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Electrical properties and microstructure of lead zirconate titanate (PZT) thin films deposited by pulsed-laser deposition

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Abstract

$Pb(Zr_{0.52}Ti_{0.48})O_3$ (PZT) thin films were prepared by pulsed-laser deposition (PLD) on $Pt/Ti/SiO_2/Si$ substrates and were crystallized by subsequent annealing at 750 °C for 90 min. Crystalline phases in the PZT films were investigated by X-ray diffraction (XRD) analysis. The microstructure and composition of the films were studied by transmission electron microscopy (TEM) and energy dispersive X-ray spectroscopy (EDS), respectively. It is found that the films consist almost entirely of the perovskite phase, but a thin layer of the pyrochlore phase exists at the surface of the films. Electrical properties of these films were evaluated by measuring *P–E* hysteresis loops and dielectric constants, and the effect of the microstructure on the electrical properties of the PZT thin films is discussed.

Keywords: B. Electron microscopy; D. PZT; Crystal structure; Ferroelectric materials

1. Introduction

There has been considerable interest in recent years in the development of lead zirconate titanate ($Pb(Zr_xTi_{1-x})O_3$: PZT) thin films, because their large number of potential applications in micro-electromechanical systems (MEMS) such as membrane-type micro-pumps [1], micro-scanning mirror devices [2,3] and atomic force microscopy (AFM) cantilevers [4,5]. Many fabrication techniques, such as the sol–gel method [6,7], pulsed-laser deposition (PLD) [8,9] and sputtering [10], have been used to fabricate PZT thin films. PLD is a promising technique for thick-PZT-film fabrication because it offers the advantage of a high deposition rate [9]. In our previous work, the effect of excess PbO in the PZT target on the electrical properties of PZT thin films were studied. It is found that the PZT films with a well-crystallized perovskite phase were obtained by adding 20 wt.% excess PbO to the PZT target and annealing at 750 °C for 90 min [9]. However, the electrical properties of the films were lower than those derived using the sol–gel process with the addition of 10 mol% excess Pb to the starting solution [7]. X-ray diffraction (XRD) analysis results show that the films derived by the sol–gel process and PLD consist almost entirely of the perovskite phase without the pyrochlore phase [7,9]. Therefore, the differences of the electrical properties between those films derived by the sol–gel process and PLD could be attributed to the differences between the microstructures of crystalline phases in those films. In order to clarify this point and obtain more detailed insight into the conditions for the formation of high-quality PZT films, it is necessary to examine the microstructure of crystalline phases of the films derived by PLD. In this work, The crystalline phases, microstructure and chemical composition of the PZT thin films fabricated by PLD were examined using XRD analysis, transmission electron microscopy (TEM) and energy dispersive X-ray spectroscopy (EDS), respectively. The dielectric constants and loss values of these films were measured at 1 kHz, and the ferroelectric properties were investigated by observing the polarization *P–E* hysteresis loop. On the basis of the obtained results, the effect of microstructures on the electrical properties of the films is discussed.

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Table 1
Deposition conditions of the PZT thin films

Target	$Pb(Zr_{0.52}Ti_{0.48})O_3$ + 20 wt.% PbO
Substrate temperature	RT
Base pressure (Torr)	10^{-7}
Gas pressure (Torr)	10^{-4}
Laser	KrF Excimer laser (248 nm)
Frequency (Hz)	10
Energy (J per shot)	0.4–0.9
Fluence (J/cm^2 per shot)	1.2
Target–substrate distance (cm)	8
Deposition time (min)	15
Film thickness (μm)	0.8

2. Experimental procedure

The laser deposition system is composed of a laser source and a deposition chamber. The light from a KrF excimer laser (wavelength: 248 nm) is introduced through a quartz SUPRASIL II window. The pumping system is composed of rotary and turbo-molecular pumps and the chamber can be evacuated to 10^{-8} Torr at room temperature. The targets used were dense ceramic pellets of $Pb(Zr_{0.52}Ti_{0.48})O_3$ (PZT) with 20 wt.% excess PbO, and their surfaces were polished prior to each ablation process. The distance from the target to the substrate was about 8 cm. A fast atom beam source (Ion Tech Ltd., FAB 110) is also available for cleaning the substrate and supplying the atoms during deposition. The applied voltage and the corresponding current were 0.5–0.8 kV and 10 mA, respectively. Chamber pressure during FAB treatment was 10^{-4} Torr. The deposition rate of the PZT films in this process was about 3 μm/h. The deposition conditions for the PZT thin films are summarized in Table 1. The films thus deposited at room temperature were annealed at 750 °C for 1.5 h.

