CHAPTER 7

RESULTS AND DISCUSSION - PART 4:

EFFECTS OF DONOR AND ACCEPTOR DOPANTS ON FATIGUE PROPERTIES IN PZT THIN FILMS

7.1 Introduction

Polarization fatigue in a ferroelectric material is defined as a systematic loss of switchable polarization under repetitive bipolar cycling [14], 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, PZT thin films coated on a metal electrode generally have a fatigue problem. There are several possible mechanisms for fatigue in the films. The most obvious candidate for fatigue mechanism is an oxygen vacancy, the only ionic species that is mobile in the lattice at ambient temperature and that can pin at the domain walls or make the space charge segregation at electrode interface during repeated switching. Numerous studies have been carried out in an attempt to reduce fatigue. One common approach for fatigue reduction is a use of metal oxide electrodes which substitute for Pt electrodes. However, this method still causes electrical leakage and makes the process more complicated and expensive [34]. The other popular approach is a use of doping aliovalent ions which distort the electroneutrality condition. In order to maintain the overall electroneutrality, higher-valence foreign cations (donors) are compensated by negatively charged defects such as Pb vacancies while lower-valence foreign cations (acceptors) create positive charged defects such as oxygen vacancies. Hence, acceptor doping normally leads to an increase in oxygen vacancy concentration [35]. Although many studies have investigated the effects of doping on fatigue in thin films, the results are contradictory [14]. For donor doping, it was reported that La showed better fatigue resistance in PZT thin films, while Nb doped PZT film was found to be independent of fatigue endurance [36]. The other acceptor dopants such as Mn, Sc, Na, Mg, Fe and Al were reported to have positive effects on fatigue resistance of the PZT thin films. These contradictory results in donor and acceptor doing remain bewildering. This study was carried out to investigate the effects of donor and acceptor doping on electrical properties, especially fatigue behaviour of the PZT films. Donor-doped PZT or soft PZT and acceptor-doped PZT or hard PZT thin films were prepared by adding WO_3 and CuO, respectively. Previous work found that the addition of WO_3 into PZT ceramics showed donor doping effect and improved mechanical and electrical properties [37] while the addition of CuO, as a sintering aid in some electroceramic materials, showed acceptor doping behaviour. The addition of CuO in some piezoelectric materials could also improve dielectric and piezoelectric properties [166]. However, similar results have not yet been reported for thin-film embodiments.

In this work, 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 nanoparticles were added into PZT films. Then, the effects of dopants on of fatigue properties were investigated and discussed.

7.2 Investigation of ferroelectric properties of PZT/WO_3 and PZT/CuO thin films

The values of remanent polarization (P_r), maximum polarization (P_{max}) and coercive field (E_c) of the composite films are given in Table 7.1. In the PZT/$x$$WO_3$ system, where x = 0, 0.1, 0.2, 0.3, 0.4, 0.5 and 1 wt%, it was found that the polarization values gradually decreased with the increase of WO_3 concentration up to 0.5 wt%. However, with further increase to 1 wt%, the P_r increased. In the PZT/xCuO system, where x = 0, 0.1, 0.2, 0.3, 0.4, 0.5 and 1 wt%, the polarization tended to reduce when the CuO concentration increased. The CuO at 0.2 wt% showed the maximum polarization value compared to the other compositions as shown in Table 7.1 In this study, therefore, the PZT/1wt% WO_3 and PZT/0.2wt% CuO films were the most preferable composition for ferroelectric properties. In addition, the coercive field (E_c) decreased with the increase of WO_3 concentration and showed the soft doping behavior in the PZT/WO_3 system (Fig. 7.1(a)). In PZT/CuO systems, E_c increased with the increase of CuO concentration, and hysteresis loop showed a hard doping behavior (Fig. 7.1(b)). The increased of oxygen vacancies in the PZT/CuO films which could pin domain walls and reduce the wall movement. This required a higher electric field for the domain wall motion, resulting in the observed hard doping behavior. Nevertheless, in the PZT/WO_3 system, the oxygen vacancies were reduced due to the charge compensated in the system, and the 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.

Table 7.1 Ferroelectric properties of PZT/xWO$_3$ 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

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 investigation of ferroelectric properties the PZT/1wt% WO$_3$ and PZT/0.2wt% CuO thin films were found to be the best representatives for donor and acceptor doping compared to the other compositions. Therefore, this work employed these two representatives to further investigate the effects of donor and acceptor doping on fatigue properties in PZT thin films.

