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Fatigue characteristics of $Pb(Zr,Ti)O_3$ capacitors on donor doping

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Abstract Fatigue characteristics of ferroelectric $Pb(Zr,Ti)O_3$ (PZT) based capacitors through donor doping is reported in this paper. La substitution up to 10% were carried out to study systematically the fatigue behaviors of epitaxial ferroelectric capacitors grown on Si using $(Ti_{0.9}Al_{0.1})N$/Pt conducting barrier composite. Ferroelectric capacitors substituted with 10% La show sufficient low voltage switched polarization and fatigue free performance. Systematic decrease in the tetragonality of the ferroelectric phase (i.e., c/a ratio) results in the corresponding reduction in coercive voltage, sufficient remnant polarization at 1.5-3V, and good fatigue property.

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Key words: cooling rate, ferroelectric, fatigue, domain, donor

1. Introduction

There is currently considerable research and development effort aimed at developing nonvolatile ferroelectric random access memories (FeRAM) using the intrinsic remnant polarization available in ferroelectric materials. Two types of materials, namely the lead zirconate titanate perovskite system (PZT family) and the layered perovskite based on strontium bismuth tantalate (SBT) are being explored.[1] Specifically in the case of the lead based perovskite, the problem of fatigue has been resolved using conducting oxide contact electrodes.[2),3)] However, the characteristics of fatigue has not been understood completely yet. Simple Pt electrode structures without additional oxide electrode are preferable for commercial ferroelectric memories due to several advantages such as low cost and simple integration. Therefore, the basic understandings of the fatigue properties for ferroelectric capacitor films are indispensable for developing the simple electrode systems without fatigue. In this paper, results of experiments aimed at addressing this understanding of fatigue properties, using La substituted PZT (PLZT) up to 10% as ferroelectric thin layers, are reported.

2. Experimental Details

The heteroepitaxial thin films of the whole stack (LSCO/PZT/LSCO) using conducting barriers ($(Ti_{1-x}Al_x)N$ composites) on Si (100) as shown in Fig. 1 were in-situ grown by pulsed laser deposition (PLD). In this technique, ~20 ns pulse width excimer laser (248 nm) beam with an energy density of 2 J/cm^2 was used in the oxygen ambient of 100 mTorr at elevated temperatures (600° to 650°C). Temperatures were controlled by a programmable circuit board. Temperature ramp up rate was 20°C/min. and cooling rate was 5°C/min. Epitaxial $(Ti_{0.9}Al_{0.1})N$ films with 600Å thickness were fabricated on hydrogen-terminated (100) Si using a target of the same composittion. $(Ti_{1-x}Al_x)N$ barriers have recently attracted attention due to their better oxidation resistance and stability at elevated temperature.[4),5)] The PLZT layer thickness

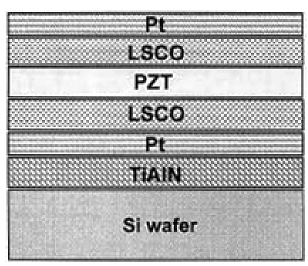

Fig. 1. Schemes showing stack structure for ferroelectric capacitor using $(Ti_{0.9}Al_{0.1})N$ diffusion barrier on Si wafer.

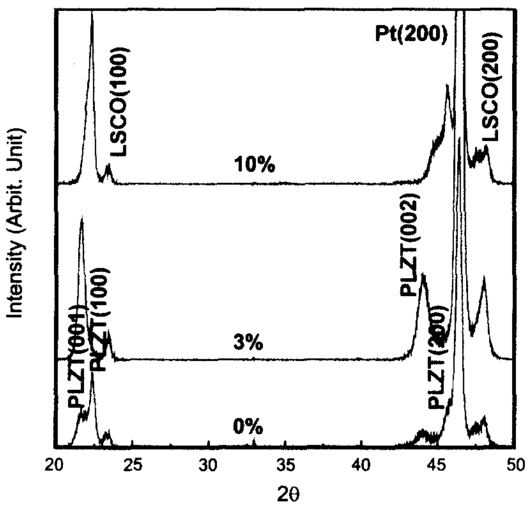

Fig. 2. X-ray θ-2θ diffraction patterns of 0%, 3%, 10% PLZT films on (100) Si / $(Ti_{0.9}Al_{0.1})N$ / Pt / $La_{0.5}Sr_{0.5}CoO_3$.

