J Mater Sci (2007) 42:7899–7905
DOI 10.1007/s10853-007-1731-6

Fatigue, retention and switching properties of PLZT(x/30/70) thin films with various La concentrations

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Received: 13 October 2006 / Accepted: 26 March 2007 / Published online: 13 June 2007

Abstract We investigated the fatigue, retention and switching properties of PLZT(x/30/70) thin films with various La concentrations. By applying 10^9 square pulse switching cycles with a voltage of ±5 V to study the fatigue properties of the film, we found that the decrease of the initial polarization is improved from 64% to 40% as the La concentration is increased from 0 mol% to 10 mol%. The retention properties are also greatly improved as the decrease of the initial polarization decrease is reduced from 47% to 9% after 10^5 s. The switching time is decreased from 0.8 μs to 0.55 μs as the La concentration is increased. While the dielectric constant of the PLZT thin films increases from 450 to 600 as the La concentration is increased, the dielectric loss and leakage current density measured at 100 kV/cm decrease from 0.075 to 0.025 and from 5.83×10^{-7} to 1.38×10^{-7} A/cm^2, respectively. By analyzing the hysteresis loops of the PLZT thin film measured at 175 kV/cm, we found that the remnant polarization and coercive electric field decrease from 20.8 μC/cm^2 to 10.5 μC/cm^2 and from 54.48 kV/cm to 32.12 kV/cm, respectively, as the La concentration is increased.

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Introduction

With the rapid development of the semiconductor and information communication industries, interest in memory devices has increased [1–3]. Especially, following the recent introduction of a new kind of non-volatile memory using the unique characteristics of ferroelectric thin films, such as their polarization reversal and hysteresis properties, many researchers have become interested in ferroelectric films. However, the development of commercial products based on ferroelectric memory is still in progress. The introduction of practical non-volatile memory based on ferroelectric film needs not only the development of a manufacturing process for ferroelectric film which is compatible with that of CMOS, but also studies designed to analyze the cause and suggest possible solutions for the fatigue in ferroelectric films, and to investigate their retention and switching properties. The fatigue property is defined as the polarization loss due to repeated bipolar pulses affecting the reliability of a ferroelectric film. The retention property is defined as the remanent polarization after an elapse of time. The switching property affects the response time of a memory device.

One of the most widely investigated ferroelectrics for non-volatile memory device application in recent years is PZT thin film, which has various merits such as a large remnant polarization and a low crystallization temperature. However, PZT thin film coated on a metal electrode has a problem related to the reliability of non-volatile memory, such as its fatigue, and retention properties, which presents a big obstacle to practical development [4]. To alleviate the problems posed by PZT thin film, investigations have been conducted in an attempt to improve its reliability using PZT thin film doped with a donor ion such as La [5]. However, systematic and integrated studies of the degradation problems related to the reliabilities of PLZT thin film, such as its fatigue and retention properties when it is applied to non-volatile memory, and of the switching properties of the film, are still in their initial stages.

In this study, PLZT(x/30/70) thin films were made with various La concentrations and their fatigue and retention properties were systematically studied. Based on these findings, we evaluated the possibility of using PLZT thin films in non-volatile memory.

Experimental

We prepared PLZT(x/30/70) thin films with various La concentrations by the sol–gel method. $Pb(CH_3COO)_2{\cdot}3H_2O$ (Aldrich), $La(OOCCH_3)_3{\cdot}1.5H_2O$ (Strem), $Zr(OC_3H_7)_4$ (Fluka) and $Ti(O\text{-}iC_3H_7)_4$ (Alpha) were used as the starting materials. Acetic acid (Acros) was used as a solvent and stabilizer. Also, *n*-propanol (Acros) was added to increase the wettability of the substrate and to control the viscosity of the solution. Pb, La, Zr and Ti stock solutions were prepared separately, and an excessive amount of Pb was added to the coating solution (as much as 12.5 mol%), in order to prevent the formation of the pyrochlore phase due to a lack of Pb. Each stock solution was mixed in accordance with its concentration, in order to prepare a 0.4 M coating solution. This coating solution was filtered by a 0.2 μm filter before spin coating. The PLZT thin film was formed on a $Pt/TiO_x/SiO_2/Si$ substrate using a two-step spin coater at 500 rpm for 5 s and 3,000 rpm for 40 s in a clean bench. After the coating process, the sample was dried at 110 °C and 450 °C for 15 and 5 min, respectively, and then coated repeatedly in order to obtain the desired thickness. The sample was annealed at 650 °C for 30 min. Top electrodes with a diameter of 0.2 mm were thermally evaporated through a shadow mask placed on the substrate, and then a planar-type capacitor was fabricated.

