIG. 2. Fatigue characteristics of the ferroelectric capacitors of (a) PZT thin film and (b) Mn-doped PZT thin film. Both films were prepoled with the  $V(-)$  connected to the top electrode. The thickness of the thin film was 300 nm.  $P^*$  and  $P^+$  represent the switching polarization between two opposite polarity pulses and nonswitching polarization between the two same polarization pulses, respectively. The values of  $P^* - P^+$  denote the switchable polarization.

PZT films. If poling with  $V_p(-)$  [Fig. 1(c)], which corresponds to poling the film along the direction of the internal bias field, a shift, with  $(|E_c(+)| = 85 \text{ kV/cm}$  and  $|E_c(-)| = 135 \text{ kV/cm}$ ), of hysteresis loop to negative field is obtained. Correspondingly, if poling with  $V_p(+)$  [Fig. 1(d)], which suppresses the film poled along the internal bias field, a large shift, with  $(|E_c(+)| = 190 \text{ kV/cm}$  and  $|E_c(-)| = 30 \text{ kV/cm}$ ), of hysteresis loop to positive field is obtained.

The defect dipole model can easily explain the phenomenon of the asymmetric hysteresis loops in poled PMZT thin films.  $\text{Mn}^{2+}$  ions are B site acceptor ions. According to the defect dipole model, an enhancement of fatigue and imprint effect would be expected. The experimental observation agrees with the defect dipole alignment model for the asymmetric hysteresis loops although not for fatigue (see below). For an unpoled PMZT thin film, defect dipoles formed by the oxygen-vacancy-acceptor-ion associates might be randomly orientated in the film. When poling the thin film, the defect dipoles orient to the poling direction forming an internal bias and leading to the asymmetric hysteresis loops.

Ferroelectric fatigue is the loss of switchable polarization with repeated polarization reversal. Figure 2 shows the normalized polarization as a function of polarization switching cycles, where  $P^*$  and  $P^+$  represent, respectively, the switching polarization between two opposite polarity pulses

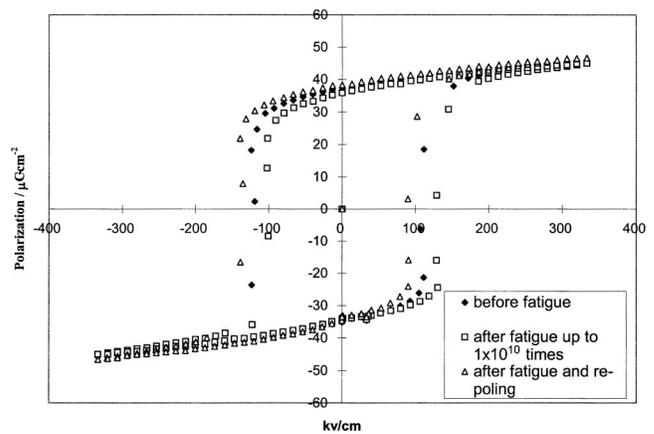


FIG. 3. Hysteresis loops of a PMZT thin film capacitor before and after fatigue test with a bipolar pulse switching up to  $10^{10}$  cycles. The film was prepoled with the  $V(-)$  connected to the top electrode. After fatigue test, the film was repoled with the same direction and electric field as before fatigue test. The 3% reduction of remnant polarization was rejuvenated.

and nonswitching polarization between two identical polarization pulses. The values of  $P^* - P^+$  denote the switchable polarization. For both Pt/PZT/Pt and Pt/PMZT/Pt capacitors, unpoled films have shown an increase of the switchable polarization up to  $10^6$  to  $10^7$  cycles while poled films did not show such an increase. This is probably because the poling process has aligned a percentage of the  $90^\circ$  domains normal to the film plane, increasing the switchable polarization. In the unpoled films, the  $90^\circ$  domains need time under successive cycling to reorient parallel to the electric field. Hence for these films the switchable polarization increases gradually with time. For the Pt/PZT/Pt capacitor [Fig. 2(a)], poling has little effect on its fatigue characteristics. The switchable polarization decreases after  $10^7$  cycles, reducing by about 50% at  $10^{10}$  cycles. This type of fatigue is well known for PZT.<sup>16</sup> For the unpoled Pt/PMZT/Pt capacitor, an increase of switchable polarization was observed before  $10^8$  cycles as shown in Fig. 2(b). After further switching, up to  $10^{10}$  cycles, only 2% to 3% reduction of the original switchable polarization was found. For the poled Pt/PMZT/Pt capacitor, no fatigue was observed at least up to  $10^8$  cycles as shown in Fig. 2(b). With further switching up to  $10^{10}$  cycles, the  $P^* - P^+$  value had reduced by only 3% of the original value. The  $P-E$  loops of a poled PMZT thin film before and after the fatigue test are shown in Fig. 3. There is no obvious reduction of switchable polarization at  $10^{10}$  cycles. This indicates that Mn doping can greatly improve the fatigue behavior of ferroelectric PZT thin films. It is worth noting that after  $10^{10}$  cycles, the  $P-E$  loop moved to positive field and towards the self-polarization direction. It is interesting to note that the  $P-E$  loop moved to negative field again if the film was repoled under the same conditions as before the fatigue test (Fig. 3).

