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Growth of Epitaxial $Pb(Zr,Ti)O_3$ Films on $Ba(Zr,Ti)O_3$ Single Crystals by Hydrothermal Synthesis

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Lead-based perovskite-structure materials, including $Pb(Zr,Ti)O_3$, have been intensively studied because of their superior ferroelectric and electromechanical properties.[1] Since the single crystals of these materials exhibit such exceptional piezoelectric responses, as compared with their polycrystalline counterparts,[2] there have been many investigations on the fabrication of single crystals and epitaxial thin films of these materials[3−6] for application to actuators, ultrasonic transducers, and other electromechanical micro devices. Among the various deposition techniques for epitaxial thin films, hydrothermal synthesis based on an aqueous method[4−8] has been of great interest for obtaining $Pb(Zr,Ti)O_3$ films because of its low processing temperature, which is critical to prevent both Pb volatilization and interfacial interaction between the film and the substrates during deposition. Chien et al.[4] successfully showed that heteroepitaxial $Pb(Zr,Ti)O_3$ thin films could be hydrothermally synthesized with high crystalline quality. In addition, a recent study by Oledzka et al.[6] demonstrated that the microstructure and the composition of hydrothermal $Pb(Zr,Ti)O_3$ films could be influenced by the starting precursors.

To grow the $Pb(Zr,Ti)O_3$ films, various substrates were used, including MgO,[9] metallic Ti,[10] $SrTiO_3$, and $LaAlO_3$.[4,6] The $Pb(Zr,Ti)O_3$ thin films could be epitaxially deposited on single-crystal $SrTiO_3$ and $LaAlO_3$ substrates, while the Ti substrates that produced the polycrystalline thin films acted as a Ti source for the film. Because of the lattice mismatch between the film and the substrates, however, the misfit strain is expected to deteriorate in terms of its piezoelectric properties and will also affect the growth behavior of the films, even on the $SrTiO_3$ and $LaAlO_3$ substrates. In the present investigation, we used a hydrothermal synthesis to produce heteroepitaxial $Pb(Zr_{0.44}Ti_{0.56})O_3$ (PZT) films on $Ba(Zr_{0.1}Ti_{0.9})O_3$ (BZT) single crystals, which resulted in a new substrate material with virtually no lattice mismatch to the films. This synthetic approach may also be used as a possible process to grow relatively thick single-crystal PZT that could potentially be applied to piezoelectric devices.

BZT single crystals were fabricated using a solid-state crystal growth technique[11,12] based on the abnormal grain growth in $BaTiO_3$. As has been recently reported,[12] when a small seed crystal is embedded in the powder compacts of some perovskite titanates, the seed crystal can be controlled so that it grows abnormally fast, at the expense of small matrix grains, resulting in a dense single crystal of considerable size. Experimental details regarding the fabrication of this single crystal can be found elsewhere.[12] $SrTiO_3$ (ST) single crystals (Shinkosha Co., Ltd., Japan) were also used as a substrate for the purposes of comparison. Both the BZT and ST single-crystal substrates were 10 mm × 10 mm in size and 1 mm in thickness and had planes with (001) orientations. PZT films were hydrothermally produced on the polished substrates, using TiO_2 powder (99 wt % purity, Yakuri Pure Chemicals Co., Ltd., Japan), ZrOCl (90%, CP grade, Junsei Chem. Co., Ltd., Japan), and $Pb(NO_3)_2$ (99.5%, GR grade, Wako Pure Chem. Ind., Ltd., Japan). The starting precursors with a molar ratio of Pb:Zr:Ti = 1:0.44:0.56 were put into a Teflon-lined vessel and were mixed with an alkaline aqueous solution of 10 M KOH with a pH of >13.9.[4] After the substrates were added to the solution in the vessel, the mixture was annealed first at 90 °C for 2 h and then, subsequently, at 150 °C for 24 h. The substrates were placed on Pt wires and were suspended in the solution to prevent sediments of PZT powder from collecting on the bottom of the Teflon liner. It was also observed that the microstructure evolution and the crystallinity of films could be influenced by the concentration of the precursors in the solution as well as by the deposition temperature and time. For effective film deposition and less sedimentation, the solutions with a concentration of 1 M were used. The deposited samples were ultrasonically cleaned and, finally, were dried at 80 °C in a box-type oven for 2 h. The films deposited at 150 °C for 24 h were $\sim 1.6\ \mu m$ in thickness.

