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Characteristics of the PLT Thin Films with Various Pb/La Ratios

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We have studied the fatigue and dielectric properties of the PLT thin films with varying the La concentration. The fatigue and the dielectric properties improve remarkably with the increase of La concentration from 5 to 28mol%. In particular, after applying of 10^9 square pulses with ±5V, the remanent polarization of the PLT(10) thin film decreases only about 20% from the initial state while that of the PLT(5) thin film decreases as much as 70%. Our results show that PLT(10) and PLT(28) thin films are potential candidates for the capacitor dielectrics of new generation of NVFRAM and DRAM, respectively.

Keywords: PLT thin film, ferroelectric, NVFRAM, paraelectric, DRAM, hysteresis, fatigue

1. Introduction

Ferroelectric thin films have received great attention for the applications in many electronic or electrooptic devices.[1-4] In particular, much effort has been made on the application in future memory devices such as dynamic random access memory (DRAM) and nonvolatile ferroelectric RAM (NVFRAM). For the application in DRAM, it is desirable to use the normal (linear) dielectric thin film with low dielectric loss. On the other hand, good fatigue endurance, low dielectric permittivity and low coercive field are key properties for the application in NVFRAM.

Among the ferroelectric thin films, La-modified $PbTiO_3$ ($Pb_{1-x}La_xTi_{1-x/4}O_3$, PLT(x)) thin film can be applied to both memory devices because it allows a wide range of dielectric and ferroelectric properties depending on the La concentration. The change of c/a ratio in the tetragonal phase through the addition of La makes PLT a versatile compound ; it can be a normal ferroelectric, linear dielectric, relaxor ferroelectric or slim loop ferroelectric depending on the La concentration.

PLT thin films have been investigated by several groups [5-8]; however, systematic investigations on the properties of PLT thin films with variation of the La concentration have been rarely performed although they are essential for the applications in devices. Recently we reported about optical and dielectric properties of PLT thin films with variation of the La concentrations x=15 to 33mol% [9]. In this study, we have studied fatigue and dielectric properties of PLT thin films with variation of La concentrations from x = 5 to 28mol%. The motivation of this study is to evaluate the possibility of the application of PLT thin films in both of DRAM and NVFRAM.

2. Experimental

We prepared the PLT thin films with various La concentrations by sol-gel method. $Pb(CH_3COO)_2{\cdot}3H_2O$ (Aldrich), $La(OOCCH_3)_3{\cdot}1.5H_2O$ (Strem) and $Ti(O\text{-}iC_3H_7)_4$ (Alpha) are used as starting materials. Acetic acid (Acros) was used as solvent and stabilizer. Pb, La and Ti stock solutions were prepared separately. Each stock solution was mixed in accordance with the concentration and then 0.4M coating solution was prepared. This coating solution was filtered by the 0.2μm filter before spin coating. Thin film was formed on $Pt/TiO_x/SiO_2/Si$ substrate using two step spin coater at 500rpm for 5sec and 3000rpm for 40sec in the clean bench. After coating process, the sample was dried at 110 and 450 ºC for 15min and 5min, respectively, and then coated repeatedly for the expected thickness. This sample was annealed at 650 ºC for 30min. Top electrodes of 0.2mm in diameter were thermally evaporated through the shadow mask placed on the substrate, then planar-type capacitor was fabricated.

The crystalline structures of PLT thin films were determined by X-ray diffractometer (PHILIPS PW3020, CuKα), and the surface morphologies were observed using AFM (Atomic Force Microscopy : Park Science, AP2000L). The thickness of PLT thin film was obtained by using ellipsometer (PLASMOS, SD2300) and SEM (Scanning Electron Microscopy : Hitachi S-4200), and the variation of concentration across a depth of thin film and at the interface were investigated by using AES (Auger Electron Spectroscopy : VG Microlab, 310F). The dielectric properties and leakage current density was measured by using LCR meter (Stanford Research, SR720) and Parameter analyzer (HP4145B), respectively. Hysteresis loop and fatigue properties of PLT thin films were evaluated using RT66A standardized ferroelectric test system (Radiant technologies).

3. Results and Discussions

The XRD patterns of PLT thin films with the La concentration ranging from 5 to 28mol% are shown in Fig. 1. Since XRD patterns show peaks of (100), (110), (111), (200) and (211) planes in all concentrations, we know that these thin films crystallize into perovskite structure and do not have a certain preferred orientation with the La concentration. When applying ferroelectric thin films to the devices, the surface morphology is one of the major factors to influence the leakage current and dielectric breakdown properties of the thin film.Fig. 2 shows AFM surface images of PLT thin films with various La concentrations. As can be seen in Fig. 2, the grain size of thin film decreases and so the surface morphology becomes smoother with the increase of La concentration.