There is considerable debate regarding the mechanisms that cause fatigue in PZT thin films with Pt electrodes.<sup>17</sup> Because the fatigue behavior in PZT is different for samples prepared by various techniques and on various substrates, it is difficult to give a universally accepted model to explain the fatigue behavior of ferroelectric thin films.<sup>18</sup> The two

TABLE I. Pyroelectric and dielectric properties of unpoled and poled PZT and PMZT with different film thickness. Dielectric constant  $\epsilon_f$  was deduced by extrapolating the thickness to zero in Eq. (1).

Sample	Unpoled PZT			Poled PZT			Unpoled PMZT			Poled PMZT		
Thickness (nm)	300	500	700	300	500	700	140	300	700	140	300	700
$\epsilon$	327	378	405	313	340	372	320	325	325	257	252	255
$\tan \delta$	0.026	0.02	0.025	0.023	0.018	0.016	0.023	0.01	0.01	0.013	0.008	0.006
$\frac{p}{\text{C K}^{-1} \text{m}^{-2}}$						$2.11 \times 10^{-4}$						$3.52 \times 10^{-4}$
$F_D$ (Pa <sup>-0.5</sup> )						$1.07 \times 10^{-5}$						$3.85 \times 10^{-5}$
33 Hz												
$\epsilon_f$		526			476			322			256	

basic models are summed up here. First, internal fields due to space charge segregation at both electrode interfaces can reduce the 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, oxygen vacancies may be transported toward the electrode interface to set up a space charge layer that has the same characteristic as a Schottky barrier. Assuming there is a thin interfacial layer between Pt and the ferroelectric film in the PZT and PMZT thin films under investigation, the equivalent circuit consists of two capacitors in series. A simple model can be constructed with this thin interfacial layer of thickness  $\delta$  and dielectric constant  $\epsilon_b$ , and with the rest of the film, dielectric constant  $\epsilon_f$ . If the measured dielectric constant is  $\epsilon$  and the total film thickness is  $d$  then we can write:

$$d/\epsilon = d/\epsilon_f + d(\epsilon_f - \epsilon_b)\epsilon_b\epsilon_f. \tag{1}$$

Hence we can use  $\epsilon$  vs  $d$  data to determine  $\epsilon_f$ . Table I lists the values of dielectric constant ( $\epsilon$ ) and loss ( $\tan \delta$ ) of the PZT and PMZT thin films with different thickness. The apparent  $\epsilon$  of PZT was found to increase with the thickness of the film, while it remained constant for the PMZT film. From an extrapolation of graphs of  $d/\epsilon$  vs  $d$  to  $d=0$  a dielectric constant  $\epsilon_f$  can be determined. The obtained  $\epsilon_f$  values of the unpoled and poled PZT and PMZT thin films are also shown in Table I. It was found that the experimentally obtained values of dielectric constant  $\epsilon$  of Pt/PZT/Pt capacitors at 33 Hz are significantly lower than  $\epsilon_f$ , indicating that the assumption of an interfacial layer is reasonable. However, the experimentally obtained values of dielectric constant  $\epsilon$  of Pt/PMZT/Pt capacitors at 33 Hz are similar to  $\epsilon_f$ . This indicates that in the Pt/PMZT/Pt capacitors, this interfacial layer is too thin for the present experiments to detect. It has also been noted that the apparent dielectric constant ( $\epsilon$ ) of a 300 nm PZT thin film decreases after the fatigue test ( $10^{10}$  cycles) from 327 to 210, indicating a thickening of the interfacial barrier, while the dielectric constant does not change for a similar PMZT thin film after the fatigue test. This indicates that after the cycles, no interfacial layer has formed in the PMZT thin films.

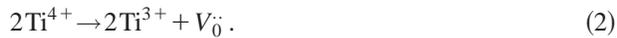
The second mechanism envisions the pinning of the domain walls by electronic carriers or, more likely, by oxygen vacancies. If defects such as oxygen vacancies segregate to the domain wall, they reduce the domain wall movement,

resulting in eventual pinning and degradation of switching ability. Unlike the first mechanism, this pinning effect is a “bulk” mechanism in the film and is not limited to the electrode interface. The fact that we observe good evidence for an interfacial barrier layer in PZT and not in PMZT, which are very similar systems apart from the Mn doping, strongly suggests that the barrier mechanism is responsible for the fatigue in the PZT films, and its absence explains the low fatigue in PMZT.

