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Effect of donor and acceptor dopants on fatigue properties in PZT thin films

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Abstract

Fatigue properties of $Pb(Zr_{0.52}Ti_{0.48})O_3$ or PZT thin films on platinized silicon substrates were investigated. Small amounts of WO_3 and CuO nano-particles were added into PZT films, which showed the results of soft and hard doping characteristics, respectively. The additions also affected the fatigue properties of PZT by showing almost no hysteresis fatigue up to 10^8 switching bipolar pulse cycles, while the fatigue of PZT started at 10^6 cycles. The results suggest that the soft and hard doping could reduce the fatigue of PZT films and the oxygen vacancies play an important role in polarization degradation of the films.

Keywords: C. Fatigue; PZT thin film; Doping

1. Introduction

Polarization fatigue in a ferroelectric material is defined as a systematic loss of the switchable polarization under a repetitive bipolar cycling [1] and it is the main limitation for applications of ferroelectric devices such as memories, electro-optical devices and actuators. One of the most widely investigated ferroelectrics for memories is PZT thin film. However, the PZT thin films coated on a metal electrode generally have fatigue problem. There are several possible mechanisms for fatigue in thin films and the most obvious candidate for fatigue mechanism is oxygen vacancy, which is the only ionic species that is mobile within the crystal lattice at ambient temperature and that it can be pinned at the domain walls or make the space charge segregation at electrode/film interfaces during repeated switching. Numerous studies have been performed to reduce the fatigue behaviors. One common approach for fatigue reduction is to use metal oxide electrodes as substitute for Pt electrodes. However, this method causes electrical leakages and makes the process more complicated and expensive [2]. The other popular approach is by doping aliovalent ions, which distort the electroneutrality condition. Higher-valence foreign cations (donors) are compensated by negatively charged defects such as Pb vacancies while lower-valence foreign cations (acceptors) create the positive charged defects, such as oxygen vacancies to maintain the overall electroneutrality. Hence, acceptor doping normally leads to an increase in the oxygen vacancy concentration [3]. Although many studies have investigated the effect of doping on fatigue in thin films or bulk materials, the results are contradictory [1]. For donor doping, it was reported that La showed better fatigue resistance in PZT thin films, but for Nb doping it was found to be independent of fatigue endurance [4]. While acceptor doping such as Mn, Sc, Na, Mg, Fe and Al were reported to have positive effects on the fatigue resistance of PZT thin films. Contradictory results in donor and acceptor remain confusing. Thus, this study was carried out to investigate the effect of donor and acceptor doping on electrical properties, especially fatigue behavior of PZT. Soft PZT and hard PZT thin films were prepared by adding WO_3 and CuO,

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respectively. Previous work found that an addition of WO_3 into PZT ceramics showed donor doping effect and improved mechanical and electrical properties [5], while an addition of CuO which is known as a sintering aid in some electroceramic materials, showed acceptor doping behavior. The addition of CuO in some piezoelectric materials could improve dielectric and piezoelectric properties [6]. However, similar results have not yet been reported in thin-film embodiments.

2. Experimental

A preparation for PZT/WO_3 and PZT/CuO films was initiated with PZT solution to reach a nominal stoichiometric composition of $Pb(Zr_{0.52}Ti_{0.48})O_3$ [7]. For a preparation of PZT/WO_3 and PZT/CuO suspended solutions, percentages by weight (0, 01, 0.2, 0.3, 0.4, 0.5 and 1) of WO_3 and CuO were ultrasonically dispersed in 2-methoxyethanol, respectively, for 30 min before mixing with PZT precursor solution. The hybrid PZT/WO_3 and PZT/CuO solutions were deposited on (111) preferred orientation platinized silicon substrates (Pt/Ti/SiO_2/Si) by a spin-coating method at 3000 rpm for 30 s [7]. The coated substrates were then pre-heated on a hot-plate at 400 °C for 30 min. After the first layer of PZT/WO_3 or PZT/CuO, a layer of PZT solution (without WO_3 or CuO) was subsequently deposited. The pure PZT precursor solution can infiltrate into pores (or defects) in the composite film to increase the film density. Lastly, the composite film was heated again at 400 °C for 30 min with a final heat treatment carried out on a hot-plate at 600 °C for 30 min.

