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The ferroelectric and electrical properties of PLZT thin films

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La-doped lead zirconate titanate (PLZT) thin films were fabricated on Pt/Ti/SiO_2/Si substrates by RF magnetron sputtering method. The crystallinity and the electrical properties of the films were investigated as a function of deposition temperature. As the deposition temperature was increased, the preferred orientation of films was changed from the (110) to the (111) plane. The (110) plane decreases with further increase of the substrate temperature to 500 °C. The PLZT films deposited to 400 °C showed good electric properties with a remnant polarization of 15.8 μC/cm^2 and a leakage current of 5.4×10^{-9} A/cm^2. As the deposition temperature was increased 500 °C, the PLZT films tended to be Pb-deficient, resulting in the degradation of electrical properties.

Keywords: ferroelectrics, PLZT ($Pb_{0.92}La_{0.08}$)($Zr_{0.65}Ti_{0.35}$)O_3, TiO_2 buffer layer, substrate temperature.

Introduction

Lead-based ferroelectric films such as lead zirconate titanate (PZT) [1] and lanthanum doped PZT (PLZT) [2] have been extensively studied for applications to dynamic random access memories (DRAM) and nonvolatile ferroelectric random access memories (FRAM) [3]. PLZT thin films have attracted much attention for memory device applications due to their higher dielectric constants, lower coercive fields, and promising fatigue, retention and aging characteristics, as compared to PZT. Ferroelectric memories can be operated in a 2 transistor/2 capacitor (2T/2C) or in a 1 transistor/1 capacitor (1T/1C) mode. The 2T/2C mode offers the benefit of a reference capacitor for each cell and therefore an increased reliability margin. For high density applications, however, a 1T/1C approach is essential. Ferroelectric films prepared by various deposition techniques such as sol-gel [4], MOCVD [5], RF magnetron sputtering [6], laser ablation [7], ion-beam deposition [8] etc. show excellent characteristics. Among these methods, RF magnetron sputtering is widely used because qualified films can be obtained by a relatively simple fabrication process. Furthermore, it is compatible with various devices processing steps. In the study the microstructural characteristics of PLZT thin films deposited by RF magnetron sputtering are presented as a function of the substrate temperature. Heating the substrates during deposition was preferred as grain growth of the thin films was observed at various substrate temperatures. The formation, microstructure, and ferroelectric properties of the sputtered PLZT (8/65/35) thin films were analyzed using X-ray diffraction, field-emission scanning electron microscopy, and a ferroelectric tester.

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Experimental Procedure

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 allows the control of the growth axis. PLZT thin films were deposited at room temperature to 500 °C at 0.23 μPa. The target was pre-sputtered for 15 minute to eliminate contamination and maintain homogeneity of the target composition. The deposition conditions of PLZT films are summarized in Table I. The crystal structure of the PLZT films was characterized using X-ray diffractometry (XRD, Rigaku, D/MAX 2200) with Cu Kα (λ = 1.5402 Å) radiation. The film thickness and microstructure was investigated with a stylus (Dektak3) and field-emission scanning electron microscopy (FE-SEM, Hitachi-4200, JAPAN), respectively. A Pt/PLZT/Pt structure was fabricated to measure the electrical properties of the PLZT films. A Pt upper electrode a 0.3 mm in diameter was deposited

Table I. Sputtering conditions for ($Pb_{0.92}$,$La_{0.08}$)($Zr_{0.65}$,$Ti_{0.35}$)O_3 thin films.

Substrate	Pt/Ti/SiO_2/Si
Target	($Pb_{0.92}$,$La_{0.08}$)($Zr_{0.65}$,$Ti_{0.35}$)O_3
Substrate temperature	RT, 300 °C, 400 °C and 500 °C
RF power	120 W
Target-substrate distance	40 mm
Base pressure	30 μPa
Working Pressure	0.23 μPa
Working gas	Ar(9) : O_2(1)