To study the crystallization characteristics and the tetragonality of the PLZT thin films with various La concentrations, analyses were performed using X-Ray Diffraction (PHILIPS PW 3020, CuKα). The surface morphologies were inspected using AFM (Atomic Force Microscopy: Topometrix, Accurex II). The dielectric characteristics and leakage current density were measured by means of an LCR meter (Stanford Research, SR 720) and semiconductor parameter analyzer (HP4145B), respectively. The hysteresis curve and the fatigue and retention properties of the PLZT thin film were measured by a standardized ferroelectric test system (Radiant Technologies, RT66A). The switching property of the PLZT thin film was measured using a pulse generator (HP8110A) and digitizing oscilloscope (HP54522A).

Results and discussion

The X-ray diffraction (XRD) results obtained for the PLZT thin films with La concentrations in the range of 0–10 mol% annealed at 650 °C for 30 min are shown in Fig. 1a. None of the PLZT thin films had a preferred orientation or showed the presence of any undesirable second phase, such as the pyrochlore phase, except for the perovskite phase. The tetragonality (c/a) calculated from the diffraction angles corresponding to the peaks of the (100) and (001) plane obtained from the XRD results is depicted in Fig. 1b. Figure 1b shows that the tetragonality is linearly decreased from 1.032 to 1.01 as the La concentration is increased from 0 to 10 mol%. This result is almost identical to that of Klee et al. [6]. However, the tetragonality observed in the PZT(30/70) thin film having an La concentration of 0 mol% is less than the value of 1.05 obtained for bulk ceramic [7]. This can be explained by the fact that the thin film has a very fine grain in comparison with the bulk ceramic.

The surface morphology such as the roughness is an important factor to consider given that when the

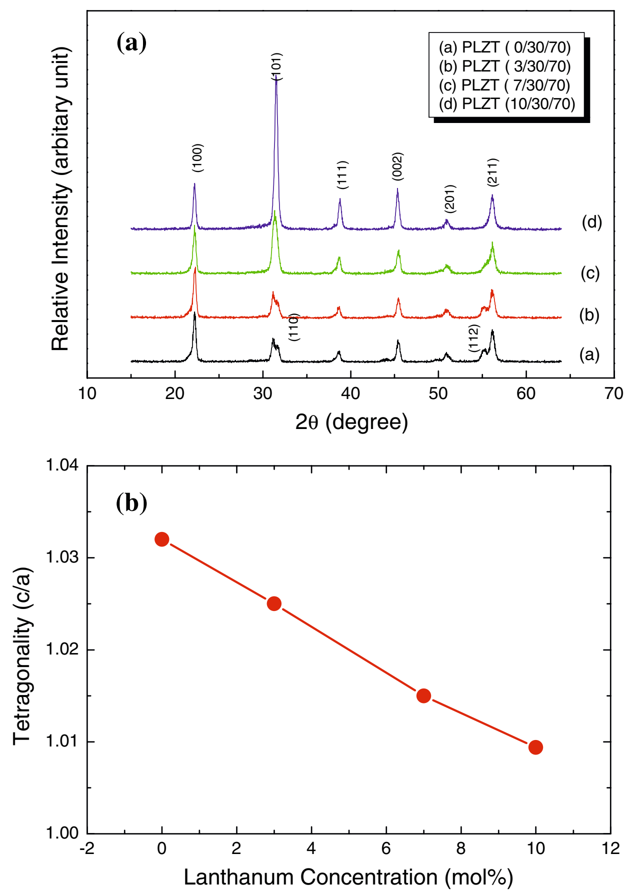


Fig. 1 (**a**) XRD patterns and (**b**) tetragonality (c/a) of PLZT(x/30/70) thin films with various La concentrations

