

PAPER REFERENCE: I-V.3

**LOW FATIGUE LEAD ZIRCONATE TITANATE-BASED CAPACITORS
MODIFIED BY MANGANESE FOR NONVOLATILE MEMORIES**

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Abstract

We have investigated the effects of Mn doping on the ferroelectric properties of $\text{Pb}(\text{Zr}_{0.3}\text{Ti}_{0.7})\text{O}_3$ (PZT) thin films on substrates Pt/Ti/SiO₂/Si. Small amount of Mn-doped (≤ 1 mol%) PZT (PMZT) showed almost no hysteretic fatigue up to 10^{10} 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^{2+} ions consume the oxygen vacancies generated during repeated switching, forming Mn^{4+} ions. These mechanisms are probably responsible for their low observed fatigue characteristics.

Keywords: PZT, Thin films, Sol-gel, Ferroelectric properties

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1. Introduction

One of the most important concerns for the ferroelectric random access memory (FERAM) is fatigue [1]. Technologically viable solutions for this problem are now at hand. For example, the use of metal oxide electrodes, replacing Pt, can reduce fatigue [2]. However, they are electrically leaky and make the process more complicated and expensive [3]. One feasible approach for reducing fatigue-related problems is donor doping (e.g. La^{3+}) without replacing the commonly used Pt electrodes with metal oxide electrodes. According to the defect dipole model, which is well known for titanate ceramics [4-5], the introduction of aliovalent dopant ions distorts the electroneutrality condition. Therefore, higher-valence foreign cations (donors), such as La^{3+} for A site modification or Nb^{5+} for B site modification, are compensated by negatively charged defects, such as Pb vacancies. Lower-valence foreign cations (acceptors), such as Li^+ for A site modification or Fe^{3+} , Mn^{3+} , Ni^{2+} 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 [6].

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 and dielectric properties.

2. Experimental procedure

All the PZT and PMZT thin films used in this study were prepared on Pt(100nm)/Ti(5nm)/SiO₂(450nm)/Si substrates using a sol gel-based process described previously [7-8]. The Pt was highly (111) orientated. The films were annealed at 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 polarisation field hysteresis and dielectric measurement methods [7-8]. The polarization fatigue tests were performed using a square wave electric field of 330 kV/cm at 60kHz. The test pulse sequence used for retention measurement was as follows: at first, a triangular pulse of -10V 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 -10V (read#1) and +10V (read#2). The pulse width for all triangular pulses is 0.5ms. The time delay between the write pulse and the first read pulse is called the retention time.

3. RESULTS AND DISCUSSION

Ferroelectric fatigue is the loss of switchable polarization with repeated polarization reversal. Fig. 1 shows the normalized polarization of a series of PZT thin

films with or without Mn doping as a function of polarization switching cycles, where P^* and P^\wedge represent respectively the switching polarization between two opposite polarity pulses and non-switching polarization between two identical polarization pulses. The values of $P^* - P^\wedge$ denote the switchable polarization. For the Pt/PZT/Pt capacitor (fig. 1a), the switchable polarisation decreases after 10^7 cycles, reducing by about 50% at 10^{10} cycles. This type of fatigue is well known for PZT [9]. For the Pt/PMZT/Pt capacitor, a 10% decrease of switchable polarisation was observed at Mn (0.2mol%) doped film after 5×10^9 cycles as shown in Fig. 1b; a 2-3% decrease of switchable polarisation was observed at Mn (0.5-1mol%) doped films after 10^{10} cycles as shown in Fig.1 c-d. With further increases in the Mn doping level, the film started to exhibit fatigue, as shown in Fig. 1e-f. A 50% decrease of switchable polarisation was observed at Mn (2-4mol%) doped films as in the case of the capacitor of PZT. The P-E loops of the PMZT (1mol%) thin film before and after the fatigue test are shown in fig. 2. There is no obvious reduction of switchable polarization at 10^{10} cycles. This indicates that small amounts of Mn doping can greatly improve the fatigue behaviour 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.