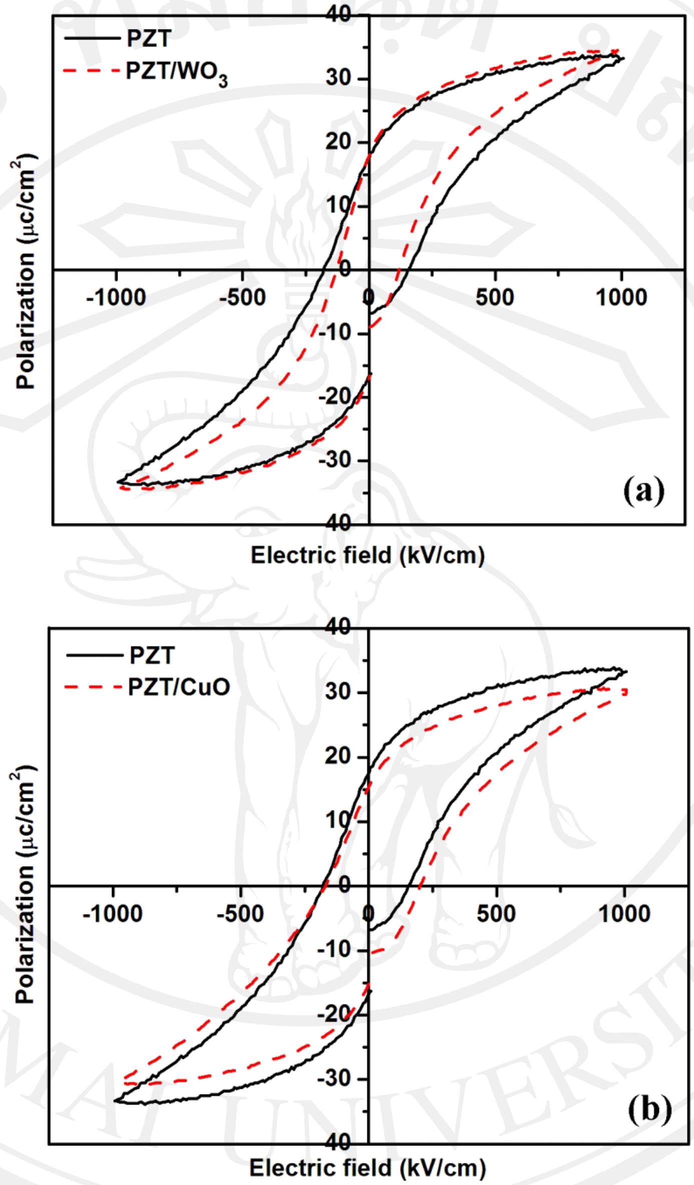

Figure 7.1 *P-E* hysteresis loops of (a) PZT donor doping and (b) PZT acceptor doping.

7.3 Fatigue behavior in donor doping and acceptor doping PZT thin films

Ferroelectric fatigue is a loss of switchable polarization (P_{sw}) [151] with repeated polarization reversal. Figure 7.2(a-c) shows the fatigue behavior of PZT, donor-doped or soft PZT (PZT/WO_3) and acceptor-doped or hard PZT (PZT/CuO) thin films, respectively. The polarization was plotted as a function of polarization switching cycles. For the PZT films, a P_{sw} decreased after 10^6 cycles and reduced by ~ 17% at 10^8 cycles. For the PZT/WO_3 film, a P_{sw} was maintained until 10^7 switching cycles. A 5% decrease of switchable polarization was observed at 10^8 cycles (Fig. 7.3). A P_{sw} of PZT/CuO film was found to decrease after 10^5 cycles and reduced by 14% at 10^8 cycles. It has been suggested that there are two basic models regarding the mechanisms for fatigue behavior of ferroelectric films [14, 35]. The first mechanism is the growth of a low-dielectric constant interface layer which becomes the internal fields created by space charge segregation at both electrode interfaces during repeated switching. This is called a dead/blocking layer model [14]. Since the interface layer grows, the field seen by the ferroelectric materials decreases and becomes insufficient to switch the domains. This lead to a suppressed polarization with cycling number [33, 101], and it was believed to be because oxygen vacancies are transported toward the electrode interface to set up a space charge layer as a consequence of cycling. Those reduced electric field in ferroelectric measurement, resulting in polarization reduction and fatigue behavior [35]. The second mechanism is the pinning of domain walls by defects. There are at least two types of defects: one is electronic charge carriers and the other is ionic defects such as oxygen vacancies [14]. This is called a domain-wall pinning model.