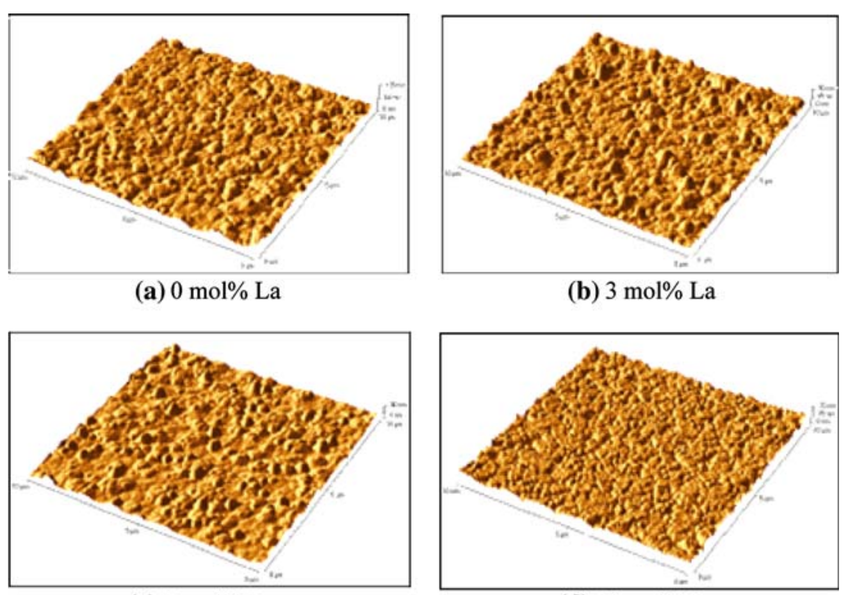
ferroelectric thin film is applied to memory devices, the electrical properties can be changed by the interfacial characteristics between the top electrode and the thin film. In particular, the enhancement of the surface morphology has a significant effect on the leakage current density of thin films. Thus in this paper, AFM was used to analyze the surface roughness of the PLZT thin films quantitatively and the results are shown in Fig. 2.

The surface roughness of the PLZT thin films decreases from 110 Å to 60 Å as the La concentration is increased from 0 mol% to 10 mol%. This improvement can be explained by the decrease in the grain size of the PLZT thin films with increasing La concentration and the decrease in the tetragonality and corresponding degradation of the crystal orientation because of the replacement of the Pb^{2+} ions having a radius of 1.19 Å by La^{3+} ions having a radius of 1.032 Å. As seen by AFM, an enhancement of the surface roughness and interactions, such as the decrease of the number of carriers due to defect compensation, improve the leakage current density. The analysis in references [8, 9] is consistent with the experiment results obtained for the leakage current density shown in Fig. 4.

The variation in the dielectric properties of the PLZT thin film due to the change of the La concentration is depicted in Fig. 3. At a frequency of 10 kHz, the dielectric constant of PLZT thin films increases from 450 to 600 as the La concentration is increased from 0 mol% to 10 mol%. This is associated with the shift of the Curie temperature toward room temperature with increasing La concentration [10]. At the atomic level, it is considered that the dielectric constant increases as the number of Pb^{2+} vacancies generated by the replacement of the Pb^{2+} ions by La^{3+} ions stimulates the polarization domain switching. However, the dielectric loss decreases from 0.075 to 0.025 as the La concentration increases (from 0 mol% to 10 mol%). This decreasing tendency of the dielectric loss with increasing La concentration can be explained by complex interactions such as the enhancement of the AC resistivity because of the improved densification of the thin film and the diminution of the influence of the domain because of the gradual increase in the paraelectricity.

The leakage current density is one of the important factors to bear in mind when considering the application of ferroelectric thin films to memory devices. As the leakage current increases, the power dissipation increases and the bias field applied to the device is limited. Therefore, it is important to keep the leakage current as low as possible. Figure 4 shows the leakage current density of the PLZT thin films with various La concentrations. The leakage current density measured at an electric field of 100 kV/cm decreases from 5.83×10^{-7} A/cm^2 to 1.38×10^{-7} A/cm^2 as the La concentration is increased from 0 mol% to 10 mol%. This improvement in the leakage current density is due to the combined effect of thee different factors. First, when a Pb-containing ferroelectric thin film is annealed at high temperature, holes are generated by the ionization of the A-site (Pb-site in PZT) vacancies due to the high volatility of PbO and, thus, the electrical conductivity increases. However, in the case of PLZT thin film, because of the substitution of La^{+3} ions for the Pb^{2+} ions in the A-sites, the creation of holes is limited in order to maintain the electrical neutrality among the atoms. Hence, the number of free carriers in the thin film decreases, so that the electrical conductivity is decreased. Second, as the La

