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Preparation and characterization of PZT thin films deposited by pulsed laser deposition on template layer

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Abstract

$Pb(Zr_xTi_{1-x})O_3$ thin films were prepared by pulsed laser deposition using the target of $Pb(Zr_{0.45}Ti_{0.55})O_3$ with excess PbO (20 wt.%) on $Pt/Ti/SiO_2/Si(100)$ substrates with and without a template layer derived by the sol-gel process. Crystalline phases and microstructure of the PZT films were investigated using X-ray diffraction analysis and scanning electron microscopy, respectively. The electrical properties of the PZT films were evaluated by measuring the polarization versus electric field hysteresis loop and the dielectric constant. In comparison with the experimental results, it was found that the template layer derived by the sol-gel process could effect the crystallographic orientation, and improve the electrical properties of the PZT films. It is clear that 1–3 μm thick films with good electrical properties can be fabricated by the pulsed laser deposition process on the template layer in a shorter time.

Keywords: Electrical properties; Electron microscopy; Films; PZT; X-ray methods

1. Introduction

Lead zirconate titanate $Pb(Zr_xTi_{1-x})O_3$ (PZT) films have attracted great interest, because of their applications in micro-electromechanical systems (MEMS) such as micro-scanning mirror devices and atomic force microscopy (AFM) cantilevers. For use in these micro-actuators, in order to obtain a large displacement, high-quality 3 μm thick PZT films on electrodes/substrates are desirable.[1] Many fabrication techniques, such as the sol-gel process,[2] pulsed laser deposition (PLD)[3] have been used to fabricate PZT films. The sol-gel method is one of the most promising techniques for PZT thin film fabrication, because it enables the realization of high purity, large deposition area and easy composition control. However, generally, the limiting thickness of a crack-free single-layered film is about 0.15 μm for the sol-gel method. The deposition of 3 microns needs more than 20 repetitions (needs over 40 h) of the coating and firing procedure, which increases the risk of contamination, and leads to Pb diffusion between the PZT layer and the bottom electrodes.[2] PLD is another promising technique for PZT film fabrication, because it offers the advantage of a high deposition rate (about 3 microns per hour), which allows a thicker PZT film to be fabricated in a shorter time.[3] However, the electrical properties of the PZT films derived by the PLD process are inferior to those of the films derived by the sol-gel process. One of the most significant reasons for this is that the post-deposition annealing temperature in the PLD process is 750 °C, and significantly higher than that of the sol-gel process (600 °C). Thus, the evaporation of Pb and PbO from the surface of the films at elevated temperature is more acute than that in the case of the sol-gel process, and leads to the formation of a thin layer of the pyrochlore phase on the surface of the films.[4] Hence, in order to improve the electrical properties of the PZT films derived by the PLD process, a lower post-deposition annealing temperature would be required.

In the synthesis and crystallization of PZT films, one of the most important factors is the control of the Pb content and the Zr/Ti ratio of the films. It is well known that the use of excess Pb in the starting solution (in sol-gel process) or target compensates (in PLD and sputtering process) for Pb loss at the surface of the PZT films and prevents the formation of a continuous layer of Pb-deficient crystal.[5, 6] In our previous work, we found that the addition of at least 20 wt.% excess PbO to the PZT target is necessary to obtain a single perovskite phase.[3] We also found that the PZT films

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fabricated from the target with Zr/Ti ratio of 45/55 exhibited better electric properties than those of the PZT films fabricated from the target with Zr/Ti ratio of 52/48, and their composition is close to the morphotropic phase boundary (52/48). Hence, in this work, we fabricated the PZT films onto $Pt/Ti/SiO_2/Si(100)$ substrates using the target of $Pb(Zr_{0.45}Ti_{0.55})O_3$ with excess PbO (20 wt.%). In order to lower the post-deposition annealing temperature and improve the electrical properties of the PZT films, a thin intermediate PZT layer was deposited on $Pt/Ti/SiO_2/Si(100)$ substrates using the sol-gel process prior to the PLD process. Based on the experimental results, the role of the template layer for PZT fabrication by the PLD process is discussed. We also attempt to fabricate the thicker PZT films using this hybrid processing.

2. Experimental

The $Pt/Ti/SiO_2/Si(100)$ substrates were prepared by sputtering the 0.05 μm thick titanium film and 0.15 μm thick platinum film onto oxidized (1.8 μm of SiO_2) Si(100) substrates.

