Preparation of Paraelectric PLT Thin Films Using Reactive Magnetron Sputtering of Multicomponent Metal Target

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Abstract

Paraelectric lead lanthanum titanate(PLT) thin films have been prepared by a reactive dc magnetron sputtering system using a multicomponent metal target. The surface area control of each element on the target markedly facilitates the fabrication of thin films of complex ceramic compounds. A postdeposition heat-treatment was applied to all as-deposited PLT thin films at annealing temperatures up to 750 ℃ for crystallization. The composition of the PLT(28) thin film annealed at 650 ℃ was: Pb, 0.73; La, 0.28; Ti, 0.88; O, 2.9. The dielectric constant and dissipation factor of the thin film(200 nm) at low field measurements (500 Vcm^{-1}) are 1216 and 0.018, respectively. The charge storage density using a typical Sawyer-Tower circuit with a 500 Hz sine wave was 12.5 μCcm^{-2} at the electric field of 200 $kVcm^{-1}$.

Introduction

In the development of ultra large scale integrated (ULSI) dynamic random access memory(RAM) technology, charge storage capacitors based on conventional dielectric materials have reached a serious limitation. Recently, many researchers have focused on ferroelectric oxides(*i.e.*, PT, PZT, PLT, and PLZT) as new dielectric materials with extremely high dielectric constant and high charge storage density. Of these ferroelectric oxides, lanthanum-doped lead titanate(PLT) has received attention due to its excellent dielectric and ferroelectric properties for memory device applications. The controllability of lanthanum(La) content within PLT ceramic oxides is applicable to nonvolatile memory devices and DRAMs. The addition of La in the Pb-La-Ti-O system has been shown to reduce transition temperature (so-called Curie temperature) and tetragonal ratio(c/a), and to increase dielectric constant[1].

The material structure with 28 mole percent(mole%) La content is transformed from tetragonal ferroelectric state to cubic paraelectric phase. The cubic paraelectric PLT thin films offer extremely high dielectric properties over nonlinear ferroelectric oxides[2].

An important factor in the preparation of ferroelectric oxide thin films is the deposition method. Results of dielectric and electrical properties for 28 mole% La-doped lead titanate deposited by sol-gel solution processing have been reported by Dey and Lee[2]. Methods of sol-gel processing in chemical solution and magnetron sputtering in physical vapor deposition have been reported as successful preparation techniques of ferroelectric ceramic films due to better control of film composition[2,3] Magnetron sputtering is a popular growth processing technique for ferroelectric oxide/semiconductor thin film-based devices when high quality and controllability of film thickness is considered. The target sources

for magnetron sputtering have used oxide alloy powder pellets and multimetal targets[4,5] In the oxide powder target, the film composition is adjusted by the amount of each component. Additional PbO is added to the target to compensate for loss of Pb caused by the evaporation from the target surface during the deposition process. However, the powder target process shows some disadvantages, including difficulty in target preparation of large-diameter powder alloy disk, reproducibility due to the altered layer on the target surface, and low deposition rate. The multicomponent metal target offers high deposition rate, possibility of a larger target, and easy control of target composition. In this paper we describe the method for preparing paraelectric lanthanum(28mole%) doped lead titanate thin films using reactive magnetron sputtering of multicomponent metal targets. Subsequently, a postdeposition annealing treatment for the as-deposited films was carried out to crystallize the film into the desired perovskite phase.

Experimental

PLT thin films were reactively deposited by a magnetron sputtering using a multicomponent metal target. The original metals of the multicomponent target consist of Pb(99.999%), La(99.9%), and Ti(99.97%). Several sectors of La, and a thin circular plate of Pb, are located on a 2.25 in. diameter and 0.25 in. thick disk-shaped Ti target. A typical schematic diagram of the multicomponent metal target is presented in Fig. 1. The content of an element in the deposited films is proportional to the fraction of the element in the multimetal target. As proposed by Fukami and Sakuma[4], and Hase and Shiosaki[6], the ratio of the Pb/La area on Ti disk target is determined by the modified Sigmund's method[7] which considers (*i*) sputtering yields for Pb, La, and Ti metal, (*ii*) Ti diameter due to (Pb +La)/Ti=1/1, and (*iii*) composition ratio of Pb/La on the deposited thin films. The film composition predicted for the *i*th element(C_i) is given by

