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# 격자 조정을 통한 PZT커패시터의 고속동작 성능

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# High speed performance of $Pb(Zr,Ti)O_3$ capacitors through lattice engineering

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## Abstract

High speed performance of ferroelectric $Pb(Zr,Ti)O_3$ (PZT) based capacitors is reported. La substitution up to 10% was performed to systematically lower the coercive and saturation voltages of epitaxial ferroelectric capacitors grown on Si using a $(Ti_{0.9}Al_{0.1})N$/Pt conducting barrier composite. Ferroelectric capacitors substituted with 10% La show significantly lower coercive voltage compared to capacitors with 0% and 3% La. This is attributed to a systematic decrease in the tetragonality (i.e., c/a ratio) of the ferroelectric phase. Furthermore, the samples doped with 10% La showed dramatically better retention and pulse width dependent polarization compared to the capacitors with 0% and 3% La. These capacitors show promise as storage elements in low power high density memory architectures.

Key words : hydrogen-terminated, ferroelectric, high speed, lattice, domin

## 1. Introduction

There is currently considerable research and development effort aimed at developing nonvolatile ferroelectric memories using the intrinsic remnant polarization available in ferroelectric materials. Two types of ferroelectric materials, namely the lead zirconate titanate perovskite system (PZT family) and the layered perovskite based on strontium bismuth tantalate (SBT) are being explored. Specifically in the case of the lead based perovskite, the problem of fatigue has been resolved using conducting oxide contact electrodes.[1,2] In conjunction with the materials and process development, other circuit related issues are also being extensively studied. One specific issue is the operability of the ferroelectric capacitors at voltage levels lower than the standard 5V operation. Low voltage operation is particularly desirable in future generation memory devices

which will function in information systems powered in the range of 1.5~3V.[3] Reduction in the operating voltage level means that the ferroelectric capacitor materials properties also have to be optimized further. Particularly, it is desirable that the hysteresis loops saturate at applied voltages of the order of 1.5~3V with coercive voltage in the range of 0.5~0.7V. Further, it is important to characterize the ferroelectric properties using test conditions within this voltage range. In this paper, results of experiments aimed at addressing this low voltage operation issue are reported, using La substituted PZT (PLZT) up to 10% as ferroelectric thin layers with La-Sr-Co-O (LSCO) electrodes.

## 2. Experimental

The heteroepitaxial thin films of the whole stack (LSCO/PZT/LSCO) using conducting barriers ($(Ti_{1-x}Al_x)N$ composites) on Si (100) 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℃. Temperatures were controlled by a programmable circuit board. Temperature ramp up rate was 20℃/min. and cooling rate was 5℃/min. Epitaxial $(Ti_{0.9}Al_{0.1})N$ films of 600Å thickness were deposited on hydrogen-terminated (100) Si using a target of the same nominal composition. $(Ti_{1-x}Al_x)N$ barriers have recently attracted attention due to their better oxidation resistance and stability at elevated temperature.[4, 5] The PLZT layer thickness was 1500( and the top and bottom LSCO layers were each 700Å The crystalline quality and phase purity of the ferroelectric stack was confirmed to be pure perovskite with a high degree of [100] orientation by x-ray diffraction studies. Furthermore, x-ray phi-scans revealed a strong degree of in-plane orientation in all the layers. Finally, transmission electron microscopy studies show clean interfaces between the various layers. Electrical measurements were carried out using a high speed pulsed test setup as well as a Radiant technologies RT66A tester.