The crystallographic structure of the films was examined using an X-ray diffractometer (Rigaku RINT2000, Cu Kα). The surface morphology of the films was observed by optical microscopy (OM) and scanning electron microscopy (SEM, JSM-6400F). The chemical composition of the films was studied by TEM–EDS (HF-2000). A Pt/Ti film was used for the bottom electrode, and an Au/Cr film was deposited by evaporation as the top electrode. The *P–E* hysteresis loop of these films was measured using a standardized ferroelectric test system (Radiant Technologies RT-60A), which uses the principle of a Sawyer-Tower circuit. The dielectric constant and loss values of these films were measured at 1 kHz using an impedance analyzer (Hewlett-Packard, HP4192A).

3. Results and discussion

3.1. Crystalline phases of the films

Fig. 1 shows the XRD pattern of PZT film fabricated by PLD and annealed at 750 °C for 90 min. As can be seen, no peak corresponding to the pyrochlore phase was detected. The patterns show that the films consist of mainly the perovskite phase without the pyrochlore phase. The XRD result is in good agreement with those of our previous work. Peaks for both the perovskite phase and the pyrochlore phase are observed in the films fabricated from PZT targets with 0 and 10 wt.% excess PbO and the peak of the pyrochlore phase disappeared in the films fabricated from PZT target with 20 wt.% excess PbO [9]. The XRD patterns also reveal that the film is without a strongly preferred crystalline orientation because peaks for (1 0 0), (1 1 1) planes and other planes of perovskite phase were observed.

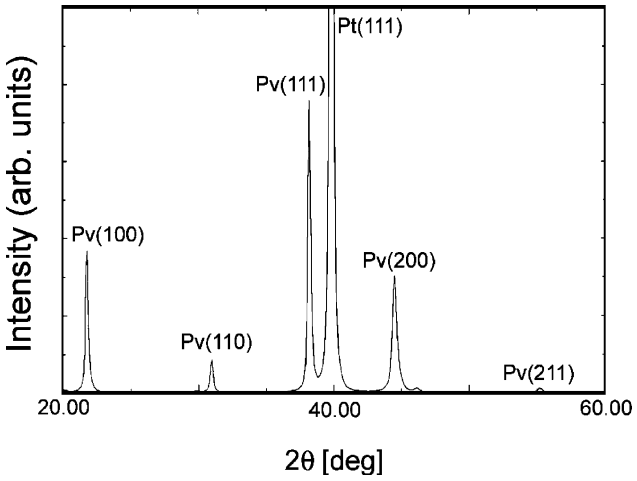

Fig. 1. XRD pattern of the PZT film fabricated from targets of $Pb(Zr_{0.52}Ti_{0.48})O_3$ with excess 20 wt.% PbO. Pv: perovskite phase.

3.2. Cross-sectional TEM observation of the films

Fig. 2 shows the cross-sectional TEM image of the PZT film. Fig. 2(a) is a bright-field TEM image and Fig. 2(b) is a dark-field TEM image. Both photographs were taken within the same area of the specimen. It can be seen that the majority of the film appears to be crystallized in the perovskite phase with columnar grains of approximately 0.3 μm size. The films deposited by PLD at room temperature exhibit a typical amorphous structure, and crystallized in the perovskite phase with columnar grains after post-deposition annealing. The columnar grain structure suggests that the nucleation of the perovskite phase began from the interface of the PZT/Pt. In our previous work [11], we observed that the films derived by a sol–gel process have a clear columnar structure with columnar grains of approximately 0.1 μm size. The difference of the width of the columnar grains between PLD and the sol–gel process may be a result of the uniformity of the chemical composition of those films, because the uniformity of the chemical composition can affect the nucleation sites of the perovskite phase. In fact, the uniformity of the chemical composition of the films derived by the sol–gel process is better than that derived by PLD. Fig. 2 also

