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# EPITAXIAL PZT FILMS DEPOSITED BY PULSED LASER DEPOSITION FOR MEMS APPLICATION

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## ABSTRACT

$Pb(Zr_{0.52}Ti_{0.48})O_3$ (PZT) thin films were in situ deposited by pulsed laser deposition (PLD) on $Pt/Ti/SiO_2/Si$ substrates using a template layer derived by a sol-gel method. A 0.15-µm-thick PZT layer with (111)-preferred orientation was first deposited onto $Pt/Ti/SiO_2/Si$ substrates using the sol-gel method, and than a PZT layer was in situ deposited by PLD on the above-mentioned PZT layer. The crystalline phases and the preferred orientations of the PZT films were investigated by X-ray diffraction analysis. Surface and cross-sectional morphologies were observed by scanning electron microscopy and transmission electron microscopy. The electrical properties of the films were evaluated by measuring their P-E hysteresis loops and dielectric constants. The preferred orientation of the films can be controlled using the template layer derived by the sol-gel method. The deposition temperature required to obtain the perovskite phase in this process is approximately 460°C, and is significantly lower than that in the case of direct film deposition by PLD on the $Pt/Ti/SiO_2/Si$ substrates.

## 1. INTRODUCTION

Lead zirconate titanate ($Pb(Zr_xTi_{1-x})O_3$: PZT) thin films have developed rapidly in recent years, because of their excellent ferroelectric, pyroelectric and piezoelectric properties. A large number of potential applications of PZT thin films in nonvolatile ferroelectric random access memories (FeRAMs) [1] and microelectro-mechanical systems (MEMS) [2], such as membrane-type micropumps [3], atomic force microscopy (AFM) cantilevers [4, 5] and microscanning mirror devices [6], have been reported. PZT films have been studied for more than one decade, and most of them are for FeRAMs less than 0.5 µm in thickness [7]. However, for use in AFM cantilevers and microscanning mirror devices, a high-quality 3-µm-thick PZT film on an electrode/substrate is desirable to obtain a larger displacement [5, 6]. Many fabrication techniques, such as the sol-gel method, pulsed-laser deposition (PLD) and jet print deposition, have been used to fabricate PZT films for microactuators [8]. However, it is not easy to obtain thick PZT films with good electrical properties due to crack formation and the volatility of lead and lead oxide in films. In our previous work, we successfully fabricated crack-free PZT films of 3 µm thickness on $Pt/Ti/SiO_2/Si$ substrates using the sol-gel method [9]. However, a deposition of 3 µm requires more than 20 repetitions of the coating and firing procedures, which increases the risk of contamination and leads to Pb diffusion between the PZT layer and Pt/Ti bottom electrodes [10]. On the other hand, PLD is a promising technique for thick-PZT-film fabrication, because it offers the advantage of a high deposition rate (approximately –3 µm/h). In PLD, films can be crystallized by two different processing methods; namely, they can be crystallized in situ as they are deposited on hot substrates, or they can be deposited amorphously at lower substrate temperatures (or room temperature) and then crystallized by postdepositional annealing. To obtain well-crystallized PZT films on $Pt/Ti/SiO_2/Si$ substrates, substrate temperatures (in the case of in situ deposition) or postannealing temperatures (in the case of films deposited at room temperature) in the range of 600 - 750°C are required [11-14]. In our previous work, we also successfully fabricated crack-free PZT films of 2 µm thickness on $Pt/Ti/SiO_2/Si$ substrates by PLD at room temperature, which were crystallized by subsequent annealing at 750°C [15]. However, the temperature of postdeposition annealing in PLD is 750°C, which is significantly higher than that in the sol-gel method (600°C). Thus the evaporation of lead and lead oxide from the surface of films at elevated temperatures is more acute than that in the case of the sol-gel process and leads to the formation of a thin pyrochlore layer on the surface of PZT films [16]. A hybrid process consisting of the sol-gel method and PLD is effective for obtaining thick PZT films with good properties, because it integrates the advantages of the sol-gel method and PLD [17]. In our previous work, we found that the temperature of postdeposition annealing in the hybrid process is lower