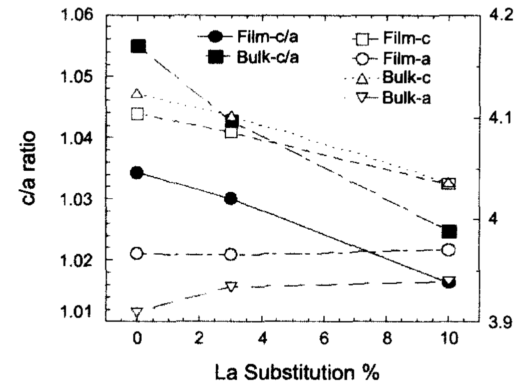

Fig. 3. A-axis and c-axis lattice constant and c/a ratio, from X-ray diffraction θ-2θ scan measurement, for both PLZT films and bulk ceramics as a function of La substitution %.

was 1500Å and the top and bottom LSCO layers were each 700Å. Electrical measurements were carried out using a Radiant technologies RT66A tester.

3. Results and Discussion

The crystalline quality and phase purity of the ferroelectric stack in both wafers was confirmed to be pure perovskite with a high degree of [100] orientation by x-ray diffraction studies shown in Fig. 2. One systematic change with La substitution is the c-axis lattice parameter and the c/a ratio. As the La content into PZT(the ratio of Zr/Ti is 20/80) capacitors increases, the c-axis parameter of bulk decreases, and the a-axis parameter of bulk increases, as shown in Fig. 3. Comparing films to bulk, c-axis parameters of films are slightly smaller, but a-axis parameters are larger, and the difference between a-axis parameters is in the range of 0.05-0.1Å. These a-axis and c-axis parameter differences can be caused by the tensile stress in the plane of PZT films resulted from the thermal expansion mismatch during cooling.[6)] The decrease of c-axis parameter in films is also observed as increasing La content.

Hysteresis loops and resistivity for 10%, 3% and 0% La substituted films are shown in Fig. 4(a) and (b), respectively. When increasing La content from 3% to 10%, the resistivity increases the order of one or two magnitudes. This result is consistent with the previous report on bulk PZT ceramics, and the improved resistivity is primarily arising from reduction of oxygen vacancies positively double-charged with increasing La contents.[7)] Polarization of 10% La substituted samples is only slightly changed in the applied voltage range of 1.5-3V, but 3% and 0% samples show rapid decrease of pulsed polarization with decreasing applied voltage. This different behavior can be explained by the different domain structures.[8)] The hysteresis loops of tweed-like domains in La substituted PZT have a lower coercive field and a slightly lower remnant polarization, similar to those of the 10%-PLZT films with 180° domains, than those of normal micron-sized ferroelectric domains (90° domains). Consequently, the lower coercive voltage and slightly lower remnant polarization can be observed in 10%-PLZT film with 180° domains, compared to 0% and 3%-PLZT films with 90°

