Impact of stress on the crystal structural nonuniformity along the film thickness direction by microfabrication of Pb(Zr,Ti)O₃ islands with morphotropic phase boundary composition

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1. Introduction

Ferroelectric materials have been used for various applications such as nonvolatile memories, actuators and sensors etc.¹⁻⁶ Pb(Zr,Ti)O₃ (PZT) is one of the most widely investigated material in ferroelectrics because of its large remanent polarization and high electromechanical coupling coefficient.⁷ It is known for PZT ceramics and powders that the tetragonal and rhombohedral phases coexist at a narrow Zr/(Zr + Ti) ratio, so called morphotropic phase boundary (MPB).⁸⁻¹⁰ The crystal structure at the MPB has attracted much interest because dielectric property and piezoelectricity show largest value at the MPB. These two phases have been reported to coexist over a relatively wider range of Zr/(Zr + Ti) ratio near the MPB in the case of thick PZT films over 1 μm in thickness as compared with that of PZT ceramics and powders.¹¹,¹² Such a wide coexistent region is considered to be caused by the stress distribution along film thickness direction induced during film growth and/or cooling process after the film deposition. The films have larger stress near the film-substrate interface than near the film surface.¹³,¹⁴ Therefore, these stress distributions induced the crystal structure non-uniformity along film thickness direction, which is considered to be results in the wide range of the coexistence region of the two phases. In fact, using transmission electron microscope (TEM), Yokoyama et al. reported that the crystal structure of a 3 μm-thick epitaxial PZT film with Zr/(Zr + Ti) ratio of 0.56 consisted of both tetragonal and the rhombohedral phases. Tetragonal phase mainly existed near the film-substrate interface, while the rhombohedral one near the surface of the film. The profile of this structural non-uniformity along the film thickness was changed by the lateral size of PZT. These phenomena can be explained by the stress distribution in PZT and the understanding of this non-uniformity is the key to control the performance of the devices using PZT.

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2. Experimental procedure

The epitaxial PZT thick film with Zr/(Zr + Ti) ratio of 0.56 was grown on a (100) SrRuO3/(100)SrTiO3 substrate at 600°C by pulsed metalorganic chemical vapor deposition (pulsed MOCVD). Pb(C11H19C2)2, Zr(O-i-C3H7)4 and Ti(O-i-C3H7)4 were used as Pb, Zr and Ti source materials, respectively, while oxygen gas was used as the oxidant.23) Film thickness was about 3 μm. The PZT islands that have square prism form with lateral size of 2 × 2, 1 × 1 and 0.5 × 0.5 μm² were fabricated by FIB (Hitachi FB-2000AB). The fabricated islands were post annealed at 600°C for 1 h to remove the process damage.

Chemical composition of the whole PZT film was measured by X-ray fluorescence analysis (XRF, PANalytical PW2404), and composition of the microscopic area was measured by energy dispersive X-ray spectrometry equipped with scanning electron microscope (SEM-EDS, Hitachi SU6600). The crystal structure of the whole PZT film was characterized by X-ray diffraction measurement (XRD, PANalytical X’Pert MRD). Microscopic structure of the PZT film and the PZT islands were investigated with micro-Raman spectroscopy (Renishaw inVia Raman spectroscopy), 514.5 nm line of an Ar + Kr mix gas laser was employed as an excitation source, and it was focused to a spot size of about 1 μm by a 250× objective lens with NA = 0.9. The laser beam was introduced from cross-sectional direction. The measurement points were accurately controlled by closed-loop control motorized stage with minimum step of 0.1 μm. The incident light was polarized circularly through a circular polarizer in order to remove an influence of the crystallographic orientation of the PZT film on the Raman spectra.

3. Results and discussion

XRD pattern of the PZT thick film grown on the (100) SrRuO3/(100)SrTiO3 substrate is shown in Fig. 1. The tetragonal h00 and 00l PZT peaks were only observed in the XRD pattern, indicating that the PZT film was single phase. Figure 2 shows high resolution XRD reciprocal space mapping (HRXRD-RSM) of the PZT thick film measured around SrTiO3 400 diffract peak. The inset in Fig. 2 shows integrated 2θ-θ spectrum of the same sample. Tetragonal 004 and 400, and rhombohedral 004 diffract peaks were observed. Although PZT powder is reported to have a rhombohedral symmetry at this composition, the present result indicates that the tetragonal and the rhombohedral phase coexist in the film (details are clearly reported elsewhere15)). The tetragonal 400 diffract peak was split into three spots, indicating the existence of twin structure. A relative volume fraction of the tetragonal phase estimated from HRXRD-RSM was 76%. Figure 3(a) shows compositional distributions of the PZT thick film along film thickness direction measured by SEM-EDS. There were no detectable dispersions in the compositions. Figures 3(b) and 3(c) respectively show the cross-sectional SEM images of the continuous PZT thick film and the 1 × 1 μm² PZT island.