## 3. Results and Discussion

La substitution in the PZT layer systematically reduces the c-axis lattice parameter and the c/a ratio. In the ceramic targets, the c-axis lattice parameter decreases while the a-axis lattice expands, as shown in Fig. 1, consistent with what is reported for other tetragonal bulk PZT ceramics.[6] The c-axis parameter of our epitaxial films is slightly smaller, but a-axis parameter is larger

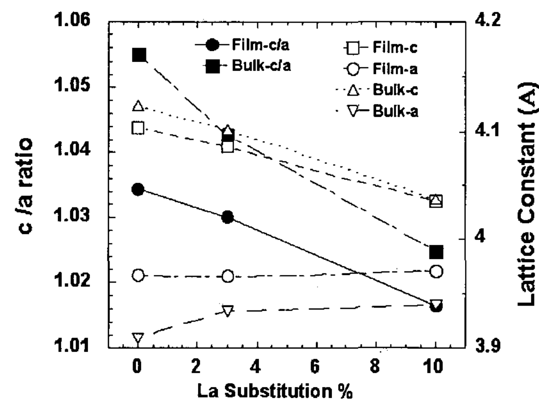


Fig. 1 a-axis and c-axis lattice constant and c/a ratio, from x-ray diffraction measurements, for both thin films and bulk PLZT ceramics as a function of La substitution.

than the bulk values by about 0.05-0.1 Å These a-axis and c-axis parameter differences can be caused by the tensile stress in the plane of PZT films resulting from the thermal expansion mismatch during cooling.[7] Finally, the c-axis parameter in our films also decreases with increasing La content, consistent with previous report for thin film.[8]

Representative hysteresis loops, pulsed polarization ($P^*$-$P^\wedge$ for a pulse width of 2 msec and coercive voltage for 10%, 3% and 0% La substituted PZT films are shown in Fig. 2. The loops for 10%, 3% and 0%-PLZT films are well saturated at 3V with coercive voltages of the order of 0.7V, 1.3V and 1.4V, respectively. Pulsed polarization values of 10 % La substituted samples changed slightly in the applied voltage range of 1.5-3V, but 3 % and 0% samples showed a rapid decrease in pulsed polarization with decreasing applied voltage. This is an important indicator of the effect of

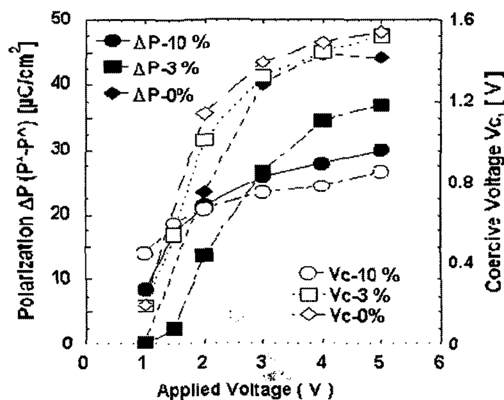


Fig. 2 Pulsed polarization, $\Delta P$ ($P^*$, switched-$P^\wedge$, nonswitched) and coercive voltage as a function of applied voltage for epitaxial LSCO/PLZT (10%, 3% and 0% La substitution)/LSCO capacitors using Pt/($Ti_{0.9}$ $Al_{0.1}$)N conducting barriers on Si (100). Inset shows the hysteresis loops, measured at applied voltage of 3V.

La substitution on the switching characteristics of the ferroelectric film. The pulse polarization data show that although the hysteresis loops seem to indicate saturation at approximately 3V, the capacitors with lower La substitution switch reluctantly at lower voltages.

This difference in field dependent switching behavior can be understood through the effect of the c/a ratio on domain structures. For example, TEM studies of bulk PLZT show that in tetragonal[9] and rhombohedral[10, 11] PZT systems, the domain structure gradually changed from normal micron-sized domains (i.e., 90° domains) through tweed-like domains to nanodomains with increasing La content. We expect that the 10% La PLZT thin films have a tweed-like domain structure while the 0% and 3%-PLZT films have the normal micron-sized ferroelectric domains. As in the case of the bulk materials, this progressive change in domain structure with La substitution is a direct consequence of the effective c/a ratio of the tetragonal structure. The x-ray Bragg scans for our films clearly show that as La content is increased up to 10%, the broadening of x-ray peaks due to splitting into a- and c-domains is gradually reduced. It has been reported earlier that the reduction of the x-ray broadening is a result of the change of domain structure towards nano polar domains.[9] Thus, the structural evidence strongly suggests that 10%-PLZT films have the tweed-like domain structure.