For the phase analysis, X-ray diffractometry (KFX-987288-SE, Mac Science Co., Japan) with Cu Kα radiation was utilized. The crystallographic orientation between the

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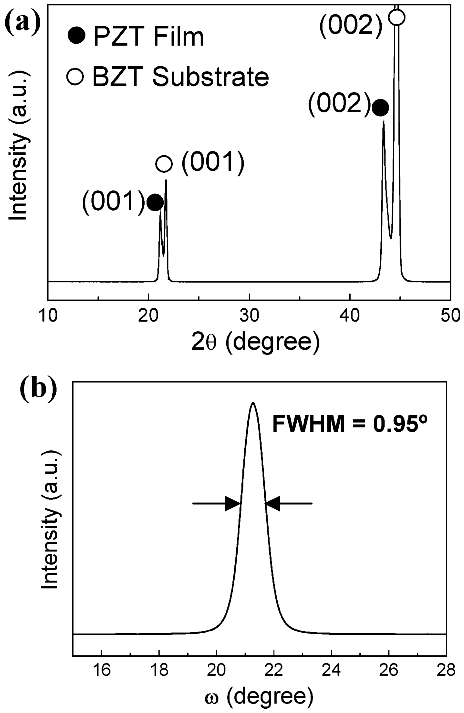

Figure 1. (a) X-ray diffraction pattern of PZT film grown on a BZT single-crystal substrate at 150 °C for 24 h, showing that the films are *c*-axis oriented. (b) Rocking curve of (002) PZT showing that the fwhm is 0.95°.

film and the substrates were examined with a ω-scan using a double-crystal diffractometer (D/max-rc, Rigaku, Japan) and also by pole figure measurements (D/max-IIIc, Rigaku, Japan). The lattice parameters of the tetragonal BZT single crystals and the PZT films were also measured by X-ray diffraction with high-purity Si and LaB_6 powder as standard specimens for precise calibration. The lattice parameter of BZT along the *a*-axis was measured to be 4.023 Å. Since the PZT films were epitaxially deposited on the (001) surface of the substrate, the lattice parameter along the *c*-axis was measured for comparison with that in a JCPDS file (a = 4.027 Å and c = 4.139 Å, JCPDS 50-0346). The lattice parameter measured 4.140 ± 0.006 Å, consistent with the value in the literature. The surface and cross-sectional microstructures of the films were observed using a scanning electron microscope (SEM, SM-300, Topcon, Tokyo, Japan). In addition, high-resolution electron microscopy (HREM, JEM-4010, JEOL Ltd., Tokyo, Japan) operated at 400 kV was used to investigate the interface structures between the PZT films and the substrates.

A typical X-ray diffraction pattern of PZT film grown on a (001) BZT substrate at 150 °C for 24 h is shown in Figure 1a. Only (00*l*) peaks appear in the pattern, indicating that the film has grown epitaxially on the substrate with *c*-axis orientation. Also, the rocking curve measurements shown in Figure 1b indicate that the full width at half-maximum (fwhm) of the PZT film's (002) peak is as narrow as 0.95 (the fwhm of the substrate (0.38) is not shown here). Thus, it can be inferred that the film has a high degree of crystallinity and a low defect density. For further examination of the epitaxial quality between the film and the substrate, a pole figure analysis was used. Figure 2 shows the reflections from the {101} poles of the BZT substrate only (Figure 2a) and of the deposited film on it (Figure 2b). Compared with the spots in Figure 2a, the pole figure reflections from the PZT film of Figure 2b remain sharp with no satellites, confirming the excellent in-plane alignment of the film to the substrate lattice.

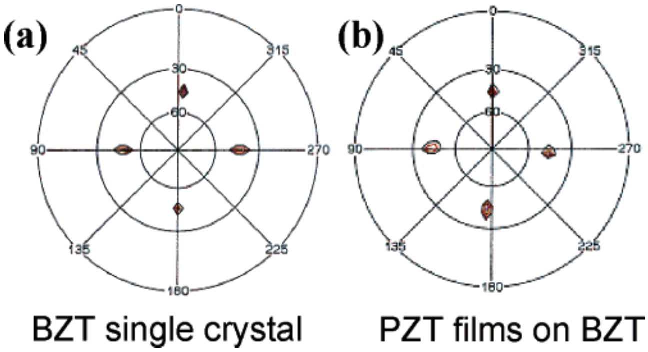

Figure 2. Pole figure reflections from {101} planes of (a) the BZT single-crystal only and of (b) the PZT films on the BZT substrate.

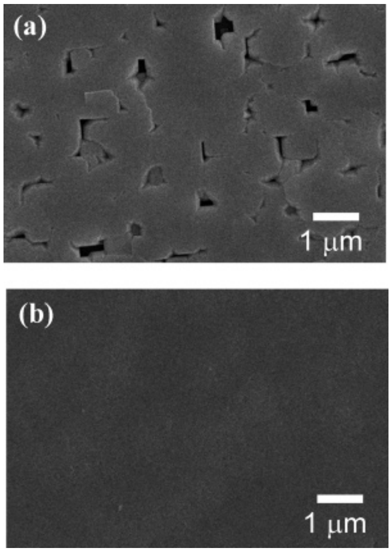

Figure 3. SEM images showing the surface morphology of the PZT films on (a) (001) ST and on (b) (001) BZT at 150 °C for 24 h.