There are several possible reasons for the low fatigue behavior in PMZT thin films: first, according to the quantitative model proposed by Arlt and coworkers for Ni-doped BaTiO<sub>3</sub> ceramics, the acceptor ions and the compensating oxygen vacancy are most likely allocated at the same lattice cell and act as a defect dipole.<sup>19,20</sup> These defect dipoles align in the direction of the external field. The strong voltage offset and fatigue resistance in PMZT compared with PZT indicates that the defect dipoles formed in PMZT thin films are alignable but less mobile. It is quite well known in perovskite oxides such as barium titanate that some dopants in the position of Ti<sup>4+</sup> can bind oxygen vacancies through dipolar interaction.<sup>21</sup> It is possible that a similar mechanism operates here, leading to deeper potential wells for oxygen vacancies in the units containing substitutional Mn. Hence it is expected that the effective drift mobility of oxygen vacancies would reduce with the increase in the probability of encounter with Mn-modified unit cells during its transport. The migration of oxygen vacancies to the interface is probably the rate limiting process in the growth of the interfacial layer responsible for fatigue. Second, domain locking, due to the trapping of the injected and/or created carriers, 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.<sup>22</sup> PMZT has a higher coercive field ( $E_c$ ) than PZT. Hence if the same switching electric field (330 kV/cm) is applied to both, this field will be smaller (relative to  $E_c$ ) for PMZT than PZT. This could result in less fatigue in PMZT thin films. However, if this were the sole mechanism responsible for the very low fatigue in PMZT films, then it is unlikely that we would observe the differences in apparent barrier layer thickness. Third, it is believed that a flow of electric current, in particular, electrons, is necessary for fatigue.<sup>23,24</sup> Under this theory, electrical fatigue in PZT

thin films is predominantly due to electronic suppression of the polarization, and not from the migration and subsequent trapping of charged ionic defects such as oxygen vacancies.<sup>1,25,26</sup> dc resistivity measurements of PZT and PMZT thin films show that the small amount ( $\leq 1$  mol %) of Mn doping in PZT thin films increases the resistivity (PZT:  $4.3 \times 10^{10} \Omega \text{ m}$ ; PMZT:  $3.15 \times 10^{11} \Omega \text{ m}$ ), probably through the reduction of the carrier density in the PZT films. This reduction may be contributing to a reduced fatigue in PMZT. It has been found that doping acceptor ions, such as Mn, in (Ba,Sr)TiO<sub>3</sub> thin films also significantly reduces the leakage current.<sup>27</sup>

It seems plausible that electrons facilitate fatigue by enhancing the mobility of oxygen vacancies. It would accelerate the development of either the space-charge layer next to the electrode or the pinning effect on the domain wall. Du *et al.*<sup>17</sup> have proposed that the formation of oxygen vacancies is probably facilitated by the conversion of Ti<sup>4+</sup> to Ti<sup>3+</sup> in the following reaction:



The role of electrons in facilitating fatigue is via deionization of  $V_{\text{O}}^{\cdot\cdot}$ :



The lower valence of  $V_{\text{O}}^{\cdot}$  makes it easier to migrate by reducing the electrostatic disturbance around it. Such an enhanced mobility of  $V_{\text{O}}^{\cdot}$  makes it a more potent defect for the purposes of segregation. In the PMZT thin films, it has been proved by electron paramagnetic resonance (EPR) that there is a coexistence of Mn<sup>2+</sup> and Mn<sup>4+</sup> ions in the PMZT thin films.<sup>28</sup> We suggest that during repeated switching, the following reaction reduces the formation of oxygen vacancies induced by the conversion of Ti<sup>4+</sup> to Ti<sup>3+</sup> in the thin films under investigation through the reaction:



Combining reactions (2) and (4), we obtain a total reaction (5):



Reaction (4) actually helps to consume oxygen vacancies and may reduce the possibilities of their segregation at the electrode interfaces, or of the pinning of the domain walls during the repeated electrical cycles. Although a 3% reduction of switchable polarization for PMZT thin films after  $10^{10}$  cycles has been observed, it was found that repoling the PMZT thin films could rejuvenate this small amount of electrical fatigue. This indicates that if this small amount of fatigue is due to domain boundary pinning, the domain boundaries are weakly pinned in PMZT.