There is considerable debate regarding the mechanisms that cause fatigue in PZT thin films with Pt electrodes [10]. 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 [11]. The two 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 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 δ and dielectric constant ϵ_b , and with the rest of the film, dielectric constant ϵ_f . If the measured dielectric constant is ϵ and the total film thickness is d then we can write:

$$d/\epsilon = d/\epsilon_f + \delta(\epsilon_f - \epsilon_b)/\epsilon_b\epsilon_f \quad (1)$$

Hence, we can use ϵ vs d data to determine ϵ_f . Table 1 lists the values of dielectric constant (ϵ) of the PZT and PMZT (Mn 1mol%) thin films with different thickness. The apparent ϵ 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/ϵ vs d to $d = 0$ a dielectric constant ϵ_f can be determined. The obtained ϵ_f values of the unpoled and poled PZT and PMZT thin films are also shown in Table 1. It was found that the experimentally-obtained values of dielectric constant ϵ of Pt/PZT/Pt capacitors at 33Hz are significantly lower than ϵ_f , indicating that the assumption of an interfacial layer is reasonable. However, the experimentally-obtained values of dielectric constant ϵ of Pt/PMZT/Pt capacitors at 33Hz are similar to ϵ_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 (ϵ) of a 300nm 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 with Mn = 1 mol%.

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 (Mn = 1 mol%).

There are several possible reasons for the low fatigue behavior in small amount of Mn doped PZT thin films: firstly, according to the quantitative model proposed by Arlt and co-workers for Ni-doped BaTiO₃ ceramics, the acceptor ions and the compensating oxygen vacancy are most likely allocated at the same lattice cell and act as a defect dipole [12-13]. These defect dipoles align in the direction of external field. The strong fatigue resistance in PMZT compared with PZT indicates that the defect dipoles formed in PMZT thin films are less mobile. It is quite well known in perovskite oxides such as barium titanate that some dopants in the position of Ti⁴⁺ can bind oxygen vacancies through dipolar interaction [14]. 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. However, when further increasing the doping level above 1 mol%, the concentration of oxygen vacancies also increases, which helps speeding up the migration of oxygen vacancies to the interface and leads to rapid fatigue, 10^6 cycles and 10^4 cycles for the samples with 2mol% Mn and 4mol% Mn, respectively.

Secondly, it is believed that a flow of electric current, in particular, electrons, is necessary for fatigue [15-16]. 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 [17-19]. DC resistivity measurements of PZT and PMZT thin films show that the small amount (≤ 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)TiO₃ thin films also significantly reduces the leakage current [20].

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 [10] have proposed that the formation of oxygen vacancies is probably facilitated by the conversion of Ti⁴⁺ to Ti³⁺ in the following reaction:



The role of electrons in facilitating fatigue is via de-ionization of $V_0^{\cdot\cdot}$:



The lower valence of V_0^{\cdot} makes it easier to migrate by reducing the electrostatic disturbance around it. Such an enhanced mobility of V_0^{\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 co-existence of Mn^{2+} and Mn^{4+} ions in the PMZT thin films [21]. We suggest that during repeated switching, the following reaction reduces the formation of oxygen vacancies induced by the conversion of Ti^{4+} to Ti^{3+} in the thin films under investigation through the reaction:



Combining reaction (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 re-poling 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 (Mn 1mol%) were carried out with a negative write pulse (-330 kV/cm) and negative pulse (-330k/cmV) read 1[#], positive pulse (+330kV/cm) read 2[#] over a range of time period 1-30000s. The nonswitched polarizations and the switched polarisations of both capacitors showed good

linearity in the range of 1-30000s. The retention tests have also been performed using the write voltage of +330kV/cm and a read voltage +330kV/cm and -330kV/cm as a function of retention time and similar retention properties were obtained. No polarisation decay was found within the time range of 1-30000s for both PZT and PMZT. The normalized retaining polarisations 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 Pt/PZT/Pt capacitor within 1s. This phenomenon was widely observed [22-24] for PZT thin films. A significant improvement of the retained polarisation for Mn-doped PZT was obtained over a retention time of 30000s.