Fig. 2 3D AFM images of PLZT(x/30/70) thin films with various La concentrations



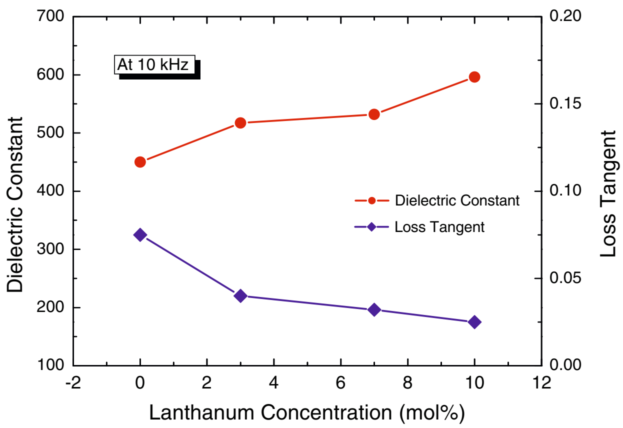


Fig. 3 Dielectric constant and loss tangent of PLZT(x/30/70) thin films with various La concentrations

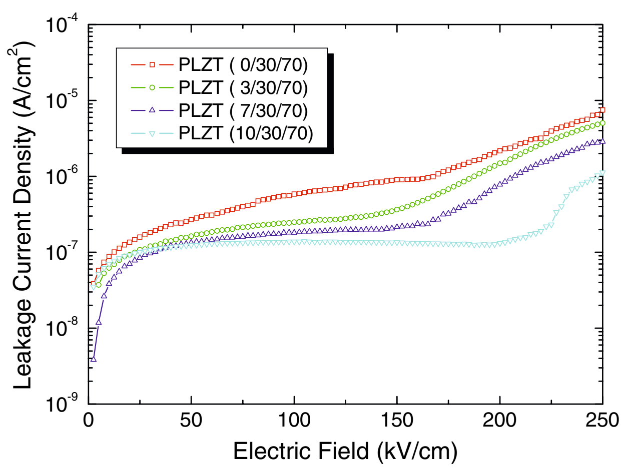


Fig. 4 Leakage characteristics of PLZT(x/30/70) thin films as a function of electric filed

concentration is increased, the lattice constant of the PLZT thin film decreases and becomes close to that of the platinum (Pt) bottom electrode. Consequently, the amount of stress due to lattice misfit decreases, so that the formation of microcracks in the thin films is minimized. Lastly, an improvement of the leakage current density results from a decrease of grain size.

Figure 5 shows the hysteresis loops of the PLZT thin films as the La concentration is increased from 0 mol% to 10 mol%. From the hysteresis loops of the thin films measured at 175 kV/cm, it was determined that the remnant polarization (P_r) and the coercive electric field (E_c) decrease from 20.8 μC/cm^2 to 10.5 μC/cm^2 and from 54.48 kV/cm to 32.12 kV/cm, respectively, as the La concentration is increased from 0 mol% to 10 mol%. These decreases of P_r and E_c can be explained by the existence of vacancies in the PLZT thin film. As the La concentration increase, the number of Pb vacancies increases so that the atomic mobility in the thin film also increases. Such a stimulated atomic mobility increases the domain activity at a lower electrical field, resulting in a decrease of the coercive electric field. Also, the decrease of the remanent polarization is due to the decrease of the tetragonality with increasing La concentration, as mentioned in the above discussion about the crystallographic characteristics.

When applying ferroelectric thin films to memory devices, repeated read/write operations cause fatigue phenomenon such as the decrease in the polarization of the ferroelectric thin film due to electrical stress, and this can become a serious problem. Hence, studying the fatigue properties of ferroelectric thin films is very important for their application to non-volatile memory. In this study, the