TEM studies for PZT films with 10% and 0% La contents were performed to investigate the systematic variation of domain structures, as shown in Fig. 3 (a) and (b), respectively. The TEM studies do indicate that the 0% PZT sample has a 90° do-

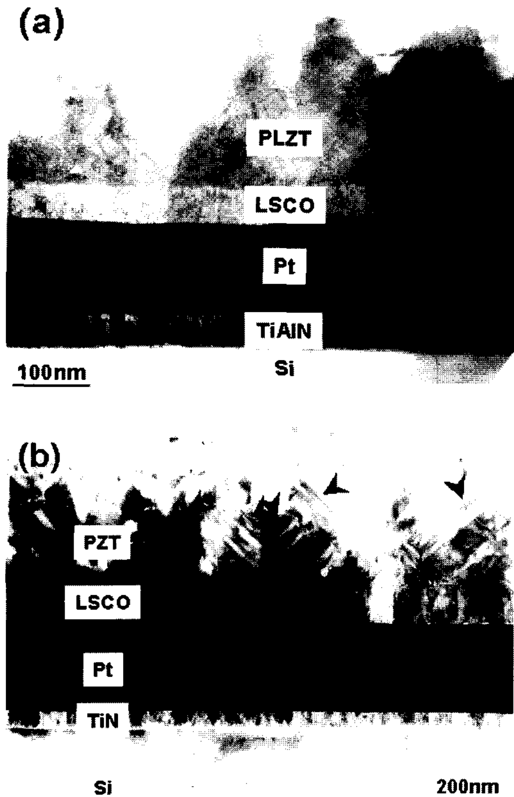


Fig. 3 Bright field TEM image of (a) epitaxial LSCO/PLZT (10% La)/LSCO/Pt/TiAlN heterostructure on Si (100), and (b) PZT(0% La)/LSCO/Pt/TiN/Si(100).

main structure while the 10% La films do not. The TEM image of PZT film with 10% La content shows similar microstructure to the nanodomains of bulk PZT reported previously,[9] which had very fine features inside the PZT. This sample also shows very clean interfaces, especially between PLZT and LSCO, and consequently no evidence for interaction between adjacent layers. However, TEM images of the PZT films and 0% La content show that much strain is involved in the PLZT and LSCO film, and high concentration of defects, such as dislocations, exists, especially in the interface between PLZT and bottom LSCO, compared to the PZT sample with 10% La content. Arrows in TEM images of the PLZT films (0% La) indicate twin boundaries slanted to 45( with the film surface. The diffraction pattern using the [110] beam direction clearly shows extra spots, indicated by arrows, due to 90° rotations of lattices resulting from twinning. These results from TEM observation confirm that the PLZT films with 3% and 0% La contents have 90° domains with twin structures. The direct correlation between the c/a ratio and the coercive voltage is important to note. The larger coercive voltage of 0% and 3%-PLZT samples seems to be related to the 90° domain structure in them, suggesting that switching of 90° domains is energetically more unfavorable compared to switching via 180° domains, as is well known in the case of bulk or single crystal materials.[12]

Another important advantage of La substitution is the dramatic improvement in the high-speed characteristics. An important manifestation of the lower c/a ratio and lower coercive voltage is that the switched polarization is not significantly influenced by the write and read pulse width. This is especially important for low power high speed memories with access times in the range of 50-100nsec. We have measured the switched polarization ($\Delta P = P^{*} - P^{\wedge}$) at 3V and 5V as a function of pulse width in a high-speed set-up, the results of which are shown in Fig. 4. As the pulse width is decreased from 1 second to 100nsec, the switched polarization of 10%-PLZT decrease from 28 to 18 $\mu C/cm^2$ at 3V, i.e., about 35% decrease. However, the pulse width dependence of 3%-PLZT at 3V is significant, i.e., about 80% decrease. It is important to note that the switched polarization at 100nsec and 3V is still large enough for high den-