4. CONCLUSIONS

This study has shown that an interfacial layer between Pt electrode and the PZT films has formed, leading to a rapid fatigue effect, but this layer was not found between Pt and PMZT (Mn=1 mol%). We propose that the defect dipoles formed in such PMZT thin films are immobile. Hence, significant improvement in PZT fatigue and retention characteristics are obtained when small amounts of Mn atoms are doped into PZT thin films. Cycling the PZT thin films doped with Mn (0.5-1 mol%) up to 10^{10} switching bipolar pulses under 330 kV/cm found only a 2-3% reduction of switchable polarization. The other reasons that lead to low fatigue effect in such PMZT thin films, include that 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.

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

ACKNOWLEDGEMENTS

The financial support of EPSRC under grant GR/N06113 and GR/R92448 is gratefully acknowledged.

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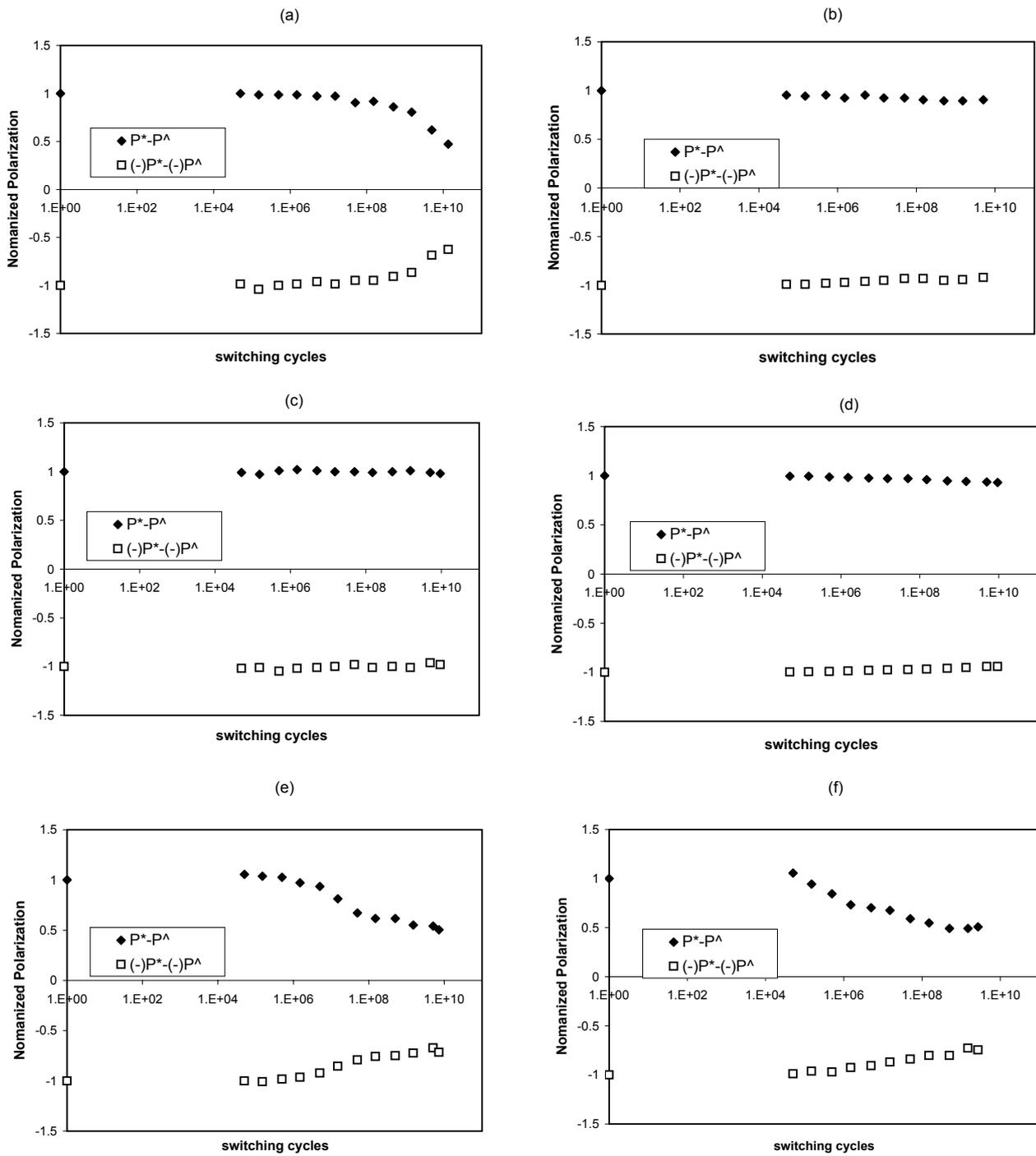