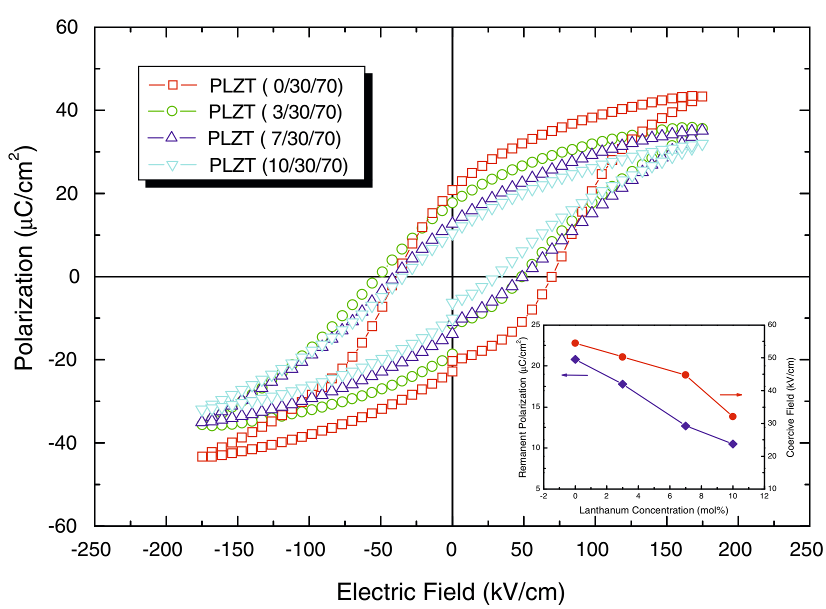


Fig. 5 Hysteresis loops of PLZT(x/30/70) thin films with various La concentrations

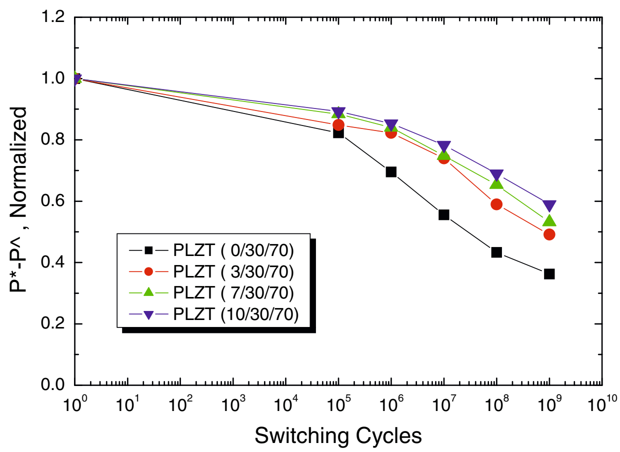


Fig. 6 Normalized fatigue properties of PLZT(x/30/70) thin films with various La concentrations

effect of the La concentration of the PLZT thin film on its fatigue properties is studied as the La concentration is increased from 0 mol% to 10 mol%. Figure 6 shows the graph of the normalized polarization ($P^* - P^\wedge$) versus the number of polarization switching cycles after applying a ±5 V square pulse to the PLZT thin films. There is an abrupt decrease in the normalized polarization of the PLZT thin film with a La concentration of 0 mol% after 10^5 cycles, and a 64% decrease from the initial polarization is observed at 10^9 cycles. However, in the PLZT thin film with a La concentration of 10 mol%, the decrease of the polarization with increasing number of polarization switching cycles is smaller than that of the thin film with a La concentration of 0 mol%, with only a 40% decrease from the initial polarization being observed at 10^9 cycles. It has been reported that the fatigue mechanism of ferroelectric thin films can be explained by either because of the domain wall pinning or because of oxygen vacancies accumulated at the interface between the bottom electrode and the ferroelectric thin film [11–13]. Hence it is necessary to suppress the creation of oxygen vacancies, in order to alleviate the fatigue phenomenon. Adding La as a donor–dopant can suppress the creation of oxygen vacancies according the following equation [14].

$$La_2O_3 + V_O^{\bullet\bullet} \rightarrow 2La_{Pb}^{\bullet} + 3O_O \quad (1)$$

According to this mechanism, as the La concentration is increased, the creation of oxygen vacancies is suppressed and the PLZT thin film is converted into a paraelectric phase. Therefore, the influence of the ferroelectric domain becomes less and the fatigue property is improved.