The retention tests for poled [V(-)] Pt/PZT/Pt and Pt/PMZT/Pt were carried out with a negative write pulse ( $-330$  kV/cm) and negative pulse ( $-330$  k/cm V) read 1<sup>#</sup>, and positive pulse ( $+330$  kV/cm) read 2<sup>#</sup> over a range of time period 1–30 000 s. The nonswitched polarizations and the switched polarizations of both capacitors showed good linearity in the range of 1–30 000 s. The retention tests have also been performed using the write voltage of  $+330$  kV/cm

and a read voltage  $+330$  and  $-330$  kV/cm as a function of retention time and similar retention properties were obtained. No polarization decay was found within the time range of 1–30 000 s for both PZT and PMZT. The normalized retaining polarizations of both capacitors were estimated by comparing these values with  $2P_r$ . This was 50% for PZT and 95% for PMZT. This indicates that there was a significant polarization decay in the Pt/PZT/Pt capacitor within 1 s. This phenomenon was widely observed<sup>29–31</sup> for PZT thin films. A significant improvement of the retained polarization for Mn-doped PZT was obtained over a retention time of 30 000 s.

Table I also shows the values of the pyroelectric coefficient and  $F_D$  for 700 nm thick films of PZT and PMZT. These figures are  $2.11 \times 10^{-4} \text{ C K}^{-1} \text{ m}^{-2}/1.07 \times 10^{-5} \text{ Pa}^{-0.5}$  and  $3.52 \times 10^{-4} \text{ C K}^{-1} \text{ m}^{-2}/3.85 \times 10^{-5} \text{ Pa}^{-0.5}$  for PZT and PMZT, respectively. The  $F_D$  for PMZT is the largest reported for any PZT-based thin film materials.<sup>9</sup> The increase in  $p$  for PMZT relative to PZT may be explained as a consequence of thermally induced changes in the defect dipole structure postulated for PMZT and outlined above. Certainly, the increase in  $p$  of ca. 72% in going from PZT to PMZT cannot be explained by the 20% increase in  $P_r$  [see Fig. 1(a)] or any change in Curie temperature, as the doping level is too low to engender any significant difference in  $T_c$ . However, a thermally induced rotation of the defect dipoles is entirely plausible—indeed to be expected. Interestingly, the pyroelectric current measurements indicate that this is no reduction in  $p$  on repeated thermal cycling in the 20–40 °C range. This implies that if the increased  $p$  is due to thermally induced rotation of the defect dipole, then the rotation is reversible, probably due to the internal electric field due to  $P_r$ .

The  $3.5 \times$  increase in  $F_D$  in going from PZT to PMZT is remarkable and only partly due to the increase in  $p$ . We also see a significant reduction in both  $\epsilon$  and  $\tan \delta$  at 33 Hz. The reduction in  $\epsilon$  is due to a reduction in the low frequency polarizability in PMZT. This may be because once the oxygen vacancies are “locked” into defect dipole pairs, they are much more immobile than in PZT. Furthermore, the effect of poling PMZT is to significantly “square-up” the hysteresis loop, further reducing the low field polarizability and hence the permittivity. This “squaring” of the loop on poling is probably due to the defect dipole pairs being locked into position by poling—an effect which is completely absent in the PZT films.

Finally, the reduction in  $\tan \delta$  in PMZT may well be due to the absence of the barrier layer that is present in PZT. Such an oxygen-vacancy rich layer would be expected to be a relatively lossy dielectric and would increase the overall loss of the PZT capacitors. Hence the mechanisms postulated for the improvement in the fatigue and retention characteristics of PMZT relative to PZT can also account for the improvements in pyroelectric characteristics.

## IV. CONCLUSIONS

This study has shown the asymmetric hysteresis loops in poled Mn-doped PZT thin films. This is due to the existence

of defect dipoles (oxygen-vacancy-acceptor-ions associates). Because, unlike the case of PZT, there is not an interfacial layer observed between Pt electrode and the PMZT films, we propose that the defect dipoles in PMZT thin films are immobile although they align in the direction of external field. Hence significant improvement in PZT fatigue and retention characteristics are obtained when Mn atoms are doped into PZT thin films. Cycling the Mn-doped PZT thin films up to  $10^{10}$  switching bipolar pulses under 330 kV/cm found only a 3% reduction of switchable polarization. Repoling the cycled thin film can rejuvenate this switchable polarization. The other reasons that lead to low fatigue 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)  $Mn^{2+}$  ions consume the oxygen vacancies generated during repeated switching, forming  $Mn^{4+}$  ions in PZT thin films. This further reduces the possibilities of oxygen vacancy segregation at both electrodes or the pinning of domain walls.
- (3) A relatively weak domain pinning situation exists in Mn-doped PZT films, which makes the domain unpinning easier.

These factors can also account for the dramatic improvement in the pyroelectric properties of PMZT relative to PZT.

The good hysteretic fatigue characteristics and excellent pyroelectric properties of the Mn-doped PZT thin films make them promising candidates as device materials for both memory and pyroelectric applications.

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