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Dielectric investigations of PLT(28) thin film prepared by reactive magnetron sputter

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Abstract

Paraelectric PLT(lead lanthanium titanate) thin films were prepared by dc magnetron sputtering with multi element metal target. In order to crystallize the as-deposited PLT thin films to the cubic perovskite phase, post-heat treatment was applied at the temperatures from 450 to 750 °C. The composition of PLT(28) thin film was: Pb, 0.72; La, 0.28; Ti, 0.88; O, 2.9. The dielectric characteristics were essentially dependent on the changes in the chemical composition and crystalline phase with variation of annealing treatment. The dielectric constant increased and dissipation factor decreased slightly, as the post-annealing temperature increased. The dielectric constant and dissipation factor at low electric field measurement of the capacitors with highest dielectric properties were 1216 and 0.018, respectively.

Keywords: PLT; Dielectric properties; Films; Electrical properties; Perovskite

1. Introduction

Since the successful development of DRAMs technology, the reduction in cell size has required the decreasing area of the planar storage capacitor. Therefore, the conventional dielectric materials such as SiO_2, Ta_2O_5, and Si_3N_4 do not appear to be sufficient for the recent trend. As a result, a new dielectric material that permits a capacitor with high charge storage density and compatible with semiconductor processing is required for DRAMs. Ferroelectrics as an alternative dielectric material with a higher dielectric constant have been widely interested by a number of researchers.[1] Ferroelectric thin films such as PZT, PLZT and PLT having the perovskite structure have been attracting great attention because of their potential applications in piezoelectric actuators, nonvolatile random access memory (NVRAM), DRAM and pyroelectric sensors.[2]

As La content in the equilibrium phase diagram of PLT system reaches to 28 mol%, it is well known that PLT film is transformed from the ferroelectric tetragonal structure into a paraelectric cubic phase, and their dielectric properties are excellent.[3] For DRAMs application, the hysteresis property of ferroelectrics is not actually desirable, and the capacitor operates only as a linear behavior. Therefore, the paraelectric PLT thin films with high dielectric constant and normal dielectric characteristics offer significant advantages for next generation of DRAMs.

An effect of La content on PLT thin films has not yet reported enough in detail.[3] In this study, a dc magnetron sputtering was utilized to deposit (Pb, La)TiO_3 thin films. PLT thin films with the La content were investigated by dielectric and electrical properties.

2. Experiments

The substrates of PLT thin film were Pt/Ti/SiO_2/Si multilayer, which consisted of (1 0 0) n-type Si with 500 nm thermally grown SiO_2, 50 nm Ti, and 200 nm Pt metal. Ti layer was used as an isolation barrier, and Pt metal was utilized as a buffer layer or a lower electrode. Ti and Pt were prepared by a dc magnetron sputtering, and PLT thin films were also deposited by a dc magnetron sputtering system. The original metals of target consist of Pb (99.999%), La (99.9%), and Ti (99.97%).

A heat treatment for the as-deposited PLT thin films (200 nm) was applied at annealing temperature ranges of 450–750 °C.

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The exact chemical formula of PLT film could be generally expressed $Pb_{1-x}La_xTi_{1-x/4}O_3$. The metal-ferroelectric-metal (MFM) configuration capacitors for the dielectric properties of ferroelectric PLT film (about 200 nm) were fabricated on multilayer. The dielectric constant with the different La concentration was measured using an impedance analyzer (HP4192A) at room temperature. The most frequently used test to characterize ferroelectric or paraelectric PLT thin films was a typical Sawyer–Tower circuit.[4] Polarization–electric field (*P*–*E*) characteristics for charge storage density were investigated by an HP54501A digitizing oscilloscope and function generator. Additional electrical properties such as current–voltage (*I*–*V*) plot for leakage current density and voltage–time (*V*–*t*) measurements for charging transient were estimated by a HP4145B semiconductor parameter analyzer.

3. Results and discussion

The dielectric constant on PLT thin films with various La contents is expressed in Fig. 1. All PLT films are annealed by the same condition of annealing heat treatment at 650 °C for 5 min. The dielectric constant of PLT films increases with a rise in La content. This phenomenon results from the lowering of Curie temperature, as shown in the results of Adachi et al.[5] It is due to the change from the ferroelectric tetragonal phase to paraelectric cubic state in the perovskite structure, as La content increases slightly in chemical composition of PLT films. Hennings and Hardtl[6] reported that the dielectric constant in PLT bulk ceramics increased with increasing La concentration, and the value was around 5500 at 20 °C. The dielectric constant and loss tangent at the La concentration of 28 mol% were 904 and 0.023, respectively.