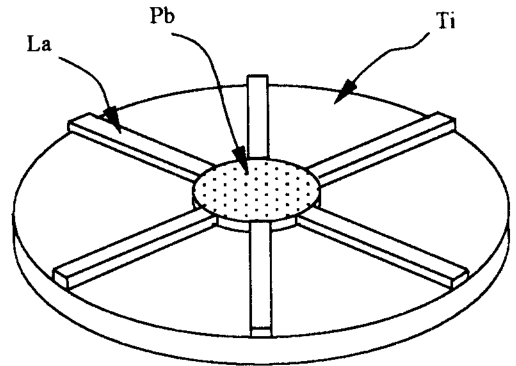


Fig. 1. Multicomponent metal target design for PLT film.

$$C_i = \frac{Y_i}{\sum y_i A_i} \times 100 \text{ [atom percent(atom\%)]}$$

where i corresponds to Pb, La, and Ti for PLT material, Y_i is the sputtering yield, and A_i is the occupied area on the target. The area ratio of each metal on the target surface is estimated from the above formula. The underlying thin films and the substrate on which the PLT thin film is deposited is $Pt/Ti/SiO_2/Si$ multilayer consisting of (100) n-type Si with 500 nm thermally grown SiO_2, 50 nm Ti, and 200 nm Pt metal. Prior to the fabrication of multilayer substrates, n-type Si (100) of 1 Ωcm resistivity is degreased in trichloroethylene for 5 min, and rinsed in acetone. The substrates are dipped in dilute HF solution($HF:H_2O$=1:10) for 30 sec, and rinsed in deionized water for 5 min.

Reactive magnetron sputtering is carried out by introducing an oxygen(purity 99.99%) and argon(99.999%) gas mixture. Sputtering parameters such as power, sputtering pressure, gas composition, substrate-target distance, and substrate temperature strongly affect the physical and chemical characteristics of the deposited PLT films. The details of sputtering conditions used in this experiment are summarized in Table I. The primary factors in the preparation and crystallization of PLT thin films are the adjustable control of oxidation kinetics and the Pb content of

Table Ⅰ. Optimized sputtering conditions for PLT deposition.

Sputtering conditions	PLT thin films
Power density (Wcm^{-1})	0.86
Gas pressure (mTorr)	20
Target-substrate distance (cm)	4
Sputtering gas	$Ar:O_2$ = 50:50
Deposition rate (nm min^{-1})	2.8
Thickness (nm)	200
Substrate temperature (℃)	160
Triode supply	
Plasma voltage (V)	60
Plasma current (A)	3

the films, since the element Pb tends to evaporate from the substrate at high temperatures. The most difficult factor to control in the stoichiometric composition of PLT films is the Pb concentration. Nonstoichiometric Pb content results from evaporation by heat-treatment, such as elevated substrate temperatures during the deposition or postdeposition annealing methods. The heated substrate process influences the overall plasma phenomena of reactive sputtering, and consequently an excess Pb content is required in the target composition. Therefore, the postdeposition annealing for as-deposited PLT thin films is not only a more preferential treatment, but also it can achieve a chemically stable compound, similar to methods used in the processing of ceramic bulk films[3]. In our experiments, the substrate heater was not used during the reactive magnetron sputtering deposition of PLT to minimize the unbalanced effect in the deposition rate of each metal element[9,10], suppress the Pb evaporation, and reduce the interreaction between the PLT film and substrate. The PLT thin films were annealed in a fused quartz tube furnace with flowing oxygen at a flow rate of 0.2 liter min^{-1}. The annealing conditions for all PLT films was set to a rate of 15 ℃ min^{-1} and a cooling rate was 5~6 ℃min^{-1}. The ranges of the annealing temperatures and annealing times were 550~750 ℃ and 5~50 min, respectively.