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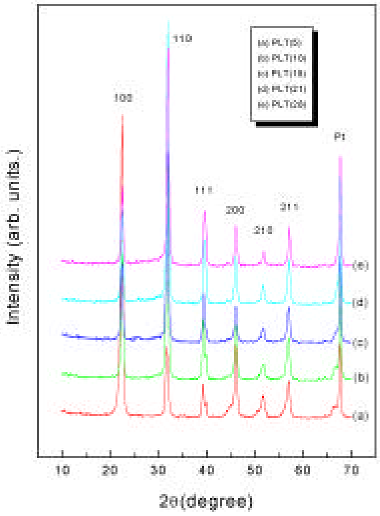


Fig. 1. XRD patterns of PLT thin films with various La concentrations.

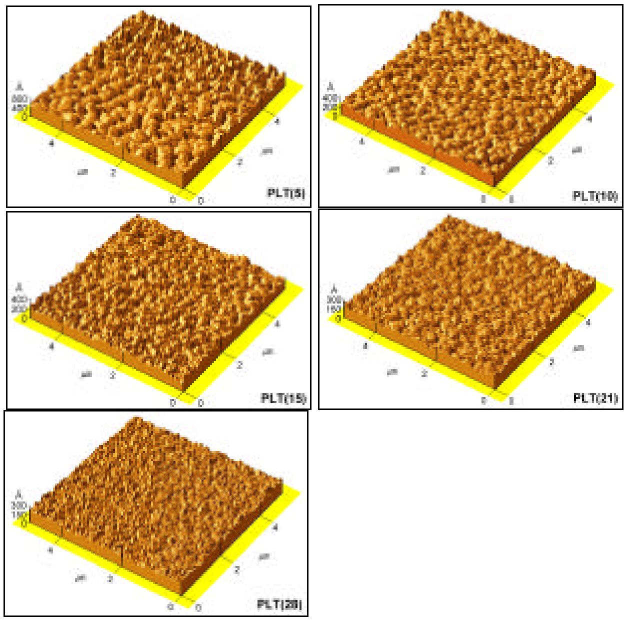
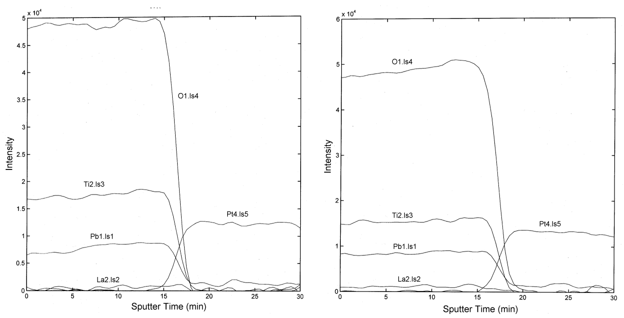


Fig. 2. The 3D AFM images of PLT thin films with various La concentrations.

The surface roughness of PLT thin film measured by AFM decreases from 98.9 to 22.0 Å as the La concentration increases from 5 to 28mol%.

Fig. 3 shows the AES depth profile of PLT(10) and PLT(28) thin films. In Fig. 3, we can see that the concentration of each component such as Pb, La, Ti, O in our PLT thin films are uniformly distributed. Since the existence of second phase is not observed in the PLT/Pt interface, it seems that the serious diffusion of Si does not occurred and the formation of low permittivity layer like silicon oxide in the PLT/Pt interface is hardly created.



(a) (b)

Fig. 3. AES depth profile of PLT thin films : (a) PLT(10), (b) PLT(28).

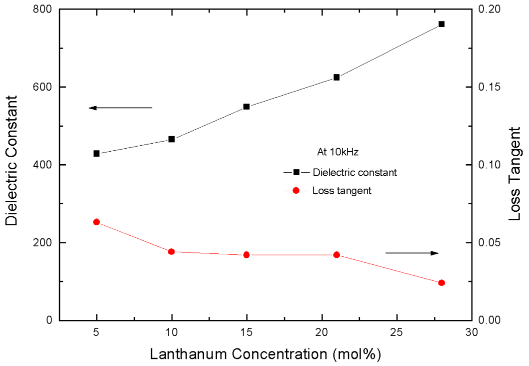


Fig. 4. Dielectric properties of PLT thin films with various La concentrations.

The dielectric properties of PLT thin films with the La concentration are shown in Fig. 4. As the La concentration increases from 5 to 28mol%, the permittivity measured at 10kHz increases from 428 to 761 whereas the loss tangent decreases from 0.063 to 0.024.