Although the retention property, which is defined as a loss of polarization after an elapse of time, is one of the main sources of reliability problem, it has not been studied intensively. In this study, the retention property of PLZT thin films with various La concentrations was studied by applying a –5 V write square pulse and +5, –5 V read square pulses. The write and read pulse widths were 8.6 μs and 2 ms, respectively. The retention time is defined as the time delay between the write pulse and read pulse. Figure 7 shows the normalized retention properties of the PLZT thin films with various La concentrations. The polarization decreases rapidly in the PLZT thin film with a La concentration of 0 mol%, with a 47% decrease from the initial polarization being observed after a retention time of 10^5 s. However, the retention property is considerably improved with increasing La concentrations. In the case of the PLZT thin film with a La concentration of 10 mol%, there is a 9% decrease from the initial polarization after a retention time of 10^5 s. It has been reported that the main cause of retention is the depolarization electric field due to the surface space charge and ferroelastic effect [15, 16]. Especially, Fridkin [17] experimentally confirmed that the depolarization electric field causing polarization loss is generated by oxygen vacancies. Aggarwal et al. [18] reported that the 90° domain inducing the depolarization electric field and ferroelastic effect has decreased with increasing La concentration. Therefore, as shown in Eq. 1, the oxygen vacancies and 90° domain decrease, so that the retention properties are improved with increasing La concentration.

The dynamic processes of the switching characteristics related to reversals of the permanent electric dipoles in ferroelectric thin films are very important from the viewpoint of their application to nonvolatile memory devices, since information about the switched charge density (Q_{sw}) and the switching time (t_s) can be obtained from them [19]. To study the switching property of the ferroelectric thin film, an RC serial circuit was used, as depicted in Fig. 8a,

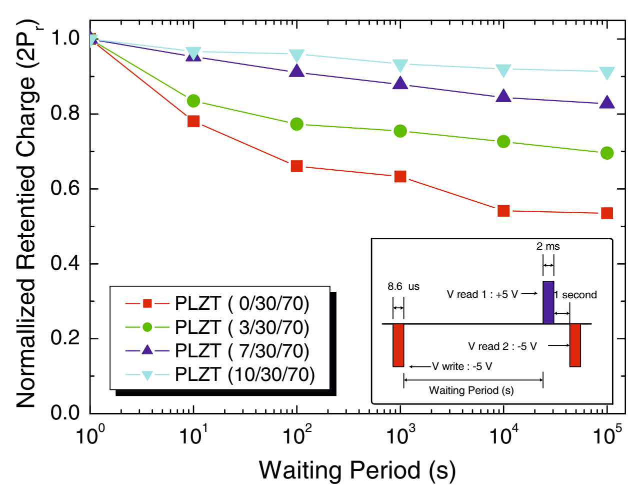


Fig. 7 Normalized retention properties of PLZT(x/30/70) thin films with various La concentrations

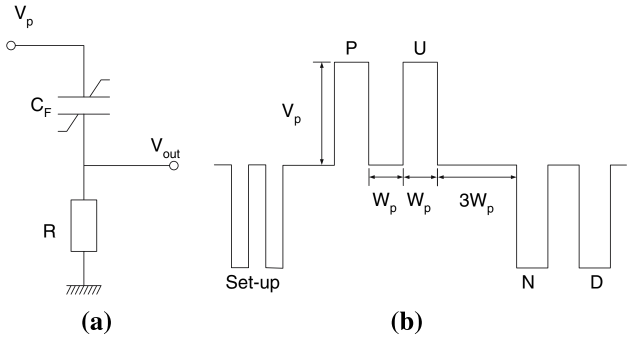


Fig. 8 (**a**) Schematic diagram of the test circuit and (**b**) input pulse waveform in pulse switching measurement

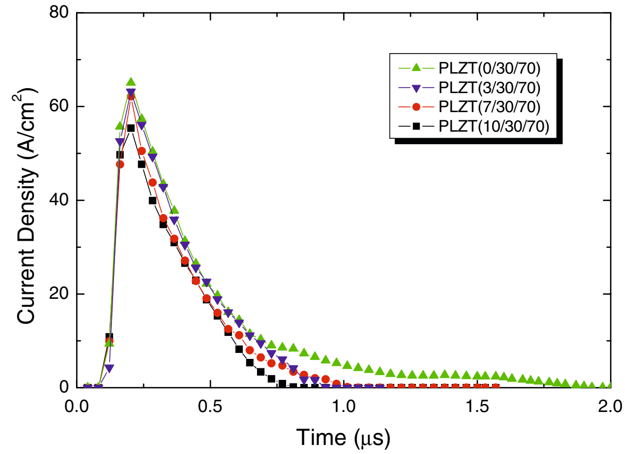


Fig. 10 Measured relative current response of PLZT(x/30/70) thin films with input pulse of 5 V

and the input signal consisted of a series of pulse wave forms, as shown in Fig. 8b. The response signal for pulse switching was measured as the transient voltage across a load resistor connected in series with the PLZT thin film capacitor.