At first, a thin PZT template layer was deposited on $Pt/Ti/SiO_2/Si(100)$ substrates using the sol-gel process. The composition of the precursor solution was controlled in the ratio of Pb:Ti:Zr = 1.2:0.48:0.52. The PZT template layer was fabricated on $Pt/Ti/SiO_2/Si(100)$ substrates using a spin coater operated at 2600 rpm for 20 s and 4000 rpm for 40 s. The coated films were dried at 120 °C for 20 min and 300 °C for 20 min, and then finally annealed at 600 °C for 30 min to crystallize the films into a perovskite-type structure.

The pulsed laser deposition system is composed of a laser source and a deposition chamber with a substrate holder for 3-inch wafers. The substrate could be rotated for deposition uniformity. Light from a KrF excimer laser (wavelength: 248 nm) was introduced through a quartz SUPRASIL II window. The pumping system was composed of rotary and turbo-molecular pumps and the deposition chamber could be evacuated to 10^{-7} Torr at room temperature. The targets used were ceramic pellets (relative density: about 85%) of $Pb(Zr_{0.45}Ti_{0.55})O_3$ with excess PbO (20 wt.%), and their surfaces were polished prior to each ablation process. The distance between the target and the substrate was approximately 10 cm. During deposition, O_2 was introduced into the deposition chamber and the partial chamber pressure was 10^{-4} Torr. The PZT films were deposited on $Pt/Ti/SiO_2/Si(100)$ substrates with and without the template layer at room temperature. After laser deposition, all of the PZT films were annealed at 700 °C for 90 min.

The crystalline structure of the PZT films was examined using an X-ray diffractometer (XRD, Rigaku RINT2000, Cu$K\alpha$). The surface and cross-section morphology of the films were observed by scanning electron microscopy (FE-SEM, JSM-6500F). The Pt/Ti film was used as a bottom electrode, and an Au/Cr film was deposited by sputtering to form the top electrode. The *P–E* hysteresis loop of these films was measured using a standard ferroelectric test system (Radiant Technologies RT-60A), which uses the principle of a Sawyer-Tower circuit. The room-temperature dielectric constant (ε_r) and loss value ($\tan\delta$) of these films were measured at 1 kHz using an impedance analyzer (Hewlett-Packard, HP4192A).

3. Results and discussion

3.1. Cross-section and surface morphology of the films

Fig. 1 shows the cross-section morphology of the PZT film fabricated by the PLD process on the template layer. The PZT film is about 0.7 μm thick and is crack free and dense. No boundary between the PZT layers derived by the sol-gel process and the PLD can be observed. This means that the adherence of the PZT layers is very good. The surface morphology of the film fabricated by the PLD process on the template layer is shown in Fig. 2. As can be seen, the film has spherulite grain structure and the most of the grain size is approximately 200 nm.

3.2. Crystalline phases of the films

Fig. 3(a) shows the XRD pattern of the template layer fabricated by the sol-gel process. The XRD pattern shows that the template layer consists of the perovskite phase without the pyrochlore phase. The peaks of the perovskite phase [(100) and (111) planes] are very small, because the thickness of the PZT template layer is very

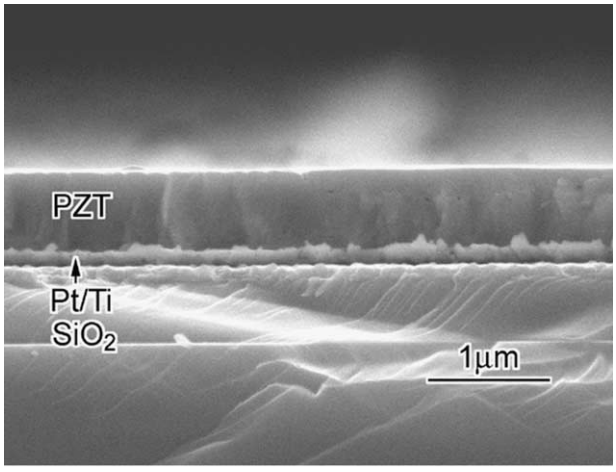

Fig. 1. Cross-section morphology of the PZT film fabricated by the pulsed laser deposition on the template layer.

thin (about 130 nm). Fig. 3(b) shows the XRD pattern of the PZT film fabricated by the PLD process on the template layer. The pattern also shows that the film consists of mainly the perovskite phase without the pyrochlore phase. Previous research conducted by our group had revealed that in the PZT films deposited by the PLD process, the peak of the pyrochlore phase disappeared after annealing at 750 °C for 90 min.[3] This means that the PZT template layer lowered the crystallization temperature to perovskite phase transformation