Fig. 2 shows the relative dielectric constant of PLT films annealed at 650 °C and 5 min at the temperature range of 30–120 °C. The dielectric constant of PLT thin film at La concentration of 28 mol% decreases as a function of temperature. The peak of dielectric constant, so-called Curie temperature, is not observed in this temperature range. It is expected that the dielectric peak with the change of temperature locates in point lower than room temperature and is similar to the Curie temperature reported by Keizer et al.[7] The dielectric constant of PLT film at La content of 22 mol% shows the broad peak between 40 and 80 °C. Thus, the Curie temperature peak of PLT films has a tendency to decrease with increasing La concentration.

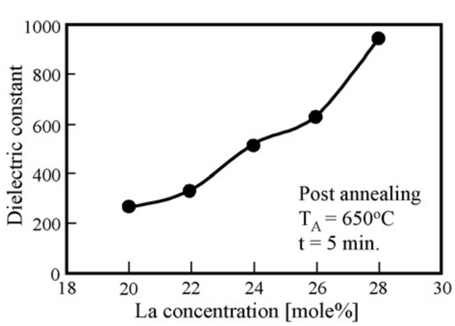

Fig. 1. Dielectric constant of PLT(28) films as a function of La concentration.

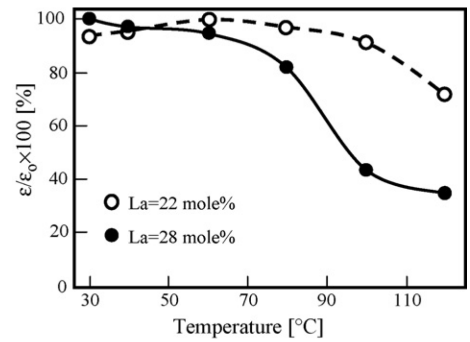

Fig. 2. Dielectric constant of PLT film with different temperature.

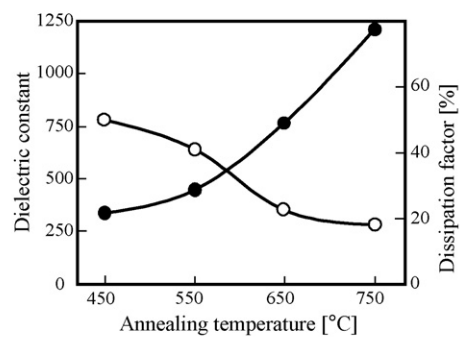

Fig. 3. Dielectric properties of PLT(28) films with post-annealing temperature.

The dielectric constant and dissipation factor of PLT films is shown in Fig. 3 as a function of post-annealing temperature. The dielectric constant increases significantly and the dissipation factor decreases slowly, as the annealing temperature increases. The dielectric properties are dependent on the changes in the stoichiometric composition as well as in relative quantities of amorphous and crystalline structures with variation of annealing treatment. With a rise in annealing temperature, the amorphous phase and the excess PbO structure disappear and transformed to the crystalline structure, i.e., the paraelectric perovskite PLT phase. However, the dissipation factor reduces from 0.051 to 0.018 with the increasing annealing temperature and the dependence on existence of the amorphous and excess PbO phases.

Fig. 4 describes the *P*–*E* characteristics as a function of annealing temperature at the same peak voltage of 4 V. The polarization of PLT(28) films with increasing post-annealing temperature is increased obviously. It is expected that some degree of crystallinity with increasing temperature have an

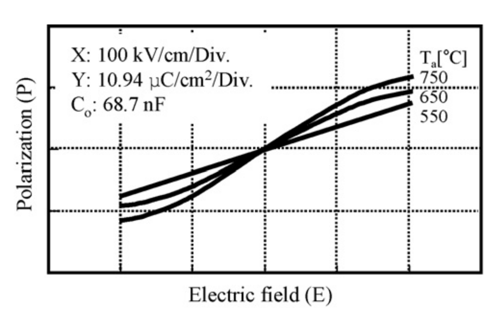

Fig. 4. *P*–*E* curves with annealing temperature for PLT films at peak voltage of 4 V (200 kV/cm).

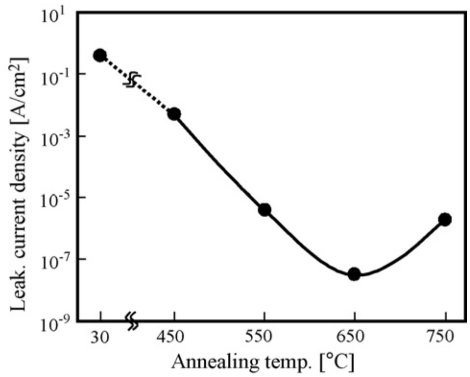

Fig. 5. Leakage current density with annealing temperature for films at 150 kV/cm.