Fig. 5 shows the leakage current density of PLT thin films with various La concentrations. As the La concentration increases from 5 to 28mol%, the leakage current density at 150kV/cm decreases from 6.96 to 0.79μA/cm^2.

There may be three possible reasons for the improvement of leakage current with the increase of La concentration. The first one is the improvement of the surface roughness with the increase of La concentration as shown in Fig. 2. Since the potential barrier height against the conduction is strongly affected by the characteristics of the interface between the electrode and the thin film, the surface morphology of PLT thin film is one of the major factors determining the leakage current of MFM capacitor. The second one is the reduction of microcracks caused by residual stress. Since tetragonality and phase transition temperature decrease with the increase of La concentration, the lattice volume change occured during cooling from annealing or deposition temperature decreases and so residual stress decreases [9]. The third one is the decrease of carrier numbers in films by the defect compensation of the added La as reported H. Maiwa et. al.[10].

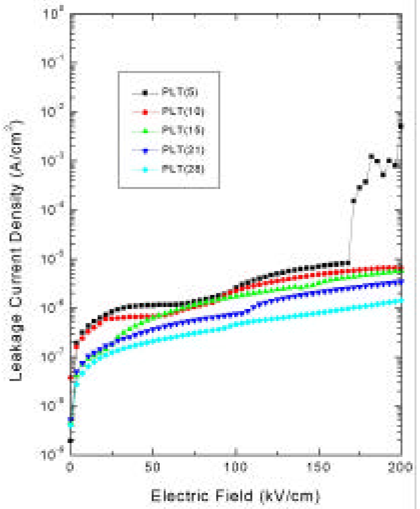
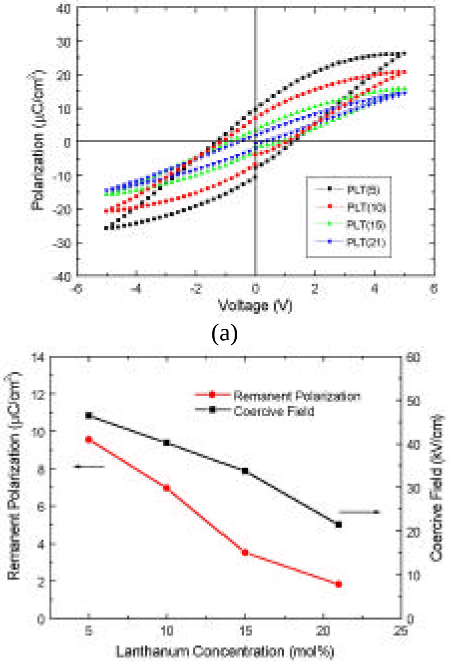


Fig. 5. Leakage characteristics of PLT thin films as a function of electric field and La concentrations.

Fig. 6(a) shows hysteresis loops of PLT thin films with various La concentrations from 5 to 21mol% measured at ±5V and Fig. 6(b) shows the remanent polarization (P_r) and the coercive field (E_c) obtained from the loops. With increase of the La concentration from 5 to 21mol%, the remanent polarization and coercive field decrease from 9.55 to 1.81μC/cm^2 and from 46.4 to 21.4kV/cm, respectively. It may be due to the decrease of tetragonality with the increase of La concentration. The applications of ferroelectric thin films to memory devices can be grouped into two, i.e. DRAM and NVFRAM.

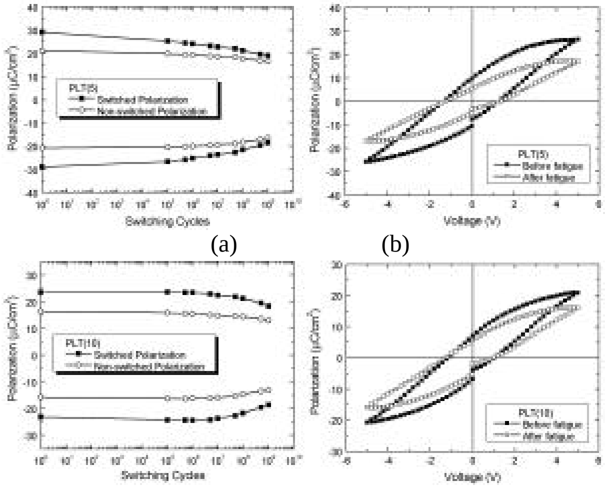

(a)

(b)

Fig. 6. Ferroelectric properties of PLT thin films with various La concentrations : (a) hysteresis loops, (b) remanent polarization and coercive field.