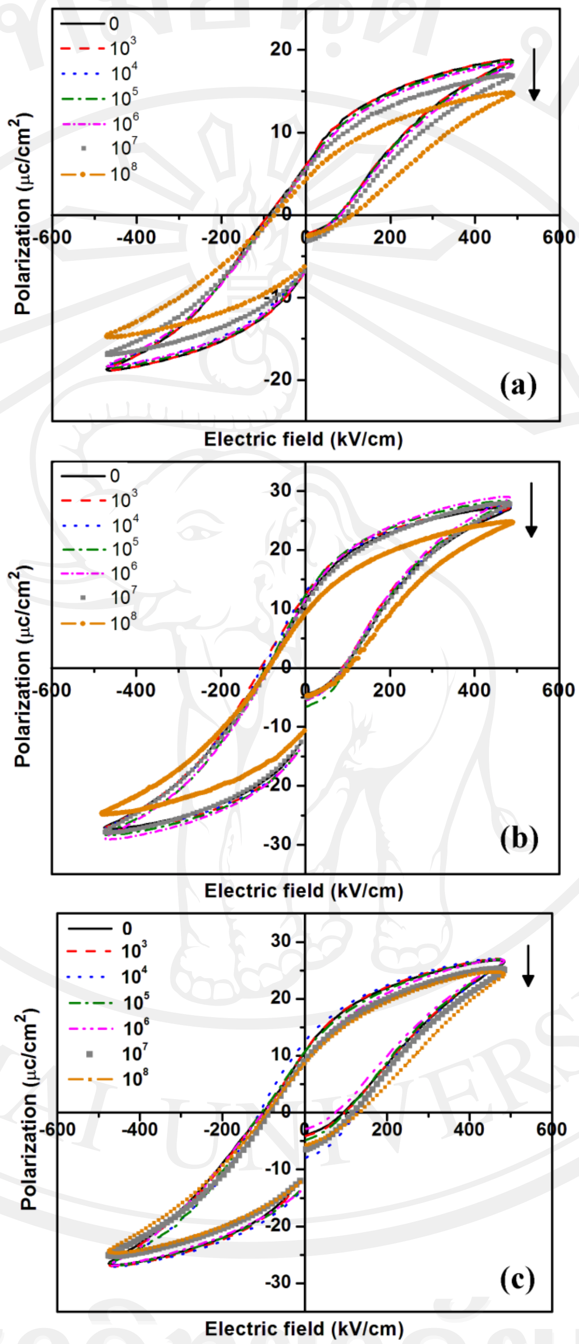

Figure 7.2 Hysteresis loops of (a) PZT, (b) PZT/1wt%WO_3 and (c) PZT/0.2 wt% CuO films plotted at different bipolar fatigue cycles under 500 kV/cm at 1 kHz.

Those defects can be trapped at electrode interfaces, grain boundaries and/or domain boundaries due to their lower potential energies at those sites [167, 168]. Since defects are segregated to the domain walls and then hinder their movement, the switching ability degrades [35]. The lack of accurate chemical control in Pb-based system during heat treatment process could cause PbO loss, resulting in the formation of lead and oxygen vacancies as shown in equation (7.1).

This was one of the causes activating the fatigue behavior in PZT thin films.

$$Pb_{Pb^x} + O_{(g)} \rightarrow PbO + V_{Pb}^{''} + V_{o}^{\cdot\cdot} \tag{7.1}$$

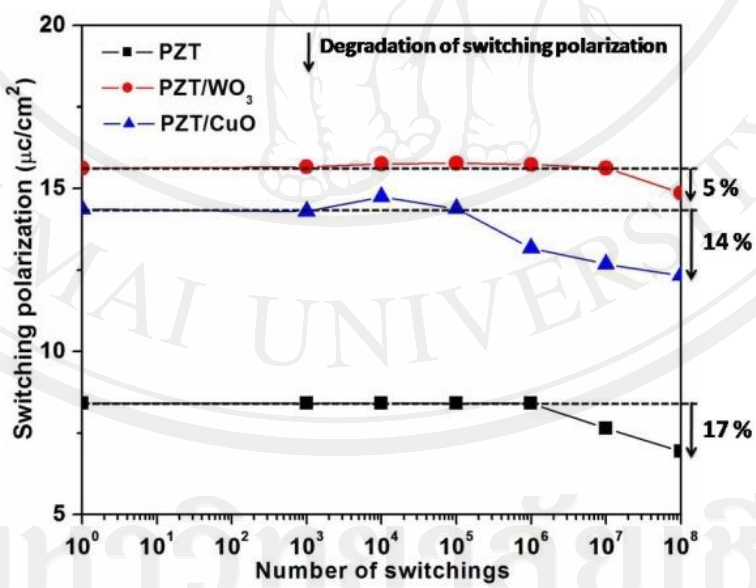

Figure 7.3 Switchable polarizations of PZT, PZTWO$_3$ and PZT/CuO thin films plotted as a function of the number of bipolar fatigue cycles.