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than that in the case of direct film deposition by PLD on a $Pt/Ti/SiO_2/Si$ substrate, and the preferred orientation of the film obtained by the hybrid process can be controlled using the layer deposited by the sol-gel method. PZT films fabricated by the hybrid process exhibit better ferroelectric properties than those directly deposited by the PLD process [18]. However, in the hybrid process, PLD is performed at room temperature and the postprocess of amorphously deposited PZT films are still required, so that an in situ deposition technique is also desirable. Hence, in this study, PZT thin films were in situ grown on $Pt/Ti/SiO_2/Si$ substrates by the hybrid process consisting of the sol-gel method and PLD. The crystalline phases and preferred orientations, as well as the microstructures of PZT films were investigated. On the basis of the experimental results, the mechanism of the in situ growth of PZT films in the hybrid process is discussed.

## 2. EXPERIMENTAL PROCEDURE

$Pt/Ti/SiO_2/Si$ substrates were prepared by sputtering 0.05 μm of titanium and 0.15 μm of platinum on oxidized (1.8 μm of $SiO_2$) silicon substrates.

First, a thin PZT layer was deposited on $Pt/Ti/SiO_2/Si(100)$ substrates using the sol-gel method. The precursor solution was prepared from lead acetate $[Pb(CH_3COO)_2]$, zirconium-n-propoxide $[Zr(C_3H_7O)_4]$ and titanium tetraisopropoxide $[Ti((CH_3)_2CHO)_4]$. 2-propanol $[(CH_3)_2CHOH]$ was used as the solvent. The solution composition was controlled at a ratio of Pb : Ti : Zr = 1.2 : 0.48 : 0.52. The PZT films were fabricated on $Pt/Ti/SiO_2/Si$ substrates using a spin coater operated at 2600 rpm for 20 s and 4000 rpm for 40 s. Before coating, the precursor solution was passed though 0.45 μm nylon filters. The coated films were dried at 250℃ for 20 min and then finally annealed at 600℃ for 30 min to crystallize the films into a perovskite-type structure with a (100)-preferred orientation. The preferred orientation of the PZT films deposited by the sol-gel method can be easily controlled by varying pyrolysis temperature [19-21]. We also found that varying pyrolysis temperature in the heat-treatment process can affect the preferred orientation of PZT films derived by the sol-gel method: 250℃ favored a (111)-preferred orientation and 400℃ favored a (100)-preferred orientation [22]. The thickness of the PZT layer deposited by the sol-gel method was approximately 130 nm.

Second, a PZT film of approximately 0.6 μm thickness was deposited by PLD on the above-mentioned PZT layer at a substrate temperature of 460℃. Figure 1 shows the pulsed laser deposition system, which is composed of a laser source and a deposition chamber with a substrate holder for 3 inch wafers. The substrate holder could be rotated for uniform deposition. 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 turbomolecular pumps and the chamber could be evacuated to $10^{-7}$ Torr at room temperature. The distance from the target to the substrate was approximately 10 cm. The targets used were dense ceramic pellets of Pb $(Zr_{0.45}Ti_{0.55})O_3$ with 20 wt% excess PbO, and their surfaces were polished with emery paper of grades up to #2000 prior to each PLD process. In our previous work, we found that the addition of at least 20 wt% excess PbO to the PZT target is required to obtain a single perovskite phase [15]. We also found that PZT films fabricated from a target with a Zr/Ti ratio of 45/55 exhibit good electric properties and their compositions are close to that of the morphotropic phase boundary (52/48)

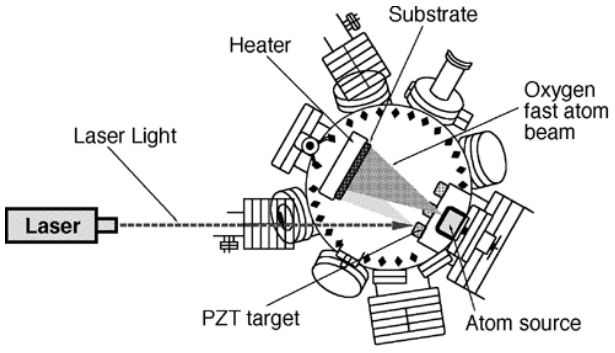


Fig. 1 Schematic of the pulsed laser deposition system.

