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Influence of the gas mixture ratio on the electrical and ferroelectric properties of PLZT thin films

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A $(Pb_{0.92}La_{0.08})(Zr_{0.65}Ti_{0.35})O_3$ (PLZT) ferroelectric thin film was deposited on deposited on TiO_2 buffered layer on top of a Pt/Ti/SiO_2/Si substrate by RF magnetron sputtering method. The effect of the Ar/O_2 partial pressure ratio on the ferroelectric properties of PLZT thin films was investigated at various Ar/O_2 partial pressure ratios such as 27/1.5, 23/5.5, 21/7.5 and 19/9.5 sccm. The crystallinities of PLZT thin films were analyzed by XRD. The surface morphology was characterized by FE-SEM. The P-E hysteresis loops, the remnant polarization characteristics and the leakage current characteristics were obtained using a precision LC. With an increase of the oxygen partial pressure ratio, the crystallinity was decreased. Also the preferred orientation of PLZT thin films was changed from the (110) plane to the (111) plane. Results indicated that the change of the oxygen partial pressure ratio significantly affects the thin film surface morphology and the ferroelectric properties.

Key words: rf magnetron sputtering, ferroelectrics thin film, PLZT.

Introduction

In recent years, considerable research has been focused on the development of ferroelectric lead zirconate titanate (PZT) and lanthanum modified PZT (PLZT) thin films due to their application in non-volatile memories, optical waveguide devices, IR detectors, piezoelectric devices, sensors and actuators, electro-optic devices, and microelectromechanical systems [1-4]. In particular, non-volatile ferroelectric random access memories using PLZT thin films have been intensively investigated because of their outstanding ferroelectric characteristics and comparatively low processing temperatures. Among the fabrication methods such as sputtering, sol-gel and chemical vapor deposition [5-8], sputtering process is the most suitable process, owing to the compatibility of the integration with IC and MEMS fabrication technology [9]. Also the sputtering process yields a more reproducible and stable film properties then other process. In this study, the crystal structure, electrical and ferroelectric properties of PLZT films prepared by RF magnetron sputtering was investigated.

Experimental Procedure

The composition of PLZT used in this study was 9/65/35 with the formula $(Pb_{0.92}La_{0.08})(Zr_{0.65}Ti_{0.35})O_3$. The substrate used was Pt (300 nm)/Ti (30 nm)/SiO_2/Si. A seeding layer of TiO_2 deposited on the Pt bottom electrode was used prior to PLZT deposition. This layer promoted the crystallization of the perovskite phase and allowed the control of the growth axis. In order to realize the effect of the Ar/O_2 partial pressure ratio on the ferroelectric properties of PLZT thin films, we deposited PLZT thin films at various Ar/O_2 partial pressure ratios of 27/1.5, 23/5.5, 21/7.5 and 19/9.5 sccm. The sputtering process was done at a base pressure of 0.2 μPa, and a working pressure of 1.3 μPa was maintained by a mixture of argon and oxygen at a given gas ratio with a total flow of 28.5 sccm. After deposition, the thin films were annealed at 700 °C by a rapid thermal annealing (RTA) method. For electrical measurements, the Pt top electrode with a diameter of 0.2 mm was deposited through a shadow mask by RF magnetron sputtering. The deposition conditions of PLZT films are summarized in Table 1.

The crystalline structure of PLZT thin films was measured by X-ray diffraction (XRD, Rigaku, D/MAX 2200) with Cu Kα (λ = 1.5402 Å). The SEM observations of the thin films were carried out using a field-emission scanning electron microscopy (FE-SEM, Hitachi-4200, Japan). The ferroelectric and leakage current properties were characterized using a ferroelectric test system (Precision LC2000,

Table 1. Deposition Conditions for PLZT thin films

Materials	Ar/O_2	Substrate temperature	Power	Annealing
Ti	30/0	300 °C	DC, 80W	×
Pt(Bottom)	30/0	300 °C	RF, 80W	×
TiO_2	27/1.5	RT	RF, 80W	×
PLZT	27/1.5 23/5.5 21/7.5 19/9.5	300 °C	RF, 120W	700 °C
Pt(Top)	30/0	RT	RF, 40W	×

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Radiant Technologies) and an HP4192A impedance analyzer, respectively.