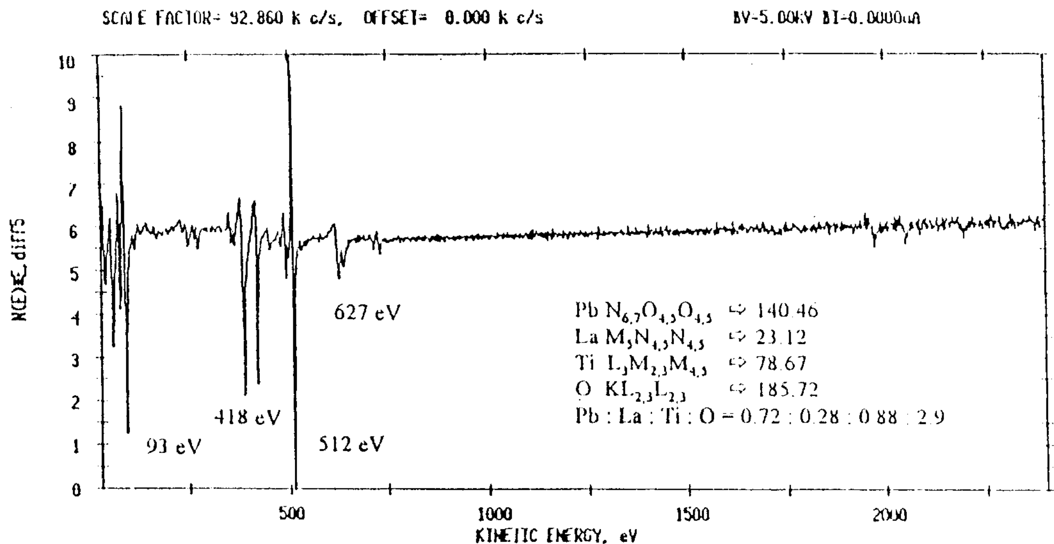


Fig. 2. AES spectrum of PLT(28) thin films deposited by the relative area ratio of sputtering target. Pb : La : Ti = 8.38 : 5.85 : 85.76 .

The primary concern in PLT(28) thin-film deposition is the stringent control of stoichiometric composition. Auger electron spectroscopy(AES; Perkin-Elmer, PHI 660, scanning Auger microscopy) was used to analyze the relative composition ratio of the Pb, La, Ti, and O content in each PLT thin films. The crystalline phases and lattice parameters of thin films were characterized using x-ray diffractometer (Rigaku D/MAX system and Phillips vertical diffractometer) with Cu-Kα radiation. The electrical properties are measured using a metal-PLT-metal configuration capacitor. Dielectric measurements are carried out on a Boonton 7200 capacitance meter with a peak voltage of 10 mV and a frequency of 1 kHz. Polarization-electric field(P-E) characteristics for charge storage density are measured by a typical Sawyer-Tower circuit.

Results and Discussion

Figure 2 shows a typical AES elemental survey for the perovskite PLT(28) thin films annealed at 650 ℃ for 5 min. Signals for elements present including Pb NOO at 93 eV, La MNN at 627 eV, Ti EMM at 418 eV, and O KLL at 512 eV. The AES signals for Ti consist of Ti LMM at 386 eV and Ti LMM at 418 eV. AES analysis indicates the composition of the PLT(28) film to be Pb, 0.73; La, 0.28; Ti, 0.88; O, 2.9. Compositional control of the PLT thin films was accompanied with the changes in relative area ratio of the multicomponent metal target. Table II shows the relationship between the relative composition of the perovskite PLT thin films annealed at 650 ℃ for 5 min and the corresponding area ratio of the multicomponent metal target.

The effect of a postannealing treatment vs. XRD patterns for several paraelectric PLT thin films is presented in Fig. 3. These films are of the same thickness(200 nm) and annealing time(5 min.). As-deposited PLT films produce XRD spectra consistent with an amorphous structure. The formation of a broad hump in the as-deposited film is presented from a 2θ of 20~

Table II. Relative composition of PLT thin films by AES analysis, and the corresponding area ratio of multicomponent metal target.

Conditions	Pb	La	Ti
Relative ratio of target area	8.38	5.85	85.76
Relative ratio of deposited film	38.62	14.81	46.56
Chemical composition	0.72	0.28	0.88

35° as shown in Fig. 3. The (100) and (110) peaks are not clear in the films treated at annealing temperatures of 450 ℃. After PLT films are annealed at a temperature above 550 ℃, XRD patterns exhibit the formation of the stable perovskite phase. Tetragonal splitting peaks of the