Table 1 Conditions of pilsed-laser deposition of the PZT thin films

| | |
|---|---|
| Target | $Pb(Zr_{0.45}Ti_{0.55})O_3$ +20 wt%PbO |
| Substrate temperature | 460℃ |
| Base pressure | $10^{-7}$ Torr |
| $O_2$ partial pressure | 200 mTorr |
| Laser | KrF Excimer laser (248nm) |
| Frequency | 10 Hz |
| Energy | 0.4-0.9 J/shot |
| Fluence | 1.2 J/cm$^2$· shot |
| Target-substrate distance | 10 cm |
| Deposition time | 30 min |
| Film thickness | 0.6μm |

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[23, 24]. Hence, in this work, we fabricated PZT films using a target of $Pb(Zr_{0.45}Ti_{0.55})O_3$ with 20 wt% excess PbO. Before starting the deposition, the vacuum chamber was evacuated up to $10^{-7}$ Torr and then filled with oxygen up to 200 mTorr. PZT films were deposited at a substrate temperature of 460℃ for 30 min so that PZT films of approximately 0.6-μm-thickness were obtained. The deposition conditions for the PZT films are summarized in Table1.

The crystalline structure of the PZT films was examined by X-ray diffractometer (XRD, Rigaku RINT2000, CuKa radiation) analysis. The surface and cross-sectional morphology of the films were observed by scanning electron microscopy (FE-SEM, JSM-6500F). Cross-sectional TEM specimens were prepared by conventional grinding and polishing. The specimens were ground and polished to a thickness of 20 μm, and were then further thinned to perforation by Ar-ion milling using a Gatan precision ion polishing system (PIPS). The microstructures of the films were studied by transmission electron microscopy (FE-TEM, HF2000, HITACHI). The Pt/Ti film was used as a bottom electrode, and a Pt film (size: 1.5mm in diameter) 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), and the dielectric constants and loss value of these films were measured at 1 kHz using an impedance analyzer (Hewlett-Packard, HP4192A).

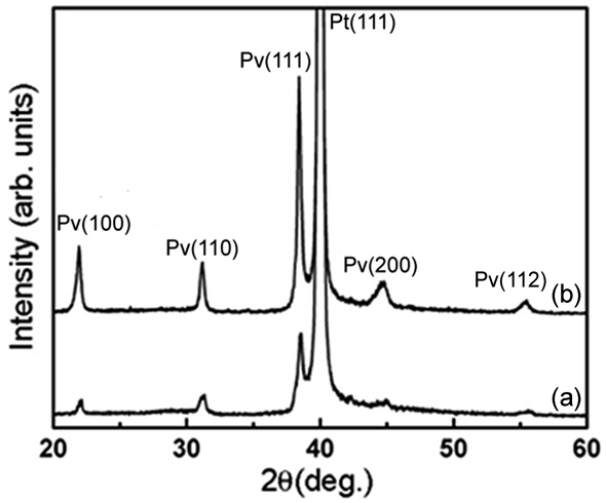


Fig. 2 XRD patterns of (100)-preferred PZT films: a) fabricated by the sol-gel method, b) fabricated by PLD on the sol-gel layer at substrate temperature of 460℃. Pv: perovskite phase.

## 3. RESULTS AND DISCUSSIN

### 3.1 Crystalline phases and preferred orientations of the PZT films

Figure 2(a) shows the XRD pattern of the PZT layer deposited by the sol-gel method, which was dried at 250℃ for 20 min and then finally annealed at 600℃ for 30 min. The PZT layer mainly consists of the perovskite phase with a (111)-preferred orientation, and no peak of the pyrochlore phase was detected in the PZT layer. These results are in good agreement with those of our previous study [22]. Varying pyrolysis temperature in the heat-treatment process can influence the preferred orientation of the PZT films obtained by the sol-gel method: 250℃ favored a (111)-preferred orientation and 400℃ favored a (100)-preferred orientation.