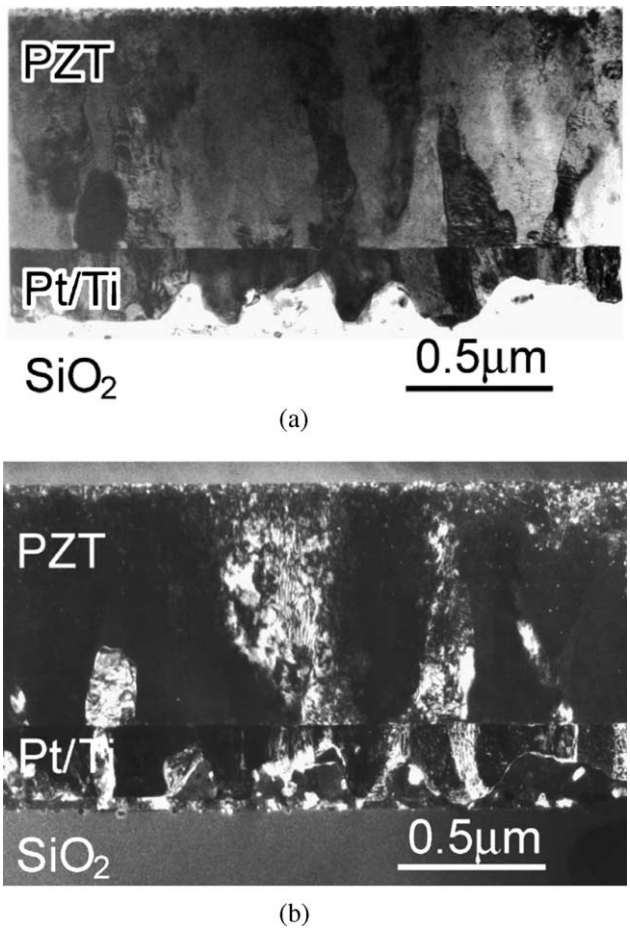

Fig. 2. TEM image showing a cross-section through the PZT/Pt/Ti/SiO_2 interfaces: (a) bright field and (b) dark field.

reveals that there is a thin layer of the second phase at the film surface.

Fig. 3 shows the cross-sectional TEM image near the surface of the film. It reveals that the thin layer of the second phase at the film surface is composed of small crystallites. HTEM micrographs of the small crystallites are showed that the measured sizes of the small crystallites are around 20 nm and are identified as the pyrochlore phase [12]. TEM–EDS analyses of this phase revealed that it was Pb-deficient compared to the perovskite phase (Fig. 4(a) and (b)). This suggests that the occurrence of the thin layer of the pyrochlore phase at the films surface could be attributed to the gradual evaporation of lead and lead oxide from the surface of the films at elevated temperatures during post-deposition annealing. In our previous work [13], the PZT films derived by the sol–gel process and annealed at 600 °C were almost fully crystallized in the perovskite phase without a thin layer of a pyrochlore phase at the film surface. In this work, the temperature of the post-deposition annealing was 750 °C, and significantly higher than that of the sol–gel process (600 °C). Thus, the evaporation of lead and lead oxide from the surface of the films at elevated temperatures is more acute than that in the case of the sol–gel process. In order to avoid the formation of a thin layer of the pyrochlore phase on the surface of the films, a lower post-deposition annealing temperature would be required.

3.3. Dielectric and ferroelectric properties

The dielectric constant and the loss value of the film measurements were carried out at a frequency of 1 kHz using

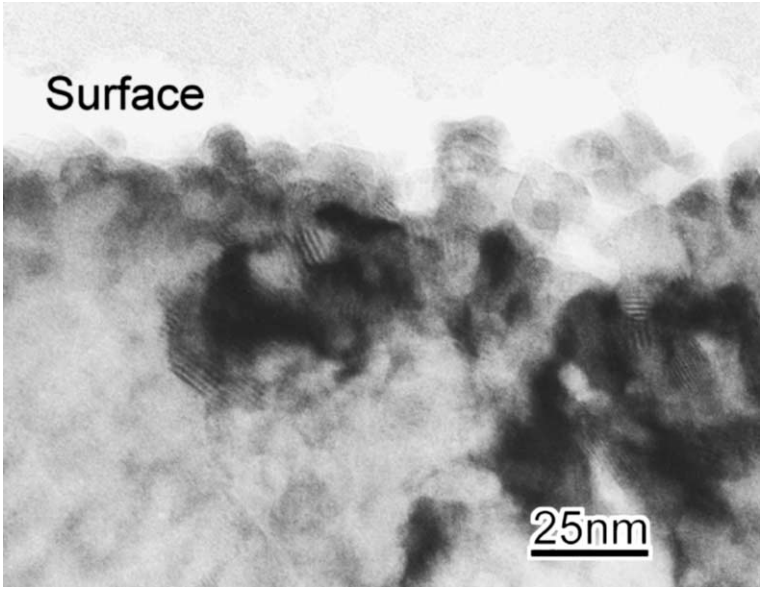

Fig. 3. Cross-sectional TEM image near the surface of the film.