Results and Discussions

Structural properties

XRD spectra of the PLZT thin films deposited at various Ar/O_2 partial pressure ratios are shown in Fig. 1. The PLZT film deposited at a 27/1.5 sccm partial pressure ratio showed a pure perovskite phase with a [110] preferred orientation. However, the thin films deposited at 23/5.5 sccm partial pressure ratio exhibited a mixture of pyrochlore phase and perovskite phase. With an increase in the oxygen partial pressure ratio, the crystallinity was decreased. Also the preferred orientation of PLZT thin films was changed from the (110) plane to the (111) plane. The presence of a pyrochlore phase in the films with an increase in the oxygen flow ratios is attributed to Pb-deficiency [10].

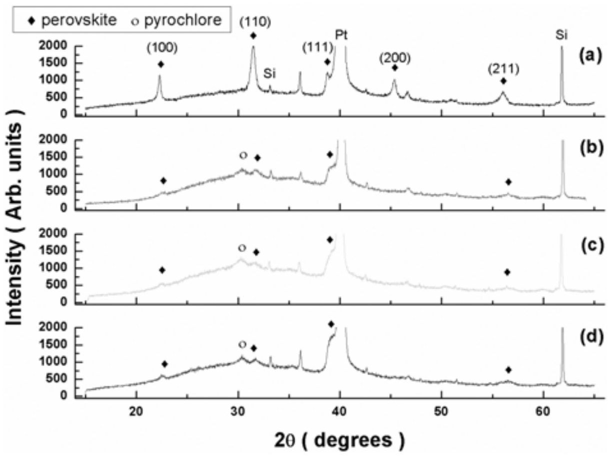

Fig. 1. XRD patterns of PLZT thin films deposited at various Ar/O_2 partial pressure ratios with (a) Ar/O_2 = 27/1.5 sccm, (b) Ar/O_2 = 23/5.5 sccm, (c) Ar/O_2 = 21/7.5 sccm, and (d) Ar/O_2 = 19/9.5 sccm.

Surface morphology

Fig. 2 shows surface micrographs of PLZT films deposited at various Ar/O_2 partial pressure ratios. The grain sizes and surface roughness of the films were investigated by FE-SEM. Results indicated that fine-sized grains grew with the decrease of the oxygen flow ratio. The roughness of the PLZT thin film also increased with the decrease of the oxygen flow during the deposition. Having in mind that the control of roughness and grain size are important parameters for application of PLZT as electrical materials, a deeper knowledge regarding the influence of the deposition atmosphere on the microstructure of PLZT thin films could obviously result in a better quality of these films [11].

Electrical properties

In order to study the resistivity of these films, I-V measurements were performed on a metal ferroelectric metal (MFM) structure. Fig. 3 shows the leakage current density of the films deposited at various Ar/O_2 partial pressure ratios. The leakage current characteristics were degraded

