Fatigue-free La-modified Pb(Zr,Ti)O₃ capacitors using a seed layer

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The development of lead zirconate titanate (PZT)-based capacitors using common Pt electrodes has been a long-time goal of ferroelectric random access memories (FRAM). In this work, a series of $Pb_{1-x}La_x(Zr_{0.55}Ti_{0.45})O_3$ capacitors (for $0.01 \le x \le 0.05$) having fatigue-free characteristics have been grown on Pt/Ti/SiO₂/Si substrates. Typically 2–3 mol% La-modified PZT capacitors fabricated at 580 °C by applying a PZT seed layer exhibited fatigue-free behavior up to 6.5×10^{10} switching cycles, a low coercive field of 50–55 kV/cm, and a stable charge retention profile with time, all of which assure their suitability for the future nonvolatile FRAM.

There is a great need to find suitable capacitors to meet the present trend in nonvolatile ferroelectric random access memories (FRAM) toward lower operating voltages.^{1,2} In this challenging search to find suitable materials, once again, we consider lead zirconate titanate (PZT)-based perovskites as potential candidates for FRAM¹⁻⁴ and microelectromechanical systems⁵ applications because of their high P_r values, easy switching characteristics, and dramatic domain refinement up to a nanometer size, in addition to relatively low processing temperatures and low costs. However, some serious problems related to the reliability must be overcome before the practical implementations. These difficulties are mainly arising from the poor fatigue resistance of PZT after a certain number of switching cycles.

To solve the problems associated with the electrical fatigue without using electrically leaky and expensive oxide electrodes,^{6–9} in this study we have focused on the intrinsic oxygen vacancies, which are known to play a key role in the ferroelectric degradation of capacitors in conjugation with film/electrode interface and domain mobility.^{10,11} The concentration of oxygen vacancies can be substantially reduced by the Pb-site vacancies (V_{Pb} ") under the condition of donor-doping. This can be predicted by considering the following intrinsic defect reaction in Pb-based perovskites: PbO = V_{Pb} " + V_{O} " with $K_{int} = [V_{Pb}"][V_{O}"]$. However, K_{int} increases rapidly with temperature. Therefore, one should reduce the processing temperature to suppress the formation of oxygen vacancies even under the donor-doping typically using

lanthanum (La). The concentrations of oxygen vacancies that are primarily responsible for the electrical fatigue can further be reduced by annealing La-modified PZT films in an oxygen-rich atmosphere. Therefore, one of the efficient ways of suppressing the formation of oxygen vacancies could be low-temperature processing in an oxygen-rich atmosphere. However, the processing temperature of La-doped PZT (PLZT) is known to be substantially higher (\geq 700 °C) than that of undoped PZT film (\leq 600 °C).¹²

In view of these requirements, one of the feasible approaches is to insert a suitable thin seed layer between the PLZT film and the electrode.^{13,14} It is well established that the PZT-based perovskite phase is evolved from the pyrochlore phase by nucleation and grain growth.¹⁵ The nucleation is strongly dependent upon the underlying layer. Therefore, a low-temperature processing can be achieved if the underlying seed layer provides favorable nucleation sites that tend to reduce the activation energy for perovskite crystallization. Thus, we have chosen PZT as a seed layer with an anticipation of its three important functions because of compositional and structural similarities between PZT and PLZT. They are (i) lowering the processing temperature by reducing the activation energy required for the nucleation/growth of the perovskite phase, (ii) maximizing the preferential growth of the PLZT film to a desired direction by suitably controlling the growth direction of this template PZT layer, and (iii) practically acting as a buffer layer between the PLZT film and the electrode.

The main purpose of this study is to demonstrate fatigue-free behavior of PZT-based capacitors with a series of different La contents. The composition of the ferroelectric layer can be summarized as $Pb_{1-x}La_x(Zr_{0.55}Ti_{0.45})O_3$

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with x between 0.01 and 0.05 (i.e., PLZT with 1 to 5 mol% of La). For the structural and compositional similarities between the seed layer and the active PLZT layer, we have employed the PZT layer having the composition of Pb($Zr_{0.55}Ti_{0.45}$)O₃ as a seed layer on (111) Pt/Ti/SiO₂/Si substrate.

The PZT and PLZT precursors were synthesized on the basis of the above chemical formulas using lead acetate trihydrate, zirconium propoxide, titanium isopropoxide, and lanthanum acetate hydrate in acetic acid solution. The prepared sols were diluted with alcohol and water to a concentration of 0.25 mol/l and used for the coating. The sols were spun coated at 4000 rpm for 20 s to form uniform gel films on (111) Pt/Ti/SiO₂/Si substrates. For the removal of organics, the deposited films were directly inserted into a furnace, preheated to a temperature of 500 to 650 °C for 0.5 h. The coating and firing process was repeated several times. Both the firing and annealing operations were performed in flowing oxygen ambient. The film thickness, as estimated by the cross-sectional field-emission scanning electron microscopy, was slightly less than 300 nm.