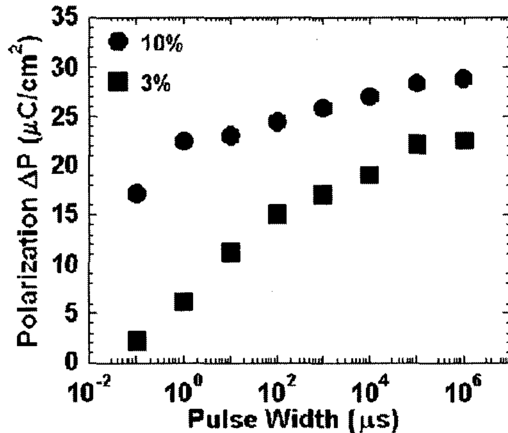


Fig. 4 The polarization, ΔP (P*, switched-P^, nonswitched), for epitaxial LSCO/PLZT (10% and 3% La substitution)/LSCO capacitors using (TiAl)N/Pt on (100) Si as a function of pulse width tested at 3V.

sity applications. Switched polarization (ΔP) values of about 10μC/cm² were obtained for 10 % PLZT capacitors at a lower operating voltage of 2V with high speed pulses of 1 μsec.

Consequently, the improved switching properties for 10% PLZT capacitors result from the low resistance of domain wall movement due to the strain reduction of tetragonal distortion.[9] The dramatic difference in the high speed polarization is also the most important consequence of the lattice engineering approach that La substitution enables.

## 4. Summary

The integration of ferroelectric capacitors (10 %-PLZT) with LSCO electrodes on Si using the ($Ti_{0.9}Al_{0.1}$)N/Pt conducting barrier composite has been demonstrated. Test capacitors show sufficient switched polarization at low voltage (1.5~3V) and good high speed performance. A systematic change in the memory-relevant ferroelectric properties with La content was also demonstrated. The beneficial effects of the controlled reduction in c/a ratio are clearly shown.

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## References

1. J. T. Cheung, P. E. D. Morgan, D. H. Lowndes, X. Y. Zheng, and J. Breen, Appl. Phys., Lett. 62 (1993) 2045.
2. R. Ramesh, A. Inam, B. Wilkens, W. K. Chan, D. L. Hart, K. Luther and J. M. Tarascon, Science., 252 (1991) 944.
3. R.E. Jones, P. Zurcher, P. Chu, D.J. Taylor, S. Zafar, B. Jiang, and S.J. Gillespie, Integrated Ferroelectrics., 15 (1997) 199.
4. D. McIntyre, J.E. Greene, G. Hakansson, J. -E. Sundgren and W. -D. Munz, J. Appl. Phys., 67 (1990) 1542.
5. T. Ikeda and H. Satoh, Thin Solid Films., 195 (1991) 99.
6. C.G.F. Stenger and A.J. Burggraaf, J. Phys., Chem. Solids., 41 (1980) 17.
7. J. S. Speck, A. Seifert, W. Pompe, and R. Ramesh, J. Appl. Phys., 76 (1994) 477.
8. S. B. Mah, N. W. Jang, and J. H. Park, Mater. Res. Bullet., 35 (2000) 1113.
9. X. Dai, Z. Xu and D. Viehland, J. Appl. Phys., 79 (1996) 1021.
10. B.A. Tuttle, T.J. Garino, J.A. Voigt, T.J. Headley, D. Dimos and M.O. Eatough, Science and Technology of Electroceramic Thin Films,

Edited by O. Auciello and R. Waser., 284 (1995) 117.

11. S. Takahashi, Ferroelectrics., 41 (1982) 143.
12. D. Dimos, W.L. Warren and B.A. Tuttle, Science and Technology of Electroceramic Thin Films, Edited by O. Auciello and R. Waser., 284 (1995) 291.

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