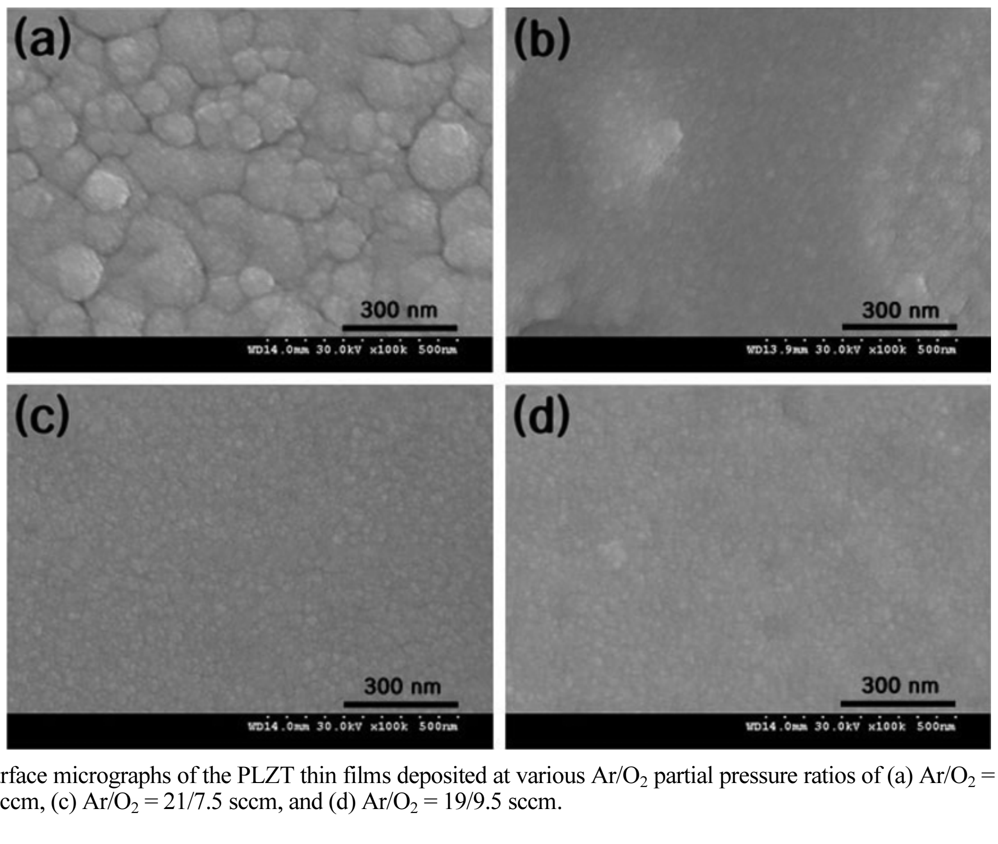

Fig. 2. SEM surface micrographs of the PLZT thin films deposited at various Ar/O_2 partial pressure ratios of (a) Ar/O_2 = 27/1.5 sccm, (b) Ar/O_2 = 23/5.5 sccm, (c) Ar/O_2 = 21/7.5 sccm, and (d) Ar/O_2 = 19/9.5 sccm.

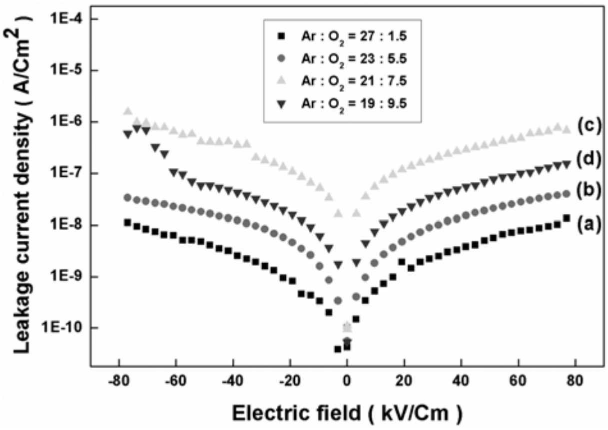

Fig. 3. Leakage current characteristics of the PLZT thin films deposited at various Ar/O_2 partial pressure ratios of (a) $Ar/O_2 = 27/1.5$ sccm, (b) $Ar/O_2 = 23/5.5$ sccm, (c) $Ar/O_2 = 21/7.5$ sccm, and (d) $Ar/O_2 = 19/9.5$ sccm.

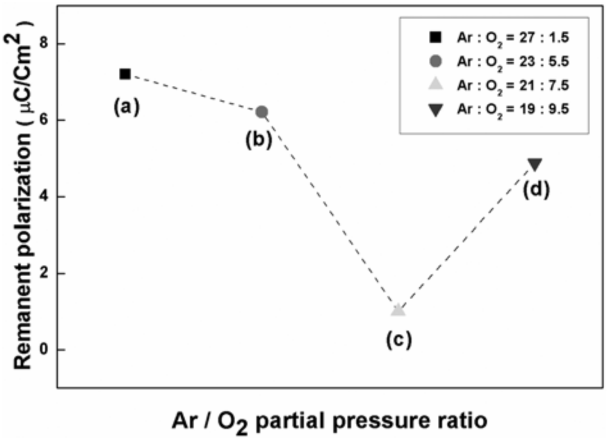

Fig. 5. Remnant polarizations of the PLZT thin films deposited in various Ar/O_2 partial pressure ratios of (a) $Ar/O_2 = 27/1.5$ sccm, (b) $Ar/O_2 = 23/5.5$ sccm, (c) $Ar/O_2 = 21/7.5$ sccm, and (d) $Ar/O_2 = 19/9.5$ sccm.