For the application to DRAM, it is desirable to use the thin film with low dielectric loss and paraelectric phase having fast switching time. Hence, as can be seen in Fig. 6(a), the 28mol% La doped PLT thin film shows paraelectric phase as well as excellent dielectric properties. Also, the charge storage density at 1V is relatively good value of 22.5fC/μm^2. Therefore, the 28mol% La doped PLT thin film is one of the excellent candidates for the capacitor dielectrics of DRAM.

In NVFRAM, the polarization of ferroelectric thin films are stressed electrically by repeating read/write cycles. Therefore, for the ferroelectric thin films to be used in NVFRAM, the most important requirement is the resistance to electrical fatigue. Figs. 7(a) and 7(c) show switched polarization (P^*) and non-switched polarization ($P^\wedge$), respectively, for the polarization reversal cycle by applying ±5V square pulse to the PLT(5) and PLT(10) thin films, and Figs. 7(b) and 7(d) show hysteresis loops before and after fatigue, respectively. P^* and $P^\wedge$ begin to decrease at 10^5 cycles and show a large drop at 10^9 cycles in the PLT(5) thin film, while they begin to decrease at 10^7 cycles and show no large decrease at 10^9 cycles in the PLT(10) thin film. The remanent polarization (P_r) of PLT(5) thin film decreases as much as 45% from 9.55 to 5.2μC/cm^2 after 10^9 cycles, while that of PLT(10) thin film decreases as much as 20% from 6.96 to 5.48μC/cm^2. As can be seen above, the fatigue property of PLT(5) thin film is not so good, while PLT(10) thin film shows relatively good fatigue property at 10^9 cycles. This indicates that if we improve the fabrication method of the thin film or use the proper electrodes, PLT(10) thin film can be successfully applied to NVFRAM.Fig. 8 shows the normalized polarization (P^*-$P^\wedge$) of the PLT thin films with various La concentrations from 5 to 21mol%. Polarization of the PLT(5) thin film at 10^9 cycles decreases as much as 70% from the initial value, while that


(a) (b)

(c) (d)

Fig. 7. Fatigue characteristics of PLT thin films on 50kHz switching cycles [(a), (c)] and hysteresis loops before and after fatigue [(b), (d)].

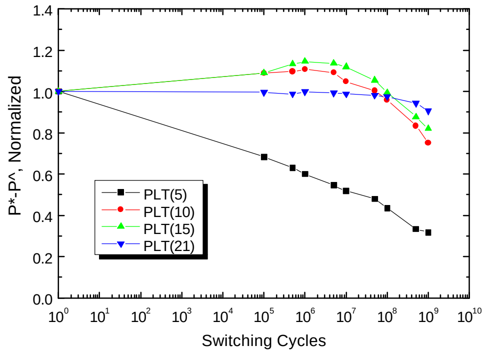


Fig. 8. Normalized pulsed fatigue data of PLT thin films with various La concentrations.

of the PLT(21) thin film decreases as much as about 9% at 10^9 cycles. The improvement of fatigue properties with the increase of La concentration seems to be due to two reasons.

The first one is that PLT thin film has more paraelectric phase with the increase of La concentration and thus the effect of ferroelectric domain decreases, and the second one is that the generation and diffusion of the oxygen vacancy known as a major cause of fatigue is more suppressed as the La concentration increases [11].

4. Conclusion

Our AFM study shows that the surface roughness and the grain size of PLT thin films decrease as the La concentration increases from 5 to 28mol%. The improvement of surface morphology with increase of La concentration may contribute to the improvement of leakage currents. As the La concentration increases from 5 to 28mol%, the dielectric constant at 10kHz increases from 428 to 761, while loss tangent and leakage current density at 150kV/cm decrease from 0.063 to 0.024 and from 6.96 to 0.79µA/cm^2, respectively. In the results of hysteresis loops of PLT thin films with various La concentrations, the remanent polarization and the coercive field decrease from 9.55 to 1.81µC/cm^2 and 46.4 to 21.4kV/cm, respectively. The PLT(28) thin film has paraelectric phase, and its charge storage density and leakage current density at 1V are 22.5fC/µm^2 and 0.15µA/cm^2, respectively. These effects must come from the decrease of tetragonality with the increase of La concentration. The fatigue properties also improve remarkably with the increase of the La concentration from 5 to 21mol%. In particular, after applying 10^9 square pulses with ±5V, the remanent polarization of the PLT(10) thin film decreases about 20% from the initial state while that of the PLT(5) thin film decreases as much as 70% from the initial state. The initial values of the remanent polarization and coercive field of the PLT(10) thin film are 6.96µC/cm^2 and 40.2kV/cm, respectively. The results of this study shows that the PLT(10) and PLT(28) thin films are excellent candidates for the capacitor dielectrics of new generation of NVFRAM and DRAM, respectively.

Acknowledgements

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