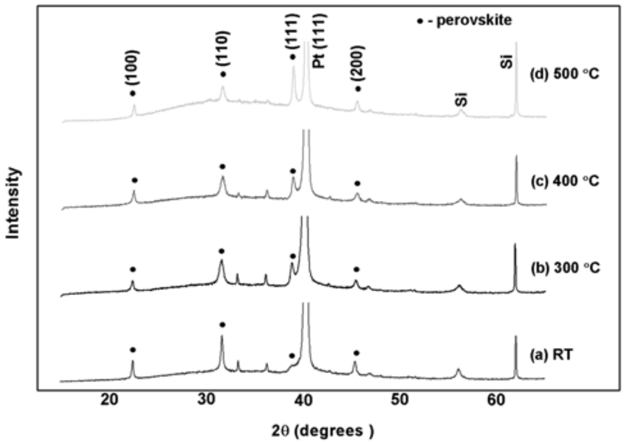

Fig. 1. XRD patterns of the films deposited at various substrate temperatures: (a)RT, (b) 300, (c) 400, and (d) 500 °C.

at room temperature using a shadow mask by RF magnetron sputtering. The leakage current density and P-E hysteresis loop were measured with a ferroelectric tester (Precision LC, Radiant Technologies). The PLZT films were rapidly annealed at 700 °C for 1 minute in air, and the concurrent changes in microstructure and electrical properties were examined.

Results and Discussions

Film crystallization

The effect of the substrate temperature during the film growth on the crystallization of PLZT films was examined by XRD. The PLZT compound has the perovskite structure. Fig. 1 shows the XRD patterns of PLZT thin films grown in situ at RT, 300, 400, and 500 °C. As the substrate temperature was increased, the PLZT thin films showed a preferred (111) orientation. When the substrate temperature increased to 500 °C, the (111) plane gave the strongest peak. The variation of the crystallographic orientation with different substrate temperatures was probably due to the different motilities of atoms on the substrate surface during the deposition process. It is known that the mobility of atoms on the substrate increases with deposition temperature [9].

Microstructure

Fig. 2 shows the surface morphology of the films deposited at RT, 300, 400, and 500 °C, respectively. With an increase in the substrate temperature, the grain size increased slightly and pin-holes appeared at temperatures above 500 °C. Also the size and density of pin-holes increased with the temperature. The substrate temperatures at which pin-holes appeared coincided with those at which a non-perovskite Pb-deficient second-phase formed. This may suggest that pin-hole generation is closely related to Pb-deficiency or to second-phase formation due to the Pb-deficiency [10].

Electrical properties

Fig. 3 shows the leakage current density of the films deposited at RT, 300, 400, and 500 °C. The leakage current characteristics were degraded with an increase in the substrate temperature and the current density at