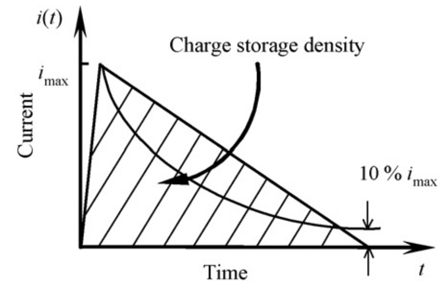

Fig. 6. The triangular area for charge storage density from *I*–*t* curve.

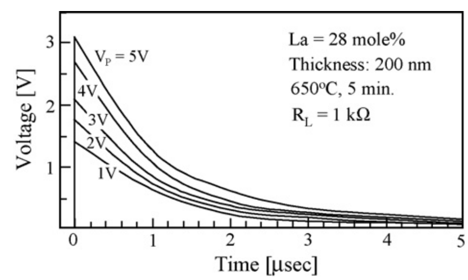

Fig. 7. *V*–*t* characteristics of PLT capacitor with different peak voltage of unipolar pulse.

influence upon the paraelectric nonlinear characteristics of the film.[3] The charge storage density at the peak voltage of 4 V is around 12.5 μC/cm^2 and the effective dielectric constant is about 706 for the PLT(28) film annealed at 750 °C for 5 min.

The leakage current density is one of important limiting factors for the DRAM capacitor dielectric. High leakage current places important limitation in the operation of a unit cell. The lowering trend of leakage current with different annealing temperature at the electric field of 150 kV/cm (3 V) is presented in Fig. 5. It is noted that the leakage current density with the increasing temperature is closely related to the degree of crystallinity. Since the intensity of each diffraction peak is proportional to the effect of a rise in post-annealing temperature, the paraelectric PLT(28) films are further crystallized into the cubic perovskite phase. The PLT film annealed at 750 °C exhibits larger leakage current density than at 650 °C. This elevation observed at high heat treatment shows a similar tendency with the results from Chikarmane et al.,[8] suggesting that the vaporization of Pb at high annealing temperature leads to the augmentation of oxygen vacancies. It is almost certain, from the results mentioned above, that the optimization between minimum leakage current density and maximum charge storage density is essentially adjusted by the conditions of post-deposition annealing process.

Voltage–time (*V*–*t*) characteristic is another method to obtain the charge storage density, and is able to calculate from the transient response of a MFM capacitor using the unipolar pulse measurement. The switching voltage is monitored with an oscilloscope by measuring the voltage drop across a grounded resistor in series with the film capacitor. The charge storage density is obtained by the measurement of the triangular area as shown in Fig. 6. The switching time (t_s) is defined as the time that decays to 90% down from the maximum current transient value. The simple approximation is estimated as the following:

$$Q'_C = \frac{1}{A}\int i\,dt = \frac{1}{A}\int_0^{\infty}\frac{V_{max}}{R_L}e^{-(t/\tau)}\,dt \cong \frac{V_{max}t_S}{2R_L A}$$

where V_{max} is the maximum response voltage, R_L the load resistance, and A is the area of the MFM capacitor.

Fig. 7 explains the *V*–*t* measurement with the different peak voltage of unipolar pulse. As the peak voltage of unipolar pulse is increased, the triangular area is not only increased but the charge storage density is also increased. The detailed results are summarized in Table 1. The charge storage densities at 1 and 5 V (250 kV/cm) peak voltages are 5.22 and 13.26 μC/cm^2, respectively.

Table 1
Charge storage density and dielectric constant estimated by *V*–*t* measurement

Peak voltage (V)	Electric field (kV/cm)	Charge storage density (μC/cm^2)	Dielectric constant
1	50	5.22	1179
2	100	6.80	768
3	150	8.59	647
4	200	11.3	638
5	250	13.26	599

4. Conclusions

The PLT films with the change of La concentration were successfully prepared by a dc magnetron sputtering. The as-deposited PLT films were annealed at the temperature ranging from 450 to 750 °C. The dielectric constant increases with a rise in La content. The dielectric constant of PLT(28) film decreases as a function of temperature. The dielectric constant increases and the dissipation factor decreases slowly, as the annealing temperature increases. The best results of dielectric constant and loss tangent in paraelectric PLT film annealed at 750 °C were 1216 and 0.018, respectively. The leakage current density in paraelectric PLT film at 650 °C was around 0.1 μA/cm^2 at 0.25 MV/cm. From *V*–*t* measurement, the charge storage density at 5 V is 13.26 μC/cm^2.

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