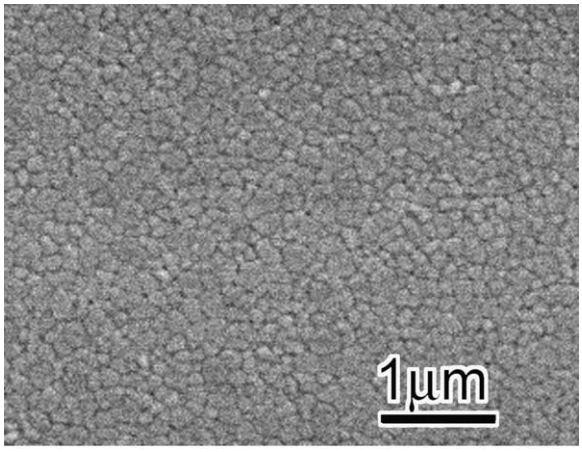

Fig. 2. Surface morphology of the PZT film fabricated by the pulsed laser deposition on the template layer.

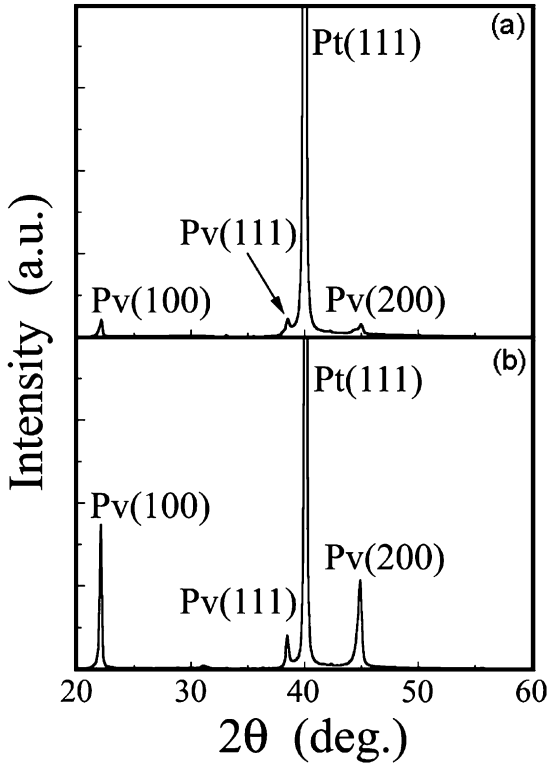

Fig. 3. XRD patterns of the template layer fabricated by (a) the sol-gel process, and (b) the PZT film fabricated by the pulsed laser deposition on the template layer. Pv: perovskite phase.

of the PZT films deposited by the PLD process. In addition, the XRD pattern only shows the strong peaks of (100) and (111) planes, and are similar to that of the template layer. This suggests that the template layer can effect the crystallographic orientation of the films derived by the PLD process. In the case of the multilayer PZT films derived by the sol-gel process, the crystallization to the perovskite phase of the subsequently coated layer is influenced by the surface of the underlying layer.[7] High-resolution electron microscope image of the interface between the layers reveals that the crystalline lattice of the layers is continuum.[8] Namely, the first spin-on layer serves as a perovskite seeding layer for subsequent layers, and the subsequent layers grow epitaxially on top. However, in order to clarify the solid-phase epitaxial effect between the PZT layers derived by the sol-gel process and the PLD process, further investigation is required.

3.3. Dielectric and ferroelectric properties

The dielectric constant and dielectric loss tangent measurements were carried out at a frequency of 1 kHz using an impedance analyzer. The dielectric constant and loss value in the films fabricated on the template layer were about 1069.11 and 0.08, respectively.

Ferroelectricity was investigated by observing the polarization hysteresis loop under the low voltage mode (maximum drive voltage: 19.9 V). Fig. 4 indicates the differences in ferroelectric properties between the PZT films fabricated by the PLD process with and without the template layer. The PZT film fabricated by the PLD process on the template layer exhibits the largest value of the spontaneous and remnant polarization. The ferroelectric parameters were as follows: spontaneous polarization $P_s = 50.53$ μC/cm^2, remanent polarization $P_r = 31.28$ μC/cm^2, and coercive field $E_c = 45.29$ kV/cm.