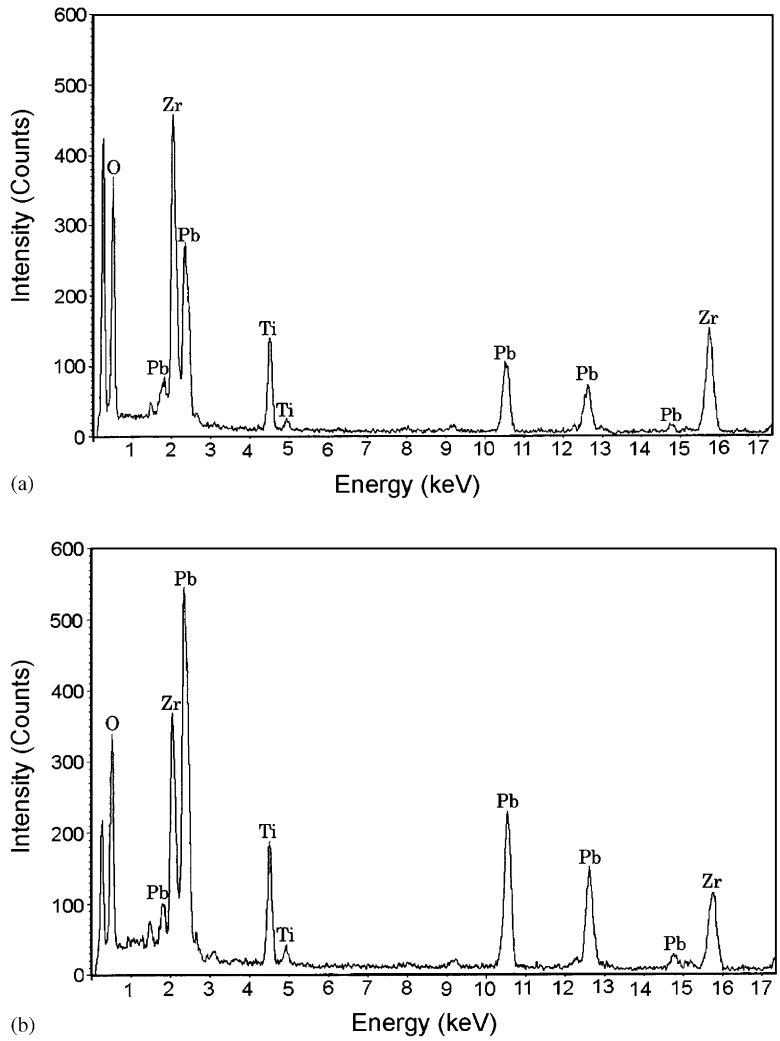

Fig. 4. Energy dispersive X-ray spectra of: (a) the small crystallites near the surface of the PZT film and (b) the perovskite phase.

an impedance analyzer. The ferroelectricity was investigated by observing the polarization hysteresis loop. The dielectric and ferroelectric parameters of the films are listed in Table 2. In order make a comparison, the dielectric and ferroelectric parameters of the PZT films deposited by the sol–gel method in our previous work [7] are also listed in Table 2. The electrical properties of the film derived by PLD in this work were lower than that of the film derived by the sol–gel method. This may be attributed to the difference between the microstructures of these films. The PZT films derived by the sol–gel process with the addition of 10 mol% excess Pb to the starting solution consist of the perovskite phase without a non-ferroelectric phase and have the (1 0 0) preferred orientation. In comparison, the film derived by PLD in this work consists almost entirely of the perovskite phase, but a thin layer of the pyrochlore phase exists at the surface of the film. The layer of the pyrochlore phase at the surface detrimental to the electrical properties of the film. In order to improve the electrical properties of the PZT films, it is necessary to prevent the formation of a thin layer of the pyrochlore phase on the surface of the films. Though the electrical properties of the PZT film derived by PLD in this work were lower than those of the films deposited by the sol–gel method, PLD for fabricating PZT films is still expected, because PLD offers the advantage of a high deposition rate. In addition, the electrical properties of the PZT films may be improved by obtaining a better microstructure, which is almost fully crystallized in the perovskite phase without a thin layer of the pyrochlore phase on the film surface.

Table 2
Dielectric and ferroelectric properties of the PZT films fabricated by PLD and the sol–gel method

Processing	ε_r	$\tan\delta$	P_r ($\mu C/cm^3$)	E_c (kV/cm)
PLD	950	0.04	23.9	60.5
Sol–gel method	1600	0.04	34.8	41.7

4. Conclusions

Thin films of $Pb(Zr_{0.52}Ti_{0.48})O_3$ were prepared by PLD on a $Pt/Ti/SiO_2/Si$ substrate and were crystallized by subsequent annealing at 750 °C for 90 min. It is found that the films mainly consist of the perovskite phase, but a thin layer of the pyrochlore phase exists at the surface of the films and the thin layer of the pyrochlore phase detrimental to the electrical properties of the PZT films. In order to avoid the formation of a thin layer of the pyrochlore phase on the surface of the films, a lower post-deposition annealing temperature would be required.

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