Figure 9 shows the positive and negative switching response of the PLZT thin film with a La concentration of 10 mol%. Here, the pulse voltage is 5 V, the pulse width (W_p) 1.5 μs, the pulse rising time 2 ns, and the load resistance (*R*) 150 Ω. The switching transient of the PLZT(10/30/70) thin film is produced by applying the first (+) pulse voltage (*P*) from the series of input pluses shown in Fig. 8b to the thin film initially polarized to the negative state by the setup pulse. The non-switching transient is generated by applying the second (+) pulse voltage (*U*). In Fig. 9, the (–) region is created by applying the reverse pulse voltage (*N* and *D*). In order to measure the essential switching property, the relative switching transient curve obtained by subtracting the non-switching transient curve from the switching transient curve is used.

Figure 10 shows the relative current response of the PLZT thin films with an input pulse of 5 V and with various La concentrations. The switched charge density can be obtained by squaring the relative current response curve in Fig. 10. The switched charge densities obtained from the polarization switching of the PLZT thin films with La concentrations of 0, 3, 7 and 10 mol% are 21.7, 19.2, 17.0 and 15.0 $\mu C/cm^2$, respectively.

Figure 11 shows the switching times of the PLZT thin films with various La concentrations obtained from the relative current response. Generally, the switching time is defined as the elapsed time between a maximum relative current and its 10% value. The switching time in Fig. 11 decreases from 0.8 μs to 0.55 μs as the La concentration is increased from 0 mol% to 10 mol% in the PLZT thin films with a top electrode having an area of 3.14×10^{-4} cm^2 and this can be explained as follows. As the La concentration increases, the number of Pb vacancies increases, so that the atomic mobility in the PLZT thin films also increases. Such a stimulated atomic mobility increases the domain activity

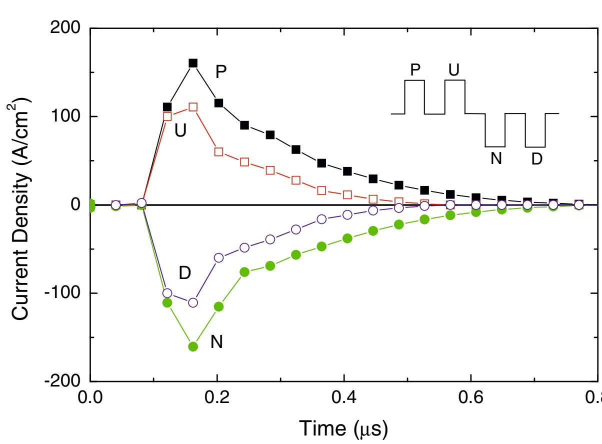


Fig. 9 Response transient current to pulse switching in PLZT(10/30/70) thin film

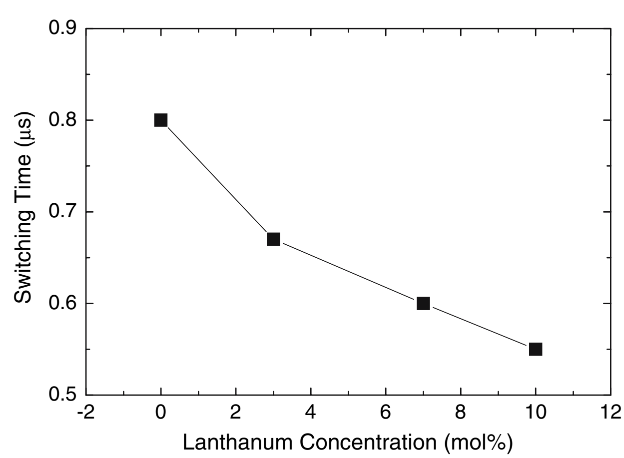


Fig. 11 Switching time of PLZT(x/30/70) thin films with various La concentrations

in an arbitrary electrical field, resulting in a speedup of the switching time.