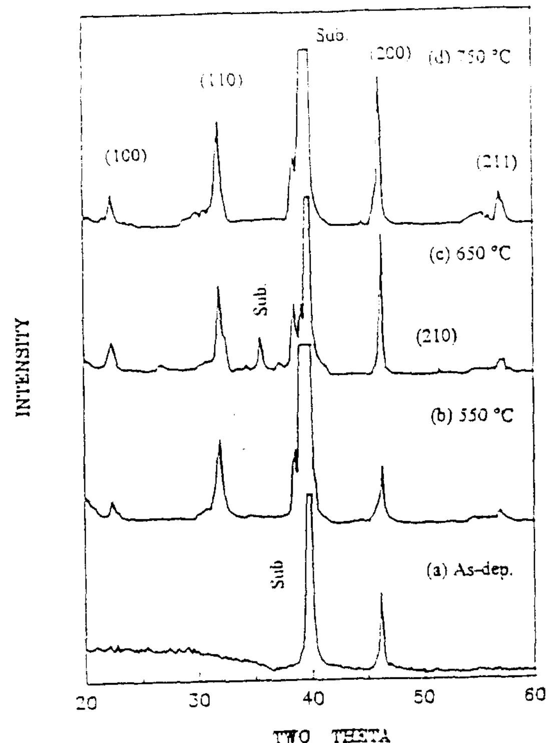


Fig. 3. XRD spectra of the paraelectric PLT(28) thin films as a function of postannealing temperature.

perovskite structure are not observed in the XRD spectra for PLT films. Typical diffraction peaks of the cubic perovskite phase such as (100), (110), (200), and (211) orientation arise completely in all PLT films. The other peaks identified are related to the substrate. It seems that the intensity of each peak in the XRD patterns increases up to the highest temperature of 750 ℃. The effect of heat-treatment with increasing annealing temperatures results in an increased intensity for each peak. Angular shifting of all diffraction peaks toward a higher angle with an increase in postannealing temperature is observed. The films may be influenced by changes of internal stress with increasing temperature[11] or by reduction of the amount of elemental Pb incorporated within the cubic perovskite structure[12]. The sharpness of the peaks indicates good crystallinity in the perovskite PLT films. The films annealed at 650 ℃ show a small (210) orientation peak of the cubic perovskite structure. The heat-treatment of PLT(28) thin films at 650 ℃ for 5 min results in the formation of the paraelectric perovskite structure with a lattice constant of $a = b = 0.394$ nm and oxygen-to-oxygen distance of 0.279 nm.

Figure 4 shows the XRD patterns of the perovskite films as a function of annealing time at a fixed annealing temperature of 650 ℃. As-deposited film shows an amorphous and a (111) peak for platinum, and all other peaks are associated with the substrate. For the PLT(28) thin films annealed at 650 ℃, an elevated annealing time shows only the typical formation of the perovskite phase, and the intensity of the diffraction peaks increases further. It is apparent that the slight shift in a typical PLT peaks occurs in the films annealed for a prolonged annealing period.

The dielectric constant and dissipation factor(or loss tangent) as a function of postannealing temperature are presented in Fig. 5. The dielectric constant increases significantly and the dissipation factor decreases slightly as the annealing temperature is increased. The dielectric properties are dependent on the changes in the stoichiometric composition as well as the relative quantities of

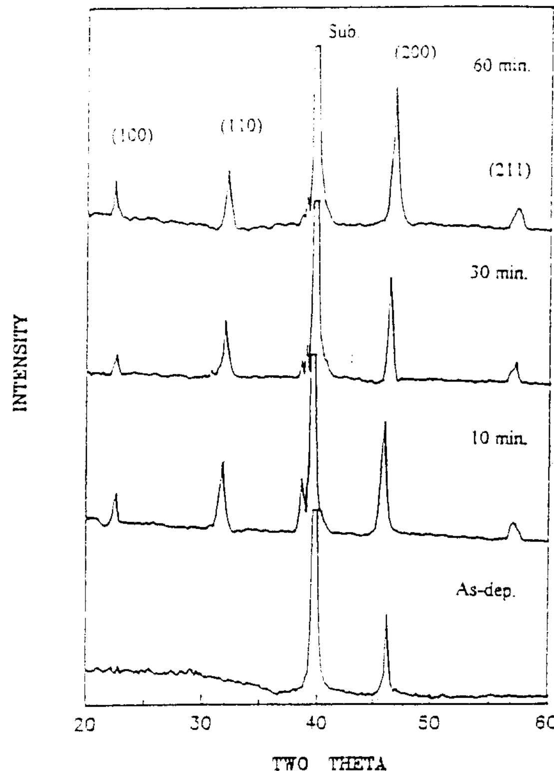


Fig. 4. XRD patterns of the paraelectric PLT(28) thin films as a function of annealing time at 650 ℃.