Ferroelectric properties of the films were measured with a HP 4192 A LCR meter and a Radiant Technology RT66B. Polarization fatigue tests were performed using a triangular pulsed electric field of 500 kV/cm at 1 kHz.

3. Results and discussion

The values of remanent polarization (P_r), maximum polarization (P_{max}) and coercive field (E_c) are shown in Table 1. In the PZT/WO_3 system, it was found the polarization values gradually decreased with WO_3 concentration up to 0.5 wt%. However, with further increase in WO_3 to 1 wt%, the P_r increased. While, in the PZT/CuO system, the polarization tend to reduce when the CuO concentration was increased. The CuO at 0.2 wt% showed the maximum polarization value compared to the other compositions as shown in Table 1 and was therefore the most acceptable composition for ferroelectric properties. In addition, the coercive field (E_c) decreased with an increase in WO_3 concentration and showed the soft doping behavior in the PZT/WO_3 system. In PZT/CuO systems, E_c increased with increasing CuO concentration and hysteresis loop showed a hard doping behavior. The PZT/CuO system increased oxygen vacancies which could pin domain walls and reduce the wall movement. This required higher electric field for the domain wall motion, resulting in the hard doping behavior. But in PZT/WO_3 system, the oxygen vacancies were reduced, and the used electric field in the films with less oxygen vacancies was less than that in the films with more oxygen vacancies, resulting in a reduction of E_c in this system. The variations of oxygen vacancies are described later.

Since polarization of ferroelectric thin films decayed under continuous bipolar cycling, the approach to fatigue problem through investigations of fatigue behavior of donor and acceptor doped PZT thin films was interesting. From the ferroelectric properties of PZT/WO_3 and PZT/CuO thin films, PZT/1 wt%WO_3 and PZT/0.2 wt%CuO thin films were found to be the best representative for donor and acceptor doping compared to other conditions in this study. Therefore, this study used these two conditions to investigate the effect of donor and acceptor doping on fatigue properties in PZT thin films. Ferroelectric fatigue is a loss of switchable polarization (P_{sw}) [8] with repeated polarization reversal. Fig. 1(a–c) shows the fatigue behavior of PZT, donor-doped PZT and acceptor-doped PZT thin films, respectively, as a function of polarization switching cycles. For the PZT films, P_{sw} decreased after 10^6 cycles and reduced by about 17% at 10^8 cycles. For the PZT/WO_3, a reduction of P_{sw} after 10^7 cycles with 5% decrease of switchable polarization was observed at 10^8 cycles as shown in Fig. 2. The switchable polarization of PZT/CuO decreased after 10^5 cycles and reduced by about 14% at 10^8 cycles. There are two basic models regarding the mechanisms for fatigue behavior of

Table 1
Ferroelectric properties of PZT/$x$$WO_3$ and PZT/xCuO films.

x (wt%)	PZT/xWO_3			PZT/xCuO		
	P_{max} (μC/cm^2)	P_r (μC/cm^2)	E_c (kV/cm)	P_{max} (μC/cm^2)	P_r (μC/cm^2)	E_c (kV/cm)
0	33.86	17.63	175	33.86	17.63	175
0.1	32.74	17.22	169	26.14	13.69	220
0.2	31.33	16.39	138	30.71	15.68	217
0.3	31.29	15.31	126	26.18	13.24	221
0.4	27.47	13.03	139	24.94	14.57	227
0.5	24.94	12.12	130	24.73	14.36	209
1	34.53	17.39	122	21.91	10.79	207