with an increase in the oxygen flow rate. The pure perovskite films deposited in a 27/1.5 sccm partial pressure ratio exhibit a low leakage current density of the order 10^{-8} A/cm^2 up to a field strength of around 80 kV/cm. Similar result reported that the resistivity in the range of 10^{-10}-10^{-6} A/cm^2 when a DC bias field of 0-80 kV/cm is applied to the capacitor [12]. These results indicate that the PLZT films have good insulating properties, which are desired for electronic applications.

Ferroelectrics properties

Fig. 4 shows the polarization-voltage characteristic of the PLZT thin films deposited at various Ar/O_2 partial pressure ratios. The shape of P-E curve indicates a classical ferroelectric nature in the films. The remnant polarization (Pr) values of the films are summarized in Fig. 5. The remnant polarization of the films deposited at ratios 27/1.5, 23/5.5, 21/7.5 and 19/9.5 sccm flow rates were 7.2, 6.4, 1.1, and 4.8 μC/cm^2, respectively. The films deposited at

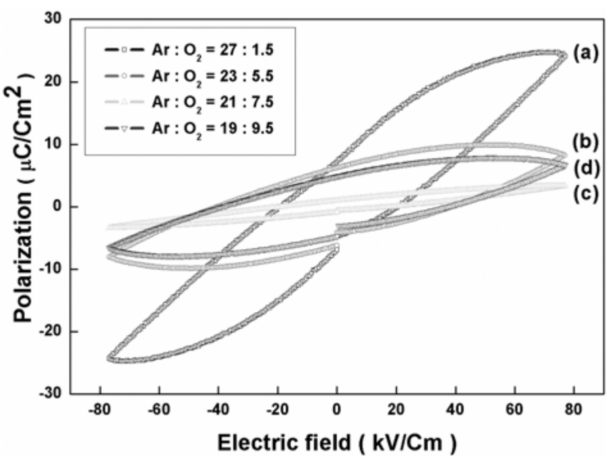

Fig. 4. Polarization-electric field characteristics of the PLZT thin films deposited at various Ar/O_2 partial pressure ratios with (a) $Ar/O_2 = 27/1.5$ sccm, (b) $Ar/O_2 = 23/5.5$ sccm, (c) $Ar/O_2 = 21/7.5$ sccm, and (d) $Ar/O_2 = 19/9.5$ sccm.

27/15 sccm partial pressure ratio exhibit good shapes of their hysteresis loops with a maximum polarization (Pmax) value of 27.4 μC/cm^2 and a coercive field (Ec) value of 19.6 kV/cm. We found that film attains a pure perovskite structure when decreasing the oxygen flow rate from 7.5 to 1.5 sccm, while the Pr value of a thin film increases from 1.1 to 7.2 μC/cm^2. This result is attributed to the appearance of a pyrochlore phase as shown in Fig. 1.

Conclusions

In this paper, PLZT thin film devices with an MFM structure were fabricated by RF magnetron sputtering method. In order to realize the effect of the Ar/O_2 partial pressure ratio on the ferroelectric properties of PLZT thin films, we deposited the PLZT thin films at various Ar/O_2 partial pressure ratios. The thin films deposited at 27/1.5 sccm, demonstrated the largest maximum polarization (Pmax), the largest remnant polarization (Pr), and the lowest leakage current density. However, ferroelectric properties of the PLZT film deposited at Ar/O_2 partial pressure ratio of 21/7.5 recorded the lowest value. In this study, the effect of Ar/O_2 partial pressure ratios significantly affects the leakage current of PLZT thin films. Generally, the formation of the perovskite phase is critically dependent on the stoichiometric composition of the films. In the case of Ar/O_2 partial pressure ratio of 21/7.5, the perovskite phase of the ABO_3 structure was not grown well, because of the inordinate inflow of oxygen.

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