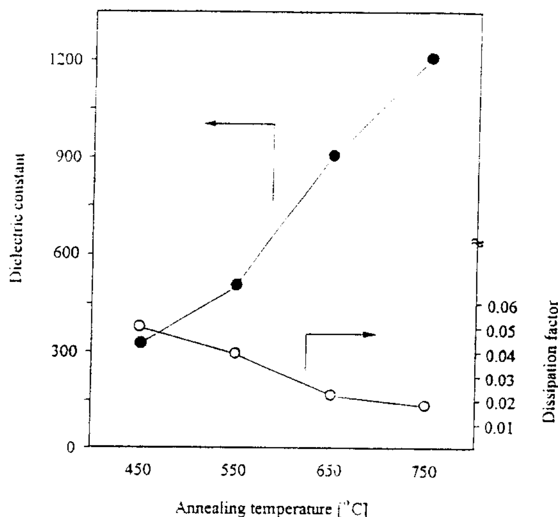
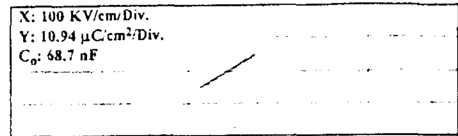


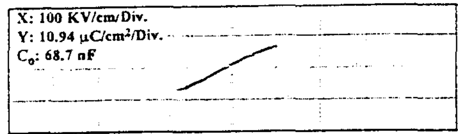
Fig. 5. Dielectric constant and dissipation factor of PLT(28) thin films as a function of postannealing temperature.

amorphous and crystalline structures with variation of annealing heat-treatment. Thus, with a rise in annealing temperature, the amorphous phase and the excess PbO structure with poor dielectric properties disappear and are transformed to the crystalline paraelectric perovskite PLT phase. Conversely, the dissipation factor decreases from 0.051 to 0.018 with the increasing annealing temperature, and with the dependence on the existence of the amorphous and excess PbO phases. The dielectric properties can be expressed by morphological conditions of the thin films with coexistence of the three phases such as perovskite PLT phase, excess PbO, and air. The excellent dielectric properties of PLT thin films are achieved by the continuity of the perovskite PLT phase. The PbO phase and porosity resulting from Pb evaporation give rise to the discontinuity of the perovskite PLT phase in the thin films. The PbO phase has a higher conductivity than the perovskite PLT phase. Therefore, the dielectric constant decreases and the dissipation factor increases due to the presence of excess PbO phases in the films annealed at lower annealing temperature.

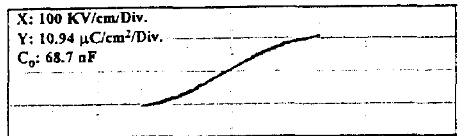
The polarization-electric field(P-E) characteristics of the paraelectric PLT(28) thin films are measured using a typical Sawyer-Tower circuit with a 500 Hz sine wave. Figure 6 shows the P-E characteristics with different peak voltage for the PLT(28) film heat-treated at 750 ℃ for 5 min. The P-E curve at low peak voltage of 1 V is similar to the linear behavior of a normal dielectric material as shown in Fig. 6 (top). The curves at a peak voltage of 2 V are gradually developed to the paraelectric state of nonlinear behavior, as the peak voltage increases enough. the charge storage density at the peak voltage of 4 V (200 $kVcm^{-1}$) is ~12.5 μCcm^{-2} as shown in Fig. 6 (bottom), and the effective dielectric constant is ~706. Recently, Adachi and Wasa[13] reported that the polarization of PLT(28) thin films exhibited a slim hysteresis loop. But the La content of 28 mole% in their films was the chemical composition in the powder target of RF magnetron sputtering. Therefore, the La content of the deposited PLT thin films was perhaps lower than that of the target material, and their P-E hysteresis with slim loop may be showing the ferroelectric behavior of PLT thin films.



(a) V_p = 1 V



(b) V_p = 2 V



(c) V_p = 4 V

Fig. 6. P-E characteristics with different peak voltages for 200 nm PLT(28) thin film at 750 ℃ for 5 min.

Conclusion

Paraelectric PLT(28) thin films were prepared successfully using reactive magnetron sputtering of multicomponent metal target. The individual control of each metal area on the sputtering target had considerable influence on the stoichiometry of the thin films. Further, the sputtering condition and postannealing treatment were important to the formation of crystalline phases and exact composition of films. The electrical characteristics were essentially dependent on the changes in the chemical composition and crystalline phase with the variation of annealing treatment. The best results of dielectric constant and dissipation factor in the film were 1216 and 0.018, respectively. The charge storage density was 12.5 μCcm^{-2} for the

200 nm PLT(28) thin film treated at an annealing temperature of 750 ℃.

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