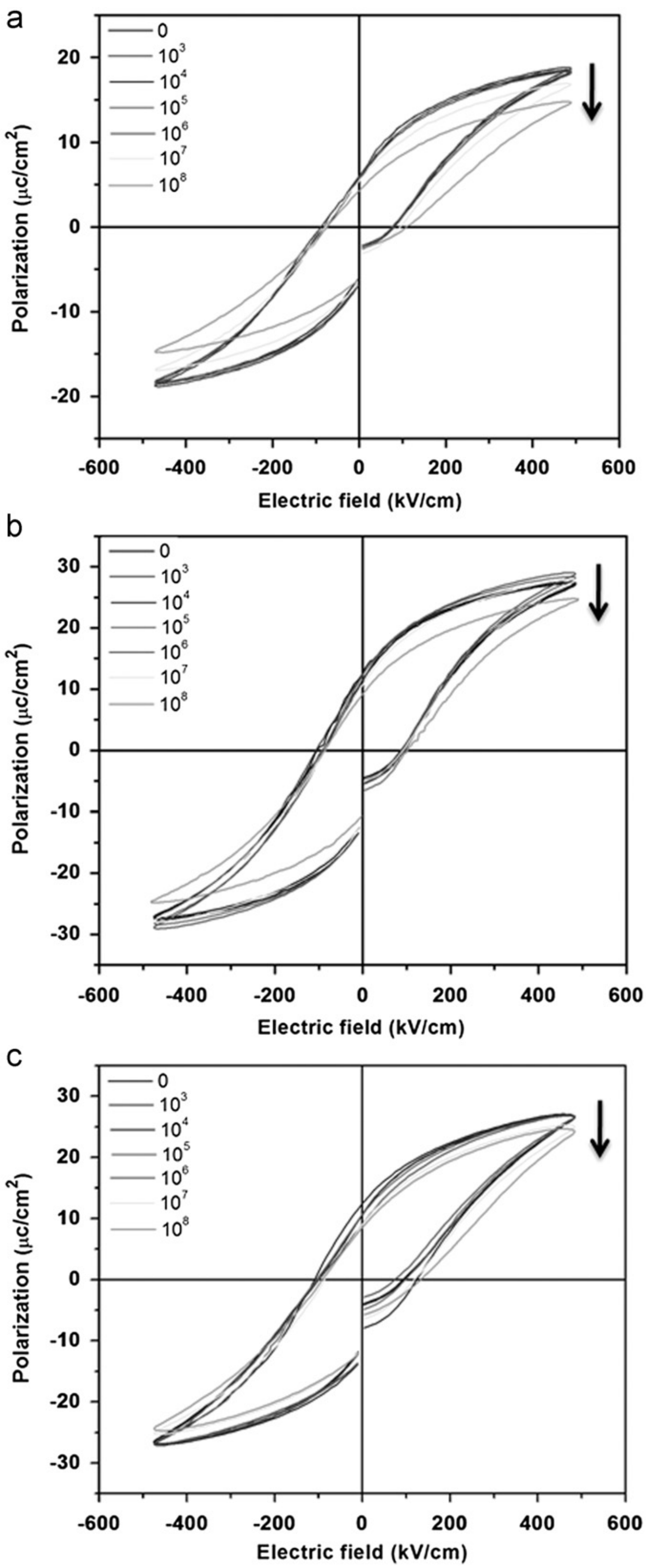

Fig. 1. Hysteresis loops of (a) PZT, (b) PZT/1 wt% WO_3 and (c) PZT/0.2 wt%CuO films plotted at different bipolar fatigue cycles under 500 kV/cm at 1 kHz.

ferroelectric films [3]. The first mechanism is to create the internal fields by space charge segregation at both electrode interfaces during repeated switching. Oxygen vacancies were transported toward the electrode interface to set up a space charge layer that could reduce the electric field in the ferroelectric measurement, resulting in the polarization reduction and showing fatigue behavior. The second mechanism is the pinning of domain walls by defects, such as electronic carriers or oxygen vacancies. These defects were segregated from the domain walls and then reduced their movement, which resulted in the degradation of switching ability. The lack of accurate chemical control in Pb-based system during heat treatment process could cause PbO loss and result in the formation of lead and oxygen vacancies as shown in Eq. (1). This is one of the causes which activate the fatigue behavior in PZT thin films.

$$Pb_{Pb}+O_o \rightarrow PbO+V''_{Pb}+V_{\ddot{o}} \quad (1)$$

In PZT/WO_3 (donor-dope PZT) thin films, donor charges were compensated by electrons or cation vacancies such as Pb, Zr or Ti vacancies. In the PZT/WO_3 system, the B-site substitution of W^{6+} for Ti^{4+} resulted in a reduction of oxygen vacancies [5] by the following equation.

