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Stress engineering for the design of morphotropic phase boundary in piezoelectric material

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ABSTRACT

Alkoxide-derived lead zirconate titanate thin films having Zr/Ti = 50/50 to 60/40 compositions with different residual stress conditions were deposited on a Si wafer to clarify the effects of the residual stress on the morphotropic phase boundary shift. The residual stress condition was controlled to −0.1 to −0.9 GPa by the design of the buffer layer structure on the Si wafer. Results show that the maximum effective piezoelectric constant d_{33} was obtained at 58/42 composition under −0.9 GPa compressive residual stress condition. Moreover, the MPB composition shifted linearly to Zr-rich phase with increasing compressive residual stress.

1. Introduction

Piezoelectric materials have been studied for various applications such as micro-actuators in micro-electromechanical systems (MEMS) [1,2]. Lead zirconate titanate (PZT) is an important piezoelectric material known for its excellent electrical properties and high Curie temperature. In addition, the highest piezoelectric property in PZT bulk ceramic has been reported at morphotropic phase boundary (MPB) composition (Zr/Ti = 53/47).

However, few researchers have reported details related to the MPB composition shifted by the residual stress condition in ferroelectric thin films such as $Pb(Mg,Nb)O_3$-$PbTiO_3$ (PMN-PT) and $Pb(Zr,Ti)O_3$(PZT). Oh et al. reported that the MPB composition in PZT should be shifted to Zr rich phase by the theoretical calculations [3]. They also showed that the MPB composition does not change in the case of hydrostatic pressure [4]. In addition, Uršič et al. reported that the MPB composition of PMN-PT shifted to PMN rich phase under weak compressive residual stress conditions. They examined this phenomenon using PMN-PT thick films on various substrates with different thermal expansion coefficients [5]. However, in almost all of those attempts, the strain effect of the MPB composition was examined in terms of the stability of the tetragonal phase using just one chemical composition under compressive residual stress. Therefore, we conducted a systematic study of the effect of the residual stress on the MPB shift in PZT materials from the perspectives of the crystal phase and electrical properties.

In general, residual stress is defined as the sum of the lattice mismatching stress, thermal stress, and the phase transition stress [6]. For the alkoxide derived thin film, the lattice mismatching stress should be omitted because of the film thickness. In addition, the phase transition stress differs depending on the crystal orientation degree. Therefore, almost all researchers have used a single-crystal substrate with a high thermal expansion coefficient to control the thermal stress in piezoelectric thin film [3,7]. However, from the viewpoint of commercial use, stress engineering should be done on a commercial Si substrate. A report of our previous study described that stress engineering was done for a Si wafer by design of the buffer layer structure [8]. Therefore, we controlled the residual stress condition in PZT thin film on a Si wafer by the design of the buffer layer structure in this study. We deposited PZT thin films of 50/50 to 60/40 compositions with controlled residual stress conditions up to −0.9 GPa to clarify the exact MPB composition in PZT thin film under controlled residual stress conditions.

2. Experimental procedure

For this study, a-axis and c-axis oriented PZT thin films with different residual stress conditions were deposited on lanthanum strontium cobalt oxide ($(La_{0.5},Sr_{0.5})CoO_3$: LSCO)/lanthanum nickel oxide ($LaNiO_3$: LNO)/Si, LNO/Si and PbO/Pt/Si substrates using chemical solution deposition (CSD) to control the residual stress condition in PZT thin films. LSCO, LNO, PbO buffer layers were also deposited using chemical solution deposition. In addition, the chemical composition of PZT thin film was changed within the range of 50/50 to 60/40. The starting reagents for the LNO precursor solution with 0.3 M concentration were lanthanum nitrate and nickel acetate. The related experimental