Figure 1 shows the XRD θ -2 θ scan results (M18XCE diffractometer, MAC Science) of the annealed PLZT films with and without the PZT seed layer. The PLZT films deposited on the PZT seed layer show a highly [111]-oriented preferential growth. If one takes the lattice match between the chosen PZT and PLZT compositions into consideration, the preferential growth along the [111] direction seems reasonable. The relative peak intensities, $I(111)/{I(111) + I(100)}$], of the seeded PLZT

Pt (111) (111)ntensity (a. u.) PLZT/PZT (100) mol% of La 5 4 3 2 1 PLZT 30 40 20 50 60 2θ (degree)

FIG. 1. XRD patterns of PLZT and PLZT/PZT films fabricated on Pt/Ti/SiO_2/Si substrates and annealed at 580 $^\circ C$ for 0.5 h.

films are all above 0.96, indicating a remarkably strong [111] orientation.¹⁶ Contrary to these, the PLZT film without the seed layer exhibited a random orientation with the presence of an amorphous phase. However, this amorphous phase gradually disappeared and the degree of [111] preferential orientation of the PLZT layer increased with the annealing temperature up to 640 °C. This suggests that the observed random orientation of the PLZT layer at 580 °C in the absence of the PZT seed layer is closely related to the higher phase-formation temperature of perovskite PLZT, as discussed previously (i.e., \leq 600 °C for PZT films versus \geq 700 °C for PLZT film).¹²

The room-temperature P-E hysteresis loops of PLZT/ PZT capacitors with a variety of the La contents are shown in Fig. 2. A typical area of the top Pt electrode was 10^{-4} cm², and measurements of ferroelectric properties were performed using a RT6000S ferroelectric tester. All of these capacitors fabricated on the bottom Pt electrode exhibited fatigue-free behavior up to, at least, 5×10^{10} switching cycles. As summarized in the inset, the remanent polarization $(2P_r)$ decreases gradually with increasing La content but the coercive field (E_c) first decreases for the La content up to 3 mol% and then increases slightly above this critical level. Considering the importance of fatigue-free capacitors with low operating voltages, we will hereafter focus on the PLZT/PZT capacitor having 3 mol% of La modification.

Figure 3 compares P-E hysteresis loops of the Pt/ PLZT/PZT/Pt capacitor at three different applied voltages. The capacitor is characterized by well-saturated P-E curves. The inset of Fig. 3 summarizes the variation of $2P_r$ and E_c with varying applied voltage. $2P_r$ of the



FIG. 2. Polarization hysteresis loops of PLZT/PZT capacitors measured at 25 °C. The inset shows variations of $2P_r$ and E_c with the La content at three different voltages.



capacitor was 30 μ C/cm² at an applied voltage of 5 V and increased to 48 μ C/cm² at 10 V. These values are substantially higher than those of the fatigue-free layered perovskites, SrBi₂Ta₂O₉ (SBT)¹⁷ and Bi_{3.25}La_{0.75}Ti₃O₁₂ (BLT),^{18,19} which range between 6 and 28 μ C/cm² at 10 V. The low coercive field of 50 kV/cm makes this capacitor especially desirable for the application to lowvoltage-driving devices.

Figure 4(a) shows the P-E hysteresis loops of the PLZT capacitor (3 mol% La) before and after the electrical fatigue test at a frequency of 1 MHz. As presented, the capacitor is characterized by a well-saturated P-Ecurve even after being subjected to 6.5×10^{10} switching cycles. The P-E curve taken after the fatigue test (filled circles) does not show any noticeable asymmetric behavior caused by imprinting failures. The fatigue-free characteristics of the PLZT capacitor (3 mol% La) are summarized in Fig. 4(b). The capacitor shows little change both in the switching polarization (P_{sw}) and in the nonswitching polarization ($P_{\rm ns}$) up to 6.5 × 10¹⁰ switching cycles. As shown in Fig. 4(b), the values of the nonvolatile charge [i.e., $(+P_{sw}) - (+P_{ns})$ or $(-P_{sw}) - (-P_{ns})$] are approximately $22 \,\mu\text{C/cm}^2$ and remain essentially constant throughout the switching cycles. Thus, the PLZT capacitor has a sufficient sensing margin for the identification of logical state throughout the read/write cycles. The fatigue-free behavior has also been observed for other switching voltages up to ± 10 V. The values of the nonvolatile charge at a lower frequency (e.g., at 1 KHz) were essentially the same as those measured at 1 MHz (approximately 22 μ C/cm²).



FIG. 3. Polarization hysteresis loops of the PLZT/PZT capacitor (3 mol% La) on a Pt/Ti/SiO₂/Si substrate at three different applied voltages.