$$WO_3+V\ddot{o} \rightarrow W^{\cdot\cdot}_{Ti}+3O_o \quad (2)$$

Reaction (2) actually helped consume oxygen vacancies. It was expected that donor-doped materials had an ability to reduce the fatigue phenomenon due to their low concentration of oxygen vacancies. In this study, it was found to reduce the fatigue by 5% of switchable polarization up to 10^8 switching bipolar pulses compared to 17% reduction of P_{sw} found in PZT films at 10^8 cycles. When considering the PZT/CuO (acceptor-doped PZT) thin films, the switchable polarization increased at 10^4 cycles and then reduced about 8% at 10^6 cycles and 14% at 10^8 cycles as shown in Fig. 2.

An increase in switchable polarization at 10^4 cycles was possibly due to the as-deposited polycrystalline films which generated a random orientation. This led to a reduction in

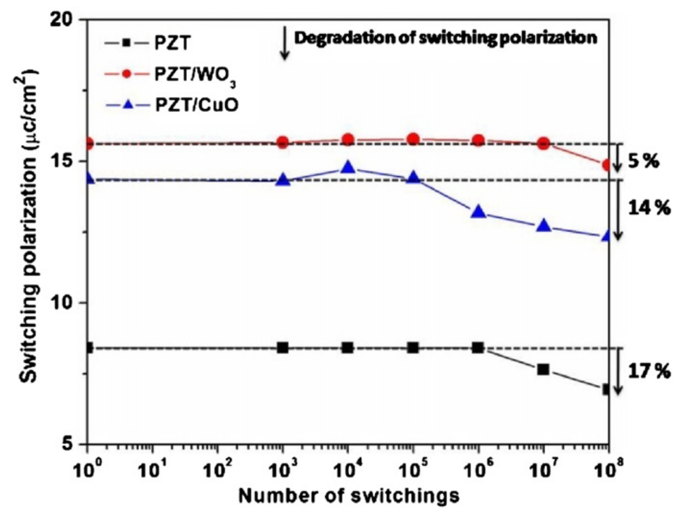

Fig. 2. Switchable polarization of PZT, PZT/1 wt% WO_3 and PZT/CuO thin films plotted as a function of the number of bipolar fatigue cycles.

the maximum possible total polarization. Moreover, acceptor doping introduced oxygen vacancies which segregated to the domain walls and reduced their motion. When the films were subject to electric field, oxygen vacancies were transported toward electrode interface. This helped ease the movement of domain wall and thus increased the polarization. However, this mechanism had to compete with the segregation of oxygen vacancies at the electrode which reduced the polarization. Nevertheless, the reduction of switchable polarization appeared earlier than that in PZT films. A possible mechanism for this phenomenon is that Cu^{2+} occupied the B-site (Ti^{4+} and Zr^{4+}) in PZT [9] and the charge difference was compensated by oxygen vacancies as shown in Eq. (3).

$$CuO \rightarrow Cu_{Zr,Ti} + O_o + V_{\ddot{o}} \tag{3}$$

Including the oxygen vacancies from PbO loss at high temperature as described in Eq. 1, the combination of oxygen vacancies from PbO loss and acceptor doping defined an approximation to bulk charge neutrality as shown in Eq. 4. These were responsible for a reduction of switchable polarization in PZT/CuO thin films. However, 14% reduction of switchable polarization at 10^8 cycles was less than 17% found at 10^8 cycles in PZT thin films. It was demonstrated that a hard PZT was more stable under a continuous cyclical drive compared to pure PZT due to their inherent polarization pinning effect and good electrical strength [10].

$$[V_{\ddot{o}}] \approx \left[V''_{Pb}\right] + \left[Cu''_{Zr,Ti}\right] \tag{4}$$

4. Conclusion

Fatigue behaviors of soft PZT (PZT/WO_3) and hard PZT (PZT/CuO) thin films were investigated. The soft PZT thin films showed a significant improvement in polarization fatigue compared to undoped PZT and hard PZT thin films. The improved fatigue behavior was also observed in the hard PZT but the magnitude was smaller than that found in soft PZT. The results showed that oxygen vacancies play an important role in polarization degradation. However, a good electrical strength of hard PZT reduced the fatigue in this compound.

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