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details have been described elsewhere [9]. The starting reagents for the LSCO precursor solution with 0.1 M concentration were lanthanum nitrate [$La(NO_3)_3 \cdot 6H_2O$], metal strontium (Sr), and cobalt acetate [$Co(CH_3COO)_2 \cdot 4H_2O$]. All reagents were dissolved separately in 2-methoxyethanol. Subsequently, La and Sr precursor solutions were mixed for 2 h at room temperature. Finally, the obtained La–Sr and Co precursor solutions were mixed for 2 h to obtain the LSCO precursor solution with $(La_{0.5},Sr_{0.5})CoO_3$ composition. The PbO precursor solution was prepared from lead acetate and ethanol. The PZT precursor solution with 0.6 M concentration was prepared from lead acetate, titanium isopropoxide, and zirconium butoxide. The experimental procedure used for this study has been explained elsewhere [10].

The LNO layer with 160 nm thickness was deposited on a Si wafer using a spin-coating process. The as-deposited LNO layers were dried, pre-annealed, and annealed, respectively, at 150, 350, and 700 °C. Subsequently, the LSCO layer was deposited on a LNO/Si structure. The film thickness of the LSCO layer was adjusted between 17 and 170 nm to control the residual compressive stress in PZT thin films. The LSCO layer was dried at 150 °C for 10 min. Final annealing was conducted at 700 °C for 5 min under O_2 flow. Finally, the PZT layer with 700 nm thickness was deposited on a LSCO/LNO/Si structure. Experimental details related to PZT deposition have been described elsewhere [10].

The composition of the obtained PZT thin films were checked by X-ray fluorescence (XRF, S8 TIGER, Bruker AXS GmbH) with Spectra Plus standard software for thin film (MLQuant G). During analysis the electric current varied between 50 and 100 mA and the voltage varied between 30 and 50 kV, though the combination during analysis could not exceed 3 kW. The residual stress in PZT thin film was determined from X-ray diffraction (XRD) using $\sin^2\psi$ method. XRD data were collected on a Bruker AXS D8 Advance using 40 kV, 40 mA, and Cu Kα radiation of wavelength Kα = 1.5406 Å. In addition, XRD measurements were performed using a polycapillary X-ray lens in the conventional geometry with θ–2θ scans. The local piezoelectric response was observed using an atomic force microscope (AFM, SPI3800N; SII Nano Technology Inc.) equipped with a piezoelectric force mode (PFM). A Rh coated Si tip with the resonant frequency of around 129 kHz (the stiffness of tip: 14 N/m) was used for this measurement (Hitach High-Tech Science Corp., Japan). The electric field was applied between the top Au electrode with 100 μm diameter and the bottom electrode of the thin film. The effective local piezoelectric response (d_{33}) was evaluated by the deflection of the cantilever by applying the triangle wave (±40 V, 10 Hz) and sin wave (1 Vrms, 10 kHz) simultaneously. The sin wave response was detected by rock-in amplifier.

3. Results

Fig. 1 presents an XRD pattern of the PZT thin films obtained with different compositions under the same residual stress condition. The obtained thin films had highly a-axis and c-axis preferred orientation, independent of their respective compositions. This result indicates that the effects of the crystal orientation on the electrical properties should be ignored in this study.

The residual stress was calculated from the lattice strain, which had been estimated using $\sin^2\psi$ method. In our previous studies, LNO and LSCO was extremely effective for application of the compressive residual stress to PZT thin films on a Si wafer because of the large thermal expansion coefficient [11]. Fig. 2 shows the change in the residual stress in PZT (53/47) thin films with increasing LSCO layer thickness. In this study, the residual compressive stress in PZT thin films on a LNO/Si substrate was −0.3 GPa and that on a LSCO/LNO/Si substrate was controlled to −0.5 to −0.9 GPa. Furthermore, the residual stress in PZT (53/47) thin film on a PbO/Pt/Si substrate was −0.1 GPa.