Figure 2(b) shows the XRD pattern of the PZT film deposited by the hybrid process on the (111)-oriented PZT layer. The film had a pure perovskite phase with a sharp and prominent diffraction peak of (111) planes. In comparison with that in Fig. 2(a), the XRD pattern of the PZT film deposited by the hybrid process is similar to that of the layer deposited by the sol-gel method. These results indicate that the grains of the perovskite phase in the layer deposited by the sol-gel method grew in situ during PLD at the substrate temperature of 460℃. In the case of PLD at room temperature in the hybrid process, we found that the lower PZT layer deposited by the sol-gel method acted as a seed layer for the crystallization of the upper PZT layer deposited by PLD during postdeposition annealing [25]. To clarify the solid-phase epitaxial effect between the PZT layers deposited by the sol-gel method and PLD, the cross-sectional microstructure of the PZT films were studied by TEM described below.

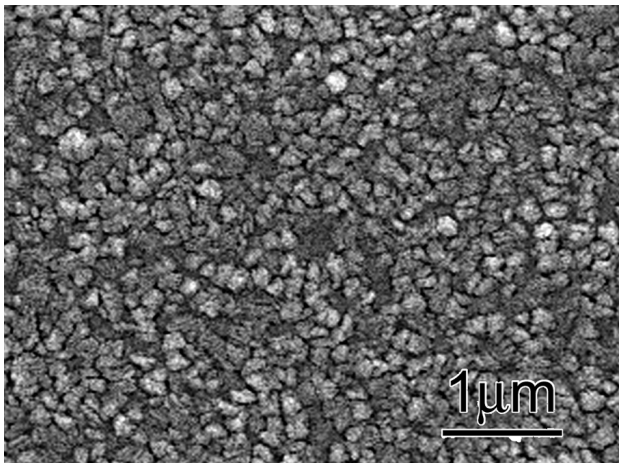


Fig. 3 Surface SEM image of PZT films fabricated by hybrid process at substrate temperature of 460℃.

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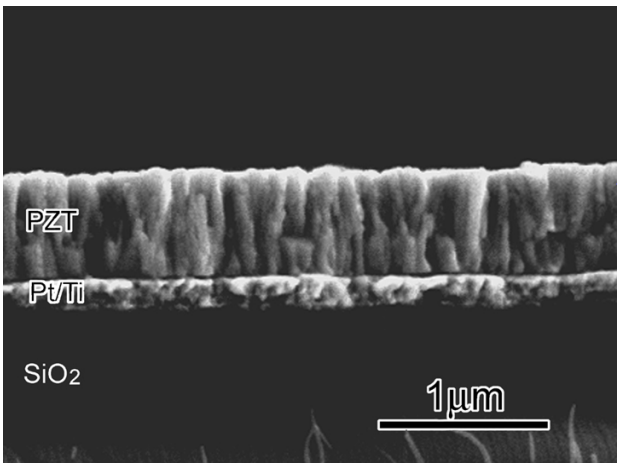


Fig. 4 Cross-sectional SEM image of PZT films fabricated by hybrid process at substrate temperature of 460℃.

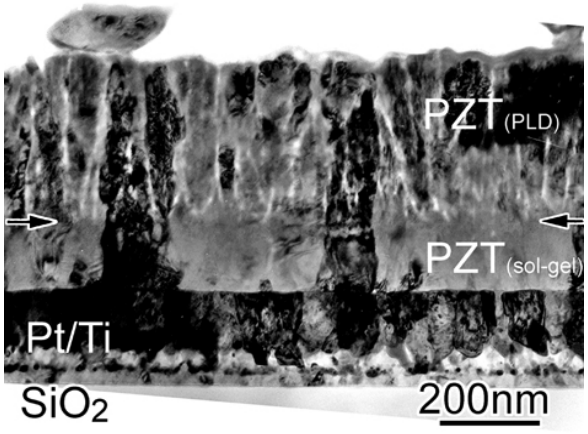


Fig. 5 Cross-sectional TEM image of PZT films fabricated by hybrid process at substrate temperature of 460℃.

On the other hand, in the case of direct film deposition by PLD on the Pt/Ti/$SiO_2$/Si substrates, to obtain well-crystallized PZT films, higher substrate temperatures in the range of 650 - 750℃ are required [11-14]. However, a pure perovskite phase can be obtained by PLD at a substrate temperature of 460℃ by the hybrid process (Fig. 2(b)). It is clear that the PZT layer deposited by the sol-gel method decreases the deposition temperature to obtain the perovskite phase during PLD.