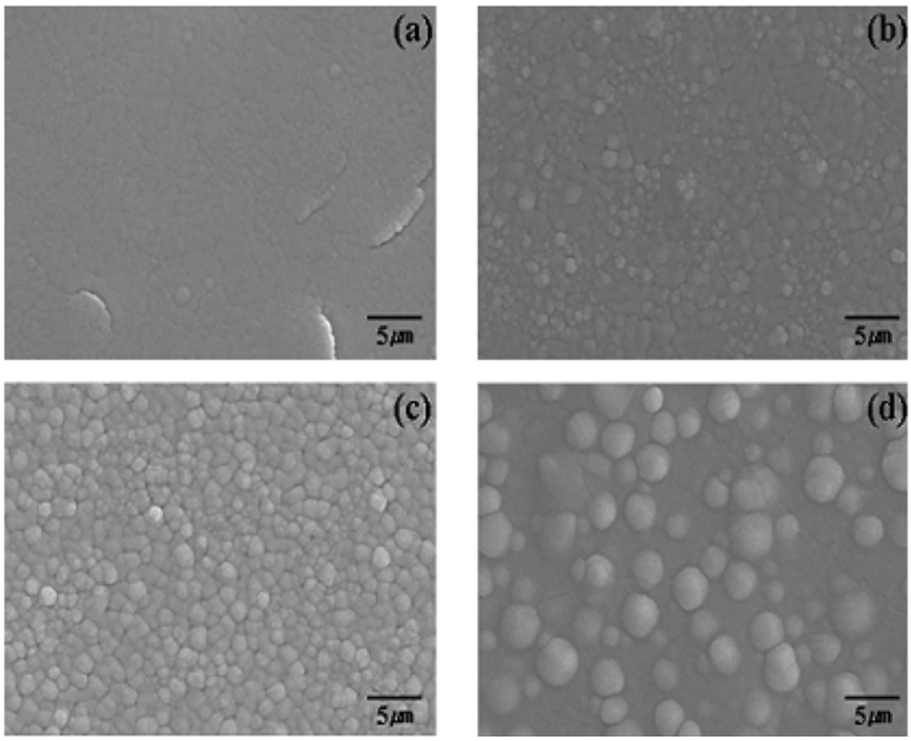

Fig. 2. SEM micrographs of the films deposited at various substrate temperatures: (a)RT, (b) 300, (c) 400, and (d) 500 °C.

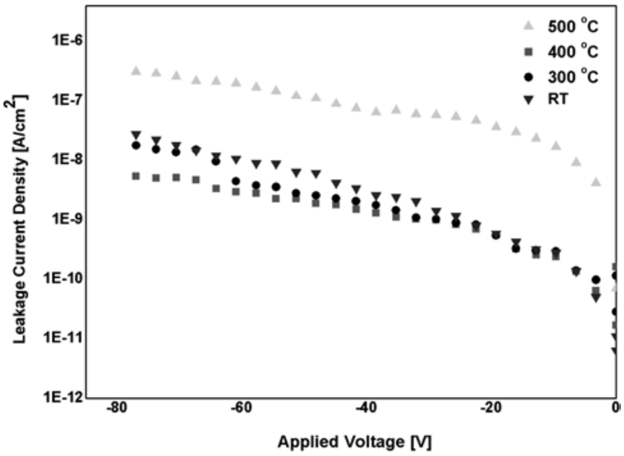

Fig. 3. I-V curves of the films deposited at various substrate temperatures: (a)RT, (b) 300, (c) 400, and (d) 500 °C.

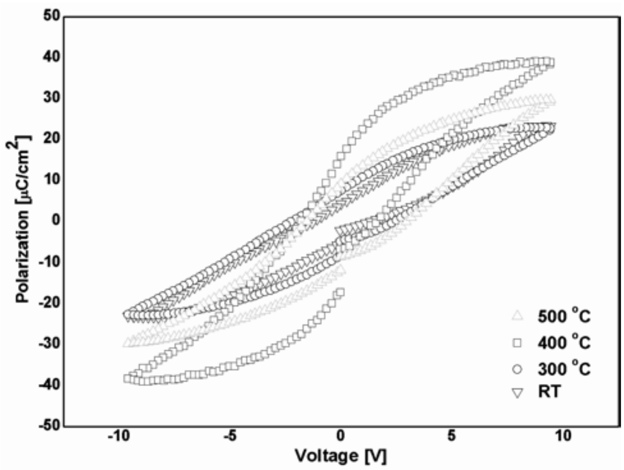

Fig. 4. P-V curves of the films deposited at various substrate temperatures: (a)RT, (b) 300, (c) 400, and (d) 500 °C.

500 °C was too high to be measured. PLZT films which were Pb-deficient contained a non-perovskite phase and a large amount of pin-holes, therefore producing significantly low leakage current characteristics.

Ferroelectrics properties

The ferroelectric behavior of the films was examined by observing the polarization-voltage characteristics. Fig. 4 shows the polarization-voltage characteristic of the PLZT thin films deposited at various temperatures. The remnant polarization of the films deposited at RT, 300, 400, and 500 °C were 4, 6, 15, and 9 $\mu C/cm^2$, respectively. The remnant polarization increased with the annealing temperature. This was probably due to the enhancement of the perovskite phase and growth of small crystallites in accordance with the XRD results.

Conclusions

In this paper, lead lanthanum zirconate titanate (PLZT) films were grown on TiO_2/Pt (111)/Ti/SiO_2/Si (100) substrates by RF magnetron sputtering. The effect of various substrate temperatures (Ts) was investigated on porevskite phase formation of PLZT films. With an increase in Ts, the preferred orientation of films was changed from (110) to (111). With an increase in Ts, most of the pyrochlore phase converted to the perovskite phase. When the growth temperature increased to 400 °C, the leakage current density and the coercive field (E_c) revealed some enhancement by a grain coarsening phenomenon.

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