Figures 4(a) and 4(b) show the Raman spectra of the continuous PZT thick film and the 1 × 1 μm² PZT island that were measured from the cross-sectional direction at the measurement points shown in Figs. 3(b) and 3(c), respectively. In the case of the film, the Raman spectra had spectral features of the rhombohedral phase near the film surface [i and ii in Fig. 4(a)]. Some of the peaks are labeled as E(2TO)-, E(2TO)-, E(1TO)-, E(1TO)-, E(2TO)- and E(1TO)- based on Ref. 24). On the other hand, the Raman spectra contained peaks of the tetragonal phase [E(2TO)-, E(2TO)-, E(1TO)-, and E(1TO)- near the film-substrate interface [iii–v in Fig. 4(a)]. However, these intensities were small. This indicates that the rhombohedral phase was dominant in the PZT thick film and the tetragonal phase with small portion was coexisted near the film-substrate interface, that is in good agreement with the result of TEM measurement.15) On the other hand, in the case of the 1 × 1 μm² island, the peak intensities of the tetragonal phase near the film-substrate interface [ii–v in Fig. 4(b)] were small compared to those of the PZT film. This indicates that phase transition from tetragonal phase to rhombohedral phase was occurred by the island formation followed by the heat treatment. The phase transition with decreasing the lateral size has been also confirmed by XRD measurement.22)
Here, peak fitting was carried out for the PZT film and the islands in order to make clear an effect of lateral size. Three Gaussian peaks (for tetragonal phase) and a function with spectral shape of the rhombohedral phase were used in this fitting. This function was obtained from peak fitting of the Raman spectrum measured at the surface of the film. We assumed that the crystal structure was single-phase of rhombohedral at the film surface because films surface was almost relaxed and the relaxed PZT with this composition was reported to have a rhombohedral symmetry. Integrated intensity ratio of the Raman peaks of the tetragonal phase to the rhombohedral phase one obtained from the peak fittings is shown in Fig. 4(c) as a function of distance from the substrate. The integrated intensity ratio of the film increased gradually with the decrease in the distance from the substrate. It reveals that the tetragonal phase exists mainly at near the film-substrate interface. In addition, these values are larger than those of the other smaller islands (2 × 2, 1 × 1 and 0.5 × 0.5 μm²) over the whole range. For the islands with smaller lateral size below 2 × 2 μm², the integrated intensity ratios also increased as the distance approached to the surface, but they were nearly constant above 1.0 μm.

Figure 5 shows stress variation with lateral size calculated by finite element method. It was calculated to reveal stress variation of the PZT islands. The calculation model is shown in Fig. 5. In this calculation, we assumed that the stress in the films occurred at cooling process due to the difference of thermal coefficients between the film and the substrate. The temperature was changed from 600°C (zero stress condition) to 30°C. Thermal coefficient of PZT and SrTiO₃ are a constant of 7.2 × 10⁻⁶/deg and 11.5 × 10⁻⁶/deg, and these materials were treated as isotropic. Dislocation was not taken into account in this calculation. Stress in the PZT islands was diminished with the decrease in the lateral size. The structural change in the PZT islands shown in Fig. 4 is considered to be caused by this stress relaxation. It must be noted that the tetragonal phase even existed at the very small islands in Fig. 4 because the stress relaxation is not perfect at the interface as suggested.
in the results shown in Fig. 5. In the case of epitaxial PZT films with \{100\} orientation, the stress applied to the PZT films is reported to stabilize the tetragonal phase for both of tensile or compressive stress.\(^{25}\) Taking account of the consideration that films were more strongly clamped at the substrate-film interface and was released along the film thickness direction, the present results about the structural change are considered to be reasonable.

These results indicate that crystal structure of the PZT films and islands is susceptibly changed with the stress condition. This crystal structure change along the film thickness direction will result in the electrical and electromechanical properties of PZT films. We must pay attention that excellent characteristics of PZT films in continuous form is not sure to remain in processed PZT films. In addition, the lateral size of the device also strongly affects the crystal structural profiles of the PZT films that must be also taken into account for the electrical and electromechanical properties of PZT films-based devices. Therefore, the changes of structural profiles are serious problem for MEMS devices, since device processing is necessary. The above mentions led to understanding this non-uniformity of the constituent phase along film thickness direction is the key to control the performance of the devices using PZT.

4. Summary

In summary, the microscopic structure of the PZT islands with various lateral sizes was investigated. The 3 μm-thick epitaxial PZT film with Zr/(Zr + Ti) ratio of 0.56 was grown on a (100)\(_3\)SrRuO\(_3\)/\(\{100\}\)SrTiO\(_3\) substrate by pulsed MOCVD and the PZT islands were fabricated using FIB. Crystal structure of the PZT film consisted of both tetragonal and rhombohedral phase. Tetragonal and rhombohedral phases mainly existed near the film-substrate interface and the surface of the interface, respectively. The profile of this structural non-uniformity along the film thickness direction was changed by the lateral size of PZT. These phenomena can be explained by the stress distribution applied to the PZT and this non-uniformity along film thickness direction is the key to control the performance of the devices using PZT.

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