### 3. 2 SEM and TEM observation of microstructure of the PZT films

Figure 3 shows the surface morphology of the PZT films fabricated by the hybrid process at the substrate temperature of 460℃. The film has a spherulite grain structure and most of the grains are approximately 250 nm in size. The cross-sectional morphology of the PZT films fabricated by the hybrid process is shown in Fig. 4. As can be seen, the film was grown as a columnar microstructure extending through its thickness, and no boundary between the PZT layers deposited by the sol-gel method and PLD can be observed. This suggests that the adherence of the layers deposited by the sol-gel method and PLD is very good.

Figure 5 shows the microstructure of the PZT films fabricated by the hybrid process at the substrate temperature of 460℃. According to the thickness of the layer deposited by the sol-gel method, the interface between the layers deposited by the sol-gel method and PLD can be assumed and is denoted by the arrows. The film showed a polycrystalline columnar grain structure, and no defects, such as pores are observed at the interface between the layers deposited by the sol-gel method and PLD. The result also indicates that perovskite grains in the PZT layer deposited by the sol-gel method grew in situ during PLD at a substrate temperature of 460℃. Taking this result together with XRD spectra shown in Fig 2, we conclude that the solid-phase epitaxial effect between the PZT layers deposited by the sol-gel method and PLD decreases the deposition temperature to obtain the perovskite phase during PLD, and causes the films to exhibit the same preferred orientation as that of the layer deposited by the sol-gel method.

### 3. 3 Electrical properties of the PZT films

The dielectric constant and loss value measurements of the films fabricated by the hybrid process were carried out at a frequency of 1 kHz using an impedance analyzer. The dielectric constant and the loss value were approximately 900 and 0.05, respectively. The ferroelectricity of the PZT

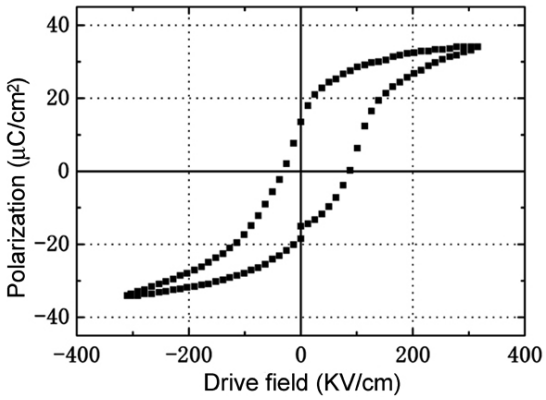


Fig. 6 P-E hysteresis loop of PZT film fabricated by hybrid processing at a substrate temperature of 460℃.

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films fabricated by the hybrid process was investigated by observing the P-E hysteresis loop (Fig. 6). The average remanent polarization $P_r$ and the coercive field $E_c$ are 15 $\mu C/cm^2$ and 45 kV/cm, respectively. We also tried to determine the ferroelectric properties of the PZT films fabricated directly on $Pt/Ti/SiO_2/Si$ substrates by PLD at the substrate temperatures of 460°C and 550°C. However, no hysteresis loops were obtained from these films, because they consist of mainly the pyrochlore phase, which is a nonferroelectric phase. It is clear that the hybrid process is effective for obtaining PZT films with good properties at lower deposition temperature.

## 4. CONCLUSIONS

$Pb(Zr_xTi_{1-x})O_3$ (PZT) thin films were in situ-deposited on $Pt/Ti/SiO_2/Si$ substrates at a substrate temperature of 460°C by the hybrid process consisting of the sol-gel method and pulsed-laser deposition (PLD). The crystalline structure and preferred orientation of the PZT films were examined by XRD analysis. The microstructures of the films were studied by TEM. XRD analysis indicated that the preferred orientation of PZT films could be controlled using the layer deposited by the sol-gel method. TEM image showed that the film had a polycrystalline columnar microstructure extending through its thickness. These results indicate that the solid-phase epitaxial effect between the PZT layers deposited by the sol-gel method and PLD decreases the deposition temperature, thereby obtaining the perovskite phase during PLD, and causes the films to exhibit the same preferred orientation as the layer deposited by the sol-gel method.

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