Conclusion

We investigated the fatigue, retention and switching properties of sol–gel derived PLZT(x/30/70) thin films with various La concentrations. From the X-ray diffraction (XRD) results of the PLZT thin films, it was confirmed that no undesirable second phases such as the pyrochlore phase were formed. The tetragonality of the PLZT thin films decreased from 1.032 to 1.01 as the La concentration increased from 0 to 10 mol%. As the La concentration was increased, the dielectric constant of the PLZT thin films at a frequency of 10 kHz increased from 450 to 600, while the dielectric loss decreased from 0.075 to 0.025. The leakage current density at 100 kV/cm decreased from 5.83×10^{-7} A/cm^2 to 1.38×10^{-7} A/cm^2 as the La concentration increased. In the hysteresis loop measured at 175 kV/cm, the remanent polarization (P_r) and coercive field (E_c) decreased from 20.8 μC/cm^2 to 10.5 μC/cm^2 and from 54.48 kV/cm to 32.12 kV/cm, respectively, as the La concentration increased. The fatigue property experiments showed that in the PLZT thin film with a La concentration of 10 mol%, the decrease of the polarization is reduced in comparison with that of the thin film with a La concentration of 0 mol%, with only a 40% decrease from the initial polarization being observed at 10^9 cycles. Hence, we found that adding La as a donor–dopant alleviates the fatigue phenomenon. The retention property experiments showed that in the PLZT thin film with a La concentration of 10 mol%, there is a 9% decrease from the initial polarization, showing that it has comparably improved retention properties. The fastest switching time is 0.55 μs in the PLZT thin film with a La concentration of 10 mol%. This can be explained as follows. As the La concentration increases, the number of Pb vacancies increases so that the atomic mobility in the PLZT thin films also increases. Such a stimulated atomic mobility increases the domain activity at an arbitrary electrical field, resulting in the speedup of the switching time. Based on the results of this study, it can be conclude that PLZT thin film with a La concentration of 10 mol% is the most suitable for use in non-volatile memory. Only the fatigue property remains to be improved. By optimizing the manufacturing process of the thin film and improving the structure of the electrode, the PLZT thin film can be rendered applicable to non-volatile memory devices.

References

1. Simoes AZ, Gonzalez AHM, Zaghete MA, Varela JA, Stojanovic BD (2001) Thin Solid Films 384:132
2. Nakada M, Ohashi K, Akedo J (2005) J Crystal Growth 275:1275
3. Tang XG, Ding AL, Ye Y, Chen WX (2003) Thin Solid Films 423:13
4. Kim CJ, Kim TY, Chung I, Yoo IK (1999) In: Tuttle BA (ed) Materials research society symposium proceedings. Boston, p 399
5. Es-Souni M, Abed M, Piorra A, Malinowski S, Zaporojtchenko V (2001) Thin Solid Films 389:99
6. Klee M, Eusemann R, Waser R (1992) J Appl Phys 72:1566
7. Xu Y (1991) Ferroelectric materials and their applications, 1st edn. Elsevier, Amsterdam
8. Maiwa H, Inchinose N (1996) Jpn J Appl Phys 35:4976
9. Kang SJ, Chang DH, Yoon YS (2000) Thin Solid Films 373:53
10. Teowee G, Boulton JM, Baerteion CD, Wade RK, Uhlmann DR (1994) Integ Ferroelectrics 4:231
11. Tagantsev AK, Stolichnov I, Colla EL, Setter N (2001) J Appl Phys 90:1387
12. Dawber M, Scott JF (2000) Appl Phys Lett 76:1060
13. Liu JM, Wang Y, Zhu C, Yuan GL, Zhang ST (2005) Appl Phys Lett 87:042904
14. Raymond MV, Chen J, Smith DM (1994) Integ Ferroelectrics 5:73
15. Tagantsev AK, Stolichnov I, Setter N, Cross JS (2004) J Appl Phys 96:6616
16. Kang BS, Yoon JG, Kim DJ, Noh TW, Song TK, Lee YK, Lee JK, Park YS (2003) Appl Phys Lett 82:2124
17. Fridkin VM (1980) Ferroelectric semiconductor, 1st edn. Consultants Bureau
18. Aggarwal S, Prakash AS, Song TK (1998) Integ Ferroelectrics 19:159
19. Chang DH, Yoon YS, Kang SJ (2001) J Kor Phys Soc 38:277