Fig. 3 presents high-angle XRD patterns of the PZT (53/47) films obtained with different residual stress conditions. The pattern is associated with the rhombohedral and the tetragonal phase (ICDD 01-070-4264, 01-070-4265), because the (53/47) composition is generally known as the MPB composition, which had the mixed-phases with tetragonal and rhombohedral. However, the peak intensity of rhombohedral (048) plane abruptly decreased concomitantly with increasing compressive residual stress. The tetragonal mono-phase was attained over −0.8 GPa residual stress condition. Fig. 4 portrays the change in the tetragonal ratio in PZT(53/47) thin films with residual compressive stress. Soares et al. reported that the tetragonal ratio of the MPB in PZT bulk materials was in the range of approximately 25–40% depending on the crystal size [12]. Under the compressive residual conditions up to −0.8 GPa, the obtained PZT(53/47) thin films were also mixed phases with tetragonal and rhombohedral components, as reported also for bulk ceramics. Although the effect of Zr/Ti composition gradient [13] is not taken into account in this research, the tetragonal ratio increased concomitantly with increasing residual compressive stress, even in the same composition. Finally, the PZT (53/47) thin film was completely tetragonal mono-phase over −0.8 GPa residual stress condition. Many research reports have described that two-dimensional compressive residual stress engenders a stable tetragonal phase [7,14]. Therefore, this result presents an almost identical tendency. Furthermore, these results strongly suggest the MPB composition shifts to Zr-rich phase under conditions of highly compressive residual stress.

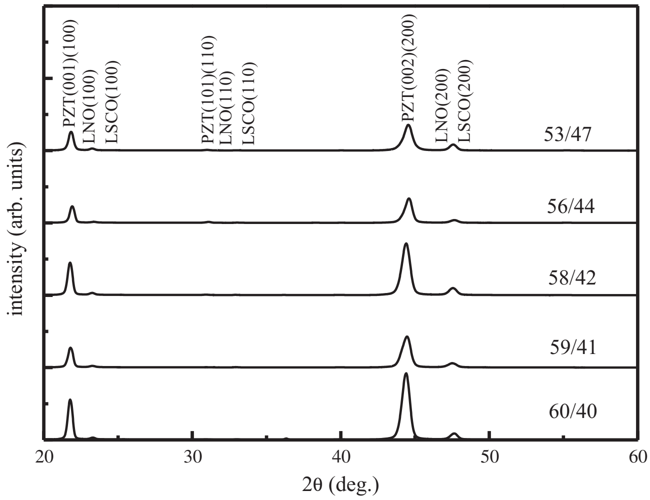

Fig. 1. XRD profiles of the PZT thin films obtained with different compositions near the reported MPB.

Fig. 5 portrays the change in the effective d_{33} value with composition under the −0.9 GPa residual stress condition. The inset shows the

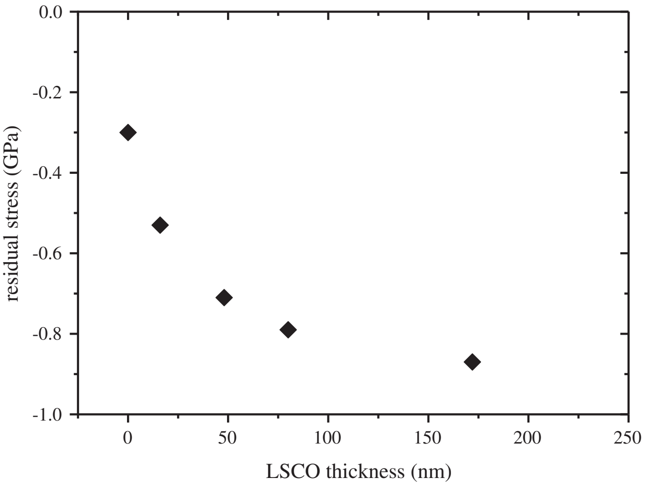

Fig. 2. Change in the residual stress in PZT thin film with LSCO buffer layer thickness.

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