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 charge compensated by the reduction of oxygen vacancies [31], expressed in equation (7.2).

$$WO_3 + V\ddot{o} \rightarrow W_{\ddot{Ti}} + 3O_{(g)} \tag{7.2}$$

Reaction (7.2) 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 (P_{sw}) up to 10^8 switching bipolar pulses compared to 17% reduction of P_{sw} found in PZT films at 10^8 cycles (Fig 7.3). However, the P_{sw} showed a very slight concave at 10^3 to 10^7 cycles, which could be due to the space charge polarization from the cation vacancies. Donor doping PZT reduced the oxygen vacancies and can concurrently create cation vacancies such as $V_{Pb''}$ and $V_{Zr/Ti''''}$ as shown in equation (7.3) and equation (7.4), respectively. When electric fields were applied, the cation vacancies could be transported toward the electrode direction and form a space charge region which increased the polarization of PZT/WO_3 system. In addition, while the cation vacancies were transported toward electrode interface by electric field, this helped ease the movement of domain wall and, thus, increased the polarization. However, the cation vacancies transportation by electric field was not as easy as oxygen vacancies transportation because the size of oxygen vacancies was bigger, and the movement of the vacancies was due to the substitution of ions in the system. Therefore, the substitution ions could easily be moved to the bigger vacancies [169]. Thus, cation vacancies may less affect polarization and coercive field compared to oxygen vacancies (described in the following section).

$$WO_3 \rightarrow W_{\ddot{Z}r,Ti} + V_{Pb}'' + 3O_{(g)} \tag{7.3}$$

$$2WO_3 \rightarrow 2W_{\ddot{Z}r,Ti} + V_{Zr/Ti}'''' + 6O_{(g)} \tag{7.4}$$

When the PZT/CuO (acceptor-doped PZT) thin films are considered, 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. 7.3. The increase in switchable polarization at 10^4 cycles was possibly due to as-deposited polycrystalline films which generated a random orientation. This led to a reduction in the maximum possible total polarization. Moreover, acceptor doping introduced oxygen vacancies which were 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 in PZT/CuO appeared earlier than that in the PZT films. A possible mechanism for this phenomenon was that the Cu^{2+}

occupied the B-site (Ti^{4+} and Zr^{4+}) in PZT [157], and the charge difference was compensated by oxygen vacancies as shown in equation (7.5).

$$CuO \rightarrow Cu''_{Zr,Ti} + O_o{}^x + V_o^{\cdot\cdot} \tag{7.5}$$

Including the oxygen vacancies from PbO loss at high temperature as described in equation 7.1, the combination of oxygen vacancies from PbO loss and acceptor doping defined an approximation to bulk charge neutrality as shown in equation (7.6). These were responsible for the 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 the PZT thin films. It was demonstrated that the 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 [165].

$$[V_o^{\cdot\cdot}] \approx [V''_{Pb}] + [Cu''_{Zr,Ti}] \tag{7.6}$$

7.4 Conclusions

Fatigue behaviors of donor-doped or soft PZT (PZT/WO_3) and acceptor-doped or hard PZT (PZT/CuO) thin films were investigated. From the ferroelectric properties of PZT/$x$$WO_3$ and PZT/xCuO films, where x = 0, 0.1, 0.2, 0.3, 0.4, 0.5 and 1 wt%, PZT/1wt% WO_3 and PZT/0.2wt% CuO thin films were found to be the best representatives for donor and acceptor doped films due to their highest polarizations. The PZT/WO_3 thin film showed a soft property with a reduction of coercive filed. But for PZT/CuO thin films, a hard property with an increase of coercive filed was observed. Therefore, these films were chosen to investigate the effects of donor and acceptor doping on fatigue properties compared to the pure PZT film. The soft PZT film showed a significant improvement in polarization fatigue compared to undoped PZT and hard PZT films. The improved fatigue behavior was also observed in the hard PZT, although the magnitude was smaller than that found in the soft PZT. The results showed that the oxygen vacancies played an important role in polarization degradation. However, a high mechanical quality factor (Q_m) of the hard PZT was found to reduce fatigue in this film.