The retention profile was fairly independent with time up to 10^4 s, as shown in Fig. 5. The normalized retaining charge of the PLZT capacitor was estimated by comparing these values with $2P_r$, and it was approximately 70%. Compared with the retention characteristics of the Pt/ PZT/Pt capacitor (approximately 45%),²⁰ this is a remarkable improvement. It is known that oxygen vacancy



FIG. 4. Results of the fatigue test at 1 MHz: (a) room-temperature P-E hysteresis loops of the Pt/PLZT/PZT/Pt/Ti/SiO₂/Si capacitor (3 mol% La) at an applied voltage of 5 V before and after being subjected to 6.5×10^{10} read/write switching cycles; (b) variation of $+P_{\rm sw}$, $+P_{\rm ns}$, $-P_{\rm sw}$, and $-P_{\rm ns}$ versus number of cycles at a switching voltage of ±5 V. The corresponding films were annealed at 580 °C for 0.5 h.



FIG. 5. Retention profile of the Pt/PLZT/PZT/Pt/Ti/SiO₂/Si capacitor (3 mol% La) measured at 25 °C.

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is one of the primary causes of the retention failure.²¹ Thus, the observed stable retention characteristics seem to be closely related to the reduced concentration of oxygen vacancies in the present PLZT capacitors. The leakage current density is another important parameter for device applications. It was as low as 5 nA/cm^2 at an applied field of 150 kV/cm (approximately 5 V).

We have reported innovative ferroelectric properties of the PLZT capacitors prepared using a PZT seed layer. The fatigue-free behavior and the stable retention profile, along with the low coercive field, observed in the PLZT capacitor (3 mol% La) potentially make it a promising capacitor for the future nonvolatile FRAM.

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REFERENCES

- 1. J.F. Scott and C.A. Araujo, Science 246, 1400 (1989).
- 2. O. Auciello, J.F. Scott, and R. Ramesh, Phys. Today **51**, 22 (1998).
- 3. G.H. Haertling, J. Am. Ceram. Soc. 82, 797 (1999).
- 4. A.J. Moulson and J.M. Herbert, *Electroceramics* (Chapman and Hall, London, United Kingdom, and New York, 1990), Chap. 6.

- 5. J.D. Olivas and S. Bolin, JOM 50, 38 (1998).
- H.N. Al-Shareef, K.R. Bellur, A.I. Kingon, and O. Auciello, Appl. Phys. Lett. 66, 239 (1995).
- K.B. Lee, S. Tirumala, and S.B. Desu, Appl. Phys. Lett. 74, 1484 (1999).
- R. Dat, D.J. Lichtenwalner, O. Auciello, and A.I. Kingon, Appl. Phys. Lett. 64, 2673 (1994).
- W-J. Lin, T-Y. Tseng, S-P. Lin, S-L. Tu, H. Chang, S-J. Yang, and I-N. Lin, J. Am. Ceram. Soc. 80, 1065 (1997).
- W.L. Warren, D. Dimos, B.A. Tuttle, R.D. Nasby, and G.E. Pike, Appl. Phys. Lett. 65, 1018 (1994).
- 11. I.K. Yoo and S.B. Desu, Phys. Status Solidi A 133, 565 (1992).
- 12. T. Tani and D.A. Payne, J. Am. Ceram. Soc. 77, 1242 (1994).
- J.S. Lee, C.J. Kim, D.S. Yoon, C.G. Choi, J.M. Kim, and K. No, Jpn. J. Appl. Phys. 33, 260 (1994).
- M. Shimizu, M. Sugiyama, H. Fujisawa, and T. Shiosaki, Jpn. J. Appl. Phys. 33, 5167 (1994).
- A.H. Carim, B.A. Tuttle, D.H. Doughty, and S.L. Martinez, J. Am. Ceram. Soc. 74, 1455 (1991).
- 16. Y.J. Song, Y. Zhu, and S.B. Desu, Appl. Phys. Lett. 72, 2686 (1998).
- C.A. Araujo, J.D. Cuchiaro, L.D. McMillan, M.C. Scott, and J.F. Scott, Nature **374**, 627 (1995).
- B.H. Park, B.S. Kang, S.D. Bu, T.W. Noh, J. Lee, and W. Jo, Nature 401, 682 (1999).
- 19. U. Chon, G-C. Yi, and H.M. Jang, Appl. Phys. Lett. 78, 658 (2001).
- J.J. Lee, C.L. Thio and S.B. Desu, Phys. Status Solidi A 151, 171 (1995).
- W.L. Warren, D. Dimos, G.E. Pike, B.A. Tuttle, M.V. Raymond, R. Rameshand, J.T. Evans, Jr., Appl. Phys. Lett. 67, 866 (1995).