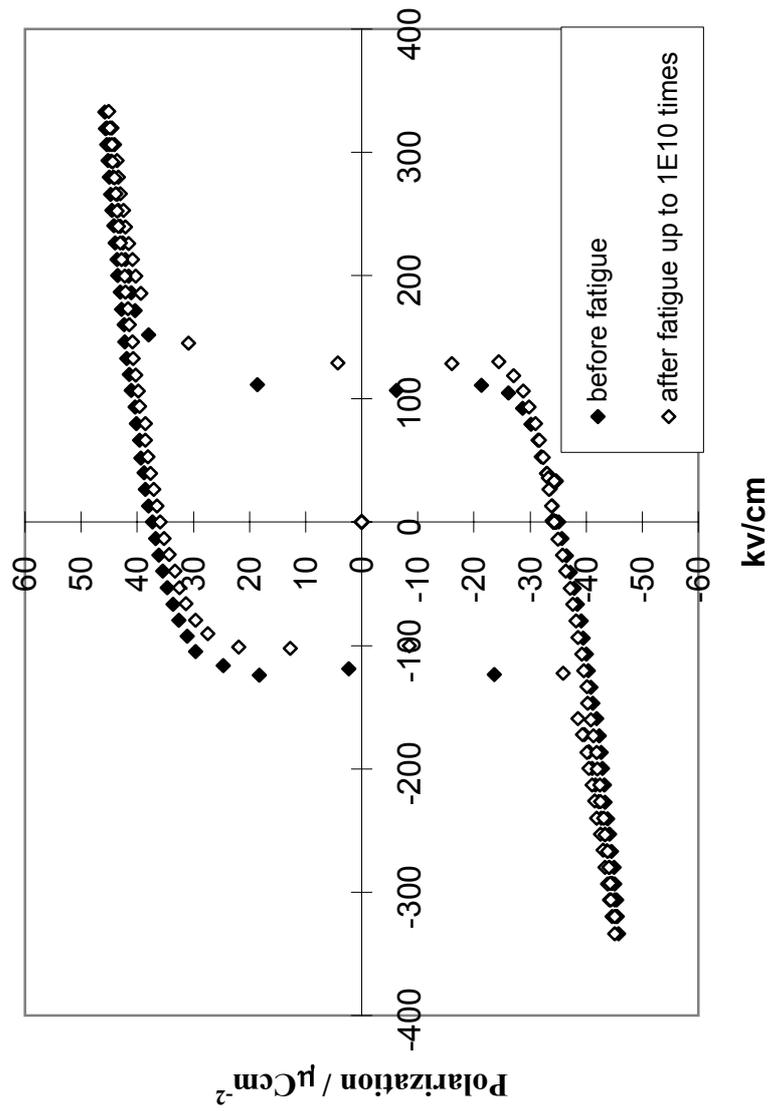


Fig. 1 Zhang & Whatmore



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Figure 2 Zhang & Whatmore

Figure Captions:

Figure 1: Fatigue tests on Mn-doped PZT thin films. Mn level (a) 0 mol% (b) 0.2% (c) 0.5 mol%; (d) 1 mol%; (e) 2 mol%; (f) 4 mol%. P^* and P^\wedge represent the switching polarisation between two opposite polarity pulses and non-switching polarisation between the two same polarisation pulses, respectively. The values of P^*-P^\wedge denote the switchable polarisation.

Figure 2: Hysteresis loops of a PMZT thin film capacitor before and after fatigue test with a bipolar pulse switching up to 10^{10} cycles.

Table 1: Dielectric properties of unpoled and poled PZT and PMZT (Mn 1 mol%) with different film thickness. Dielectric constant ϵ_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
ϵ	327	378	405	313	340	372	320	325	325	257	252	255
ϵ_f	526			476			322			256		

Table 1 Zhang & Whatmore

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