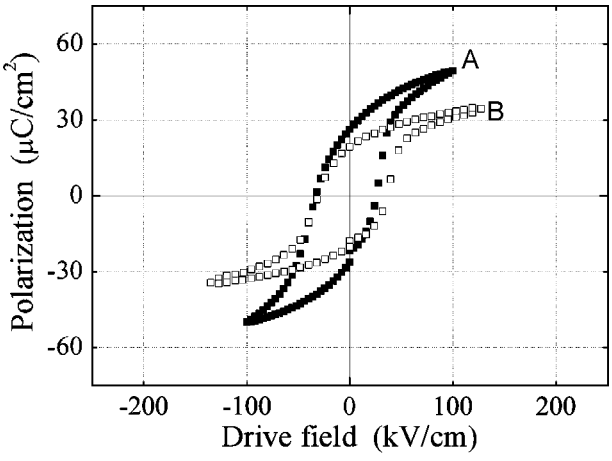

Fig. 4. Polarization versus electric field hysteresis loops of the PZT films fabricated by the pulsed laser deposition on Pt/Ti/SiO2/Si substrates with the template layer (denoted by A), and without the template layer (denoted by B).

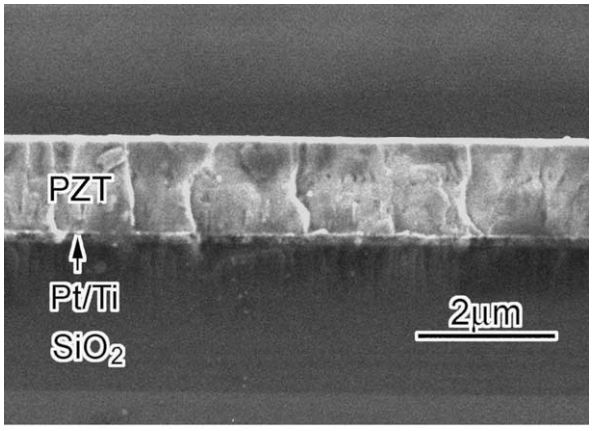

Fig. 5. Cross-section morphology of a thicker PZT film fabricated by the pulsed laser deposition on the template layer.

In the case of PZT films fabricated without the template layer, the ferroelectric parameters were as follows: spontaneous polarization $P_s = 31.32$ μC/cm^2, remanent polarization $P_r = 19.06$ μC/cm^2, and coercive field $E_c = 34.57$ kV/cm. In comparison with these results, the PZT film fabricated on the template layer exhibits better ferroelectric properties.

The increase in the electrical properties for the PZT films fabricated on template layer can be attributed to the fact that the PZT film consists entirely of the perovskite phase, as indicated by XRD data. The template layer provides the nucleation sites for crystallization of the PZT films fabricated by the PLD process and lowered post-deposition annealing temperature. The post-deposition annealing carried out at lower temperature can decrease the evaporation of Pb and PbO from the surface of the films and prevent the formation of a continuous layer of Pb-deficient crystal on the surface. The films fabricated on the template layer have spherulite grain structure of the perovskite phase and no second phase can be observed on the surface (Fig. 2).

At last, the thicker PZT films were fabricated by the PLD process on the template layer. The cross-section morphology of the PZT film fabricated on the template layer by the PLD process with deposition time of 1.5 h is shown in Fig. 5. The PZT film is about 1.5 μm thick and is crack-free and dense. As mentioned above, the thickness of a single-layered PZT film for the sol-gel process is about 0.15 μm, and the deposition of 1.5 microns needs more than 10 repetitions (needs over 20 h) of the coating and firing procedure. It is clear that 1–3 μm thick films with good electrical properties can be deposited by the PLD process on the template layer in a shorter time.

4. Conclusions

$Pb(Zr_xTi_{1-x})O_3$ thin films were prepared by pulsed laser deposition using the target of $Pb(Zr_{0.45}Ti_{0.55})O_3$ with 20 wt.% excess PbO on $Pt/Ti/SiO_2/Si(100)$ substrates with a template layer derived by the sol-gel process, and subsequently annealed at 700 °C for 90 min. The crystalline structure of the PZT films was examined using X-ray diffraction analysis. The surface and cross-section morphology of the films were observed by scanning electron microscopy. The electrical properties of the PZT films were evaluated by measuring the polarization versus electric field hysteresis loop and dielectric constant. It was found that the template layer derived by the sol-gel process could lower the post-deposition annealing temperature, effect the crystallographic orientation, and improve the electrical properties of the PZT films. It is also clear that 1–3 μm thick films with good electrical properties can be fabricated by the pulsed laser deposition process on the template layer derived by the sol-gel process in a shorter time.

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