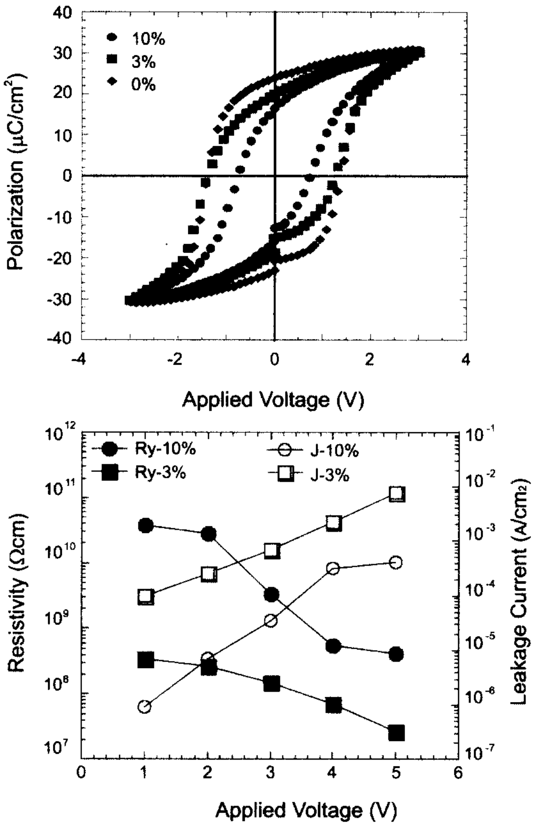

Fig. 4. a) Hysteresis loops for 10%, 3% and 0%-PLZT capacitors, measured at applied voltage of 3V. b) Resistivity and leakage current density for epitaxial $La_{0.5}Sr_{0.5}CoO_3$/PLZT/$La_{0.5}Sr_{0.5}CoO_3$ capacitor using Pt/$(Ti_{0.9}Al_{0.1})N$ conducting barriers on Si (100).

domains. Therefore, the smaller distortion (lower c/a ratio) in 10%-PLZT films leads to lower coercive voltages resulting from smaller depolarizing field.

La additions in the Pb sites in PZT films reduce the concentration of oxygen vacancies. The reduction in oxygen vacancies can diminish the voltage shifts due to the reduced defect-dipole (e.g., lead vacancy-oxygen vacancy) component of polarization.[9] The effects of this reduction in oxygen vacancies and in coercive voltage reflect in fatigue characteristics of FE capacitors. Fatigue tests were carried out at the V_{max} of 3V and 5V, which is typically 3-4 times the coercive voltage. Fig. 5 shows results of a fatigue test at ±3V

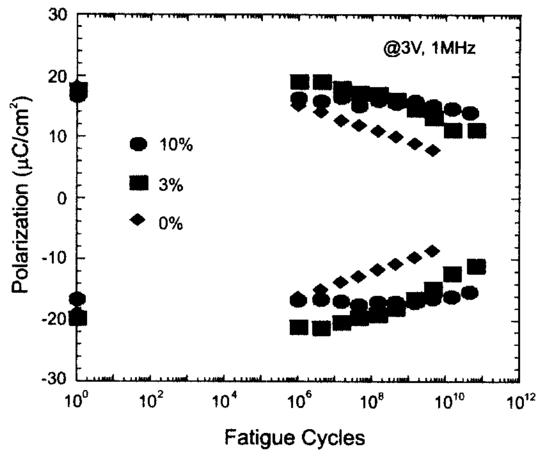

Fig. 5. The polarization, ΔP (P*, switched - P^, nonswitched), for epitaxial $La_{0.5}Sr_{0.5}CoO_3$/PLZT (10%, 3% and 0% La substitution) / $La_{0.5}Sr_{0.5}CoO_3$ capacitors using $(Ti_{0.9}Al_{0.1})N$/Pt on Si (100) as a function of fatigue cycles tested at 3 V and 1 MHz.

and 1 MHz for 10%, 3%, and 0%-PLZT capacitors. There is very little degradation of the remanent polarization for 10% PLZT samples after 10^{11} cycles. On the other hand, 0% and 3% PLZT samples show some fatigue loss after about 10^6 and 10^9 cycles, respectively, at ±3V and 1MHz. These results are consistent with earlier reports, which have been outlined in the beneficial effects of donor substitutions, such as Nb^{+5} in the Ti^{+4} site and La^{+3} in the Pb^{+2} site.[10]

However, it has not been well understood why La substitution improves fatigue in PZT. There have been several reports for fatigue mechanisms, which suggest that fatigue loss is due to pinning of domain walls, and fatigue loss is equivalent to the optically suppressed polarization.[11] Thus, these results indicate that pinning of domains by charge trapping at internal domain boundaries is a primary fatigue mechanism. In contrast to the fatigue behavior, it has been shown that PZT films with metallic oxides, such as LSCO, RuO_2, and IrO_2, can exhibit essentially fatigue-free behavior.[12),13] Recently, FE $SrBi_2Ta_2O_9$ (SBT) films with Pt electrodes have also shown fatigue-free behavior even though they underwent higher processing temperature (700°-800°C), compared to PZT processing temperature (550°–650°C). However, the illumination experiments for these samples also induced fatigue behavior during the electrical fatigue testing. These samples after this experiment showed the full restoration of the loss of polarization by applying a dc saturation bias with light or by electric field cycling without light. These results indicate that SBT with Pt and PZT with metal oxide electrodes are also susceptible to domain pinning by charge trapping. Thus, it is concluded that normal fatigue testing (without uv illumination) with these systems does not show fatigue behavior because the domain pinning rate is lower than the domain unpinning rate.

The improvement of fatigue behavior with increasing La content in PZT can be understood by the low Vö content in PZT capacitors. The sources of intrinsic oxygen vacancies in PZT are primarily from the loss of the volatile component PbO: [14)]

$$Pb_{Pb} + O_O \leftrightarrow PbO + V''_{Pb} + Vö$$

It is well known that La substitution in PZT results in the reduction of Vö. A donor impurity has a larger positive charge than the ion it replaces in the lattice. Thus, the oxide of a donor impurity (La_2O_3) contains more oxygen per cation than does the binary host oxide (PbO) it replaces. This excess oxygen can be used to reduce the concentration of oxygen vacancies:

$$2(Pb^{2+}{}_{Pb^{2+}})^x + La_2O_3 + Vö \longrightarrow 2(La^{3+}{}_{Pb^{2+}}) + (O^{2-}{}_{O^{2-}})^x + 2PbO$$

This reduction is supported by resistivity measurements as shown in Fig. 4 (b). PZT capacitors with 10% La content show at least one order of magnitude higher resistivity over 3%-PLZT films. When increasing La content up to 10% in PZT, negligible Vö accumulation at interfaces consequent of the reduction of intrinsic Vö results in almost the same unpinning rate as pinning rate at domain walls. The previous experimental study for donor impurity in bulk PZT ceramic is consistent with the results of this work.[10)]

Partial switching of domains in conjuction with the electron charge injection from Vö accumulation at interfaces during fatigue process results in the higher fatigue rate in the 0% and 3% La samples. Dimos et.al.,[13)] have shown that the largest suppression of switched polarization occurs when the capacitor is at a switching threshold (i.e., there is a high density of domain that is partly switched), leading to an environment that can lead to significant trapping of electronic defects at the polarization discontinuities between domains. As discussed previously, 10%-PLZT capacitors, well saturated at 3V, showed the coercive voltage in the order of 0.7V. However, 0%- and 3%-PLZT capacitors with the order of 1.3V were not fully saturated at 3V. These samples with low La content showed twin boundaries along with high strain in the capacitors from TEM studies.[15)] These defects in capacitors significantly contribute to the partial switching due to domain wall pinning at especially low applied voltages. Thus, this partial switching results in randomly oriented polarization domains during the fatigue cycles, and the pinning of these domains, by charge trapping at internal domain boundaries which is accelerated by charge injection from Vö accumulation at interfaces, significantly contributes to fatigue loss.

4. Summary

The minimal fatigue loss in 10%-PLZT capacitors arises from at least the same unpinning rate as the pinning rate of domains. The improvement results from both the reduction of the Vö concentration and the tetragonality, c/a ratio, resulting in low strain in the capacitor, which is consequent of the La substitution into PZT capacitors. In terms of the nucleation and growth process of ferroelctric domains, it is expected that 10%-PLZT films have higher nucleation rate due to the decreased displacement of Ti ion, and faster growth rate resulted from the tweed-like domain structures. Thus, tweed-like domains and the decreased displacement in c-domain results in sufficient remnant polarization at 1.5-3V, and no fatigue loss.

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