Figure 3 shows the SEM images for the surface morphology of the films grown on the ST (a) and the BZT substrates (b) at 150 °C for 24 h. As shown in the figure, the PZT film deposited on the BZT is smooth and has few pores on the surface, while some faceted pores and an incomplete surface coverage are observed on the film from the ST substrate. Since all the deposition conditions, including temperature, time, and solute concentration in the aqueous solution, are the same, it appears that such a difference in microstructure must be attributed to the substrates used. In fact, the lattice mismatch of the tetragonal PZT (a = 4.027 Å, JCPDS 50-0346) film to the cubic ST (a = 3.905 Å, JCPDS 35-0734) substrate is 3.3%, whereas the lattice mismatch is less than 0.1% between the PZT and BZT (a = 4.023 Å). In most of the previous reports,[3−6] $LaAlO_3$ or $SrTiO_3$ substrates were used for PZT film growth, resulting in more than 3−5% of the lattice misfit. Therefore, mosaic-like patterns during film growth[6] or faceted pores caused by the incomplete coalescence of {100} islands on the films[4] have been frequently observed when synthesis conditions were not well-controlled. In this regard, the present result demonstrates that the BZT

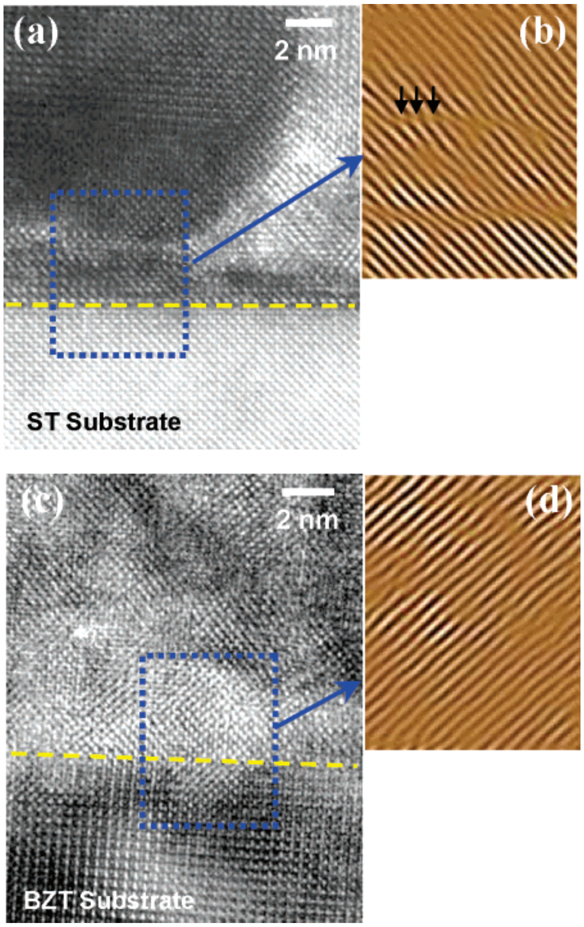

Figure 4. Cross-sectional HREM images of the interface region between the films and each substrate with their Fourier filtered images indicated by a rectangle; (a) and (b) are the ST substrate, while (c) and (d) are the BZT substrate. The broken line in (a) and (c) represents the interface between the films and the substrates. Small arrows in (b) indicate the misfit dislocations.

single crystal is a promising substrate for epitaxial PZT films with a smooth surface and little lattice misfit.

The structures around the interface between the films and the substrates can be observed in more detail using HREM. Figure 4 shows cross-sectional HREM images at the interface regions of each specimen. As shown in Figure 4a, the PZT film on the ST substrate is initially deposited up to a few nanometers, showing epitaxial growth behavior. Due to the lattice misfit between the film and the substrate, however, the observed epitaxy cannot be sustained as the film grows. This may cause misfit dislocations to form in the film, resulting in lattice mismatch. Figure 4b is a Fourier filtered image of the region marked by the rectangle in Figure 4a. Arrows indicate the formation misfit dislocations, and lattice distortion at the interface can be clearly observed as well. By contrast, when the BZT substrate is used as the substrate, an outstanding epitaxial growth behavior can be seen, as shown in the HREM image of Figure 4c. This observation is also confirmed by the Fourier filtered image in Figure 4d, which demonstrates little lattice distortion and few misfit dislocations.

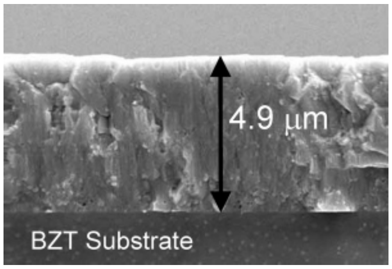

Figure 5. SEM image showing a relatively thick film grown on the BZT substrate at 150 °C for 72 h.

By variation of the deposition time, the thickness of the films can be well-controlled from a few hundred nanometers to several micrometers. Figure 5 is a cross-sectional SEM image of the film grown on the BZT substrate up to ~5 μm at 150 °C for 72 h. As indicated in the figure, a fairly thick film was easily obtained through this process. Because of the excellent lattice match between the film and the substrate, it is believed that thick films can be grown without any appreciable lattice distortion. PZT single crystals with more than several hundred micrometers, therefore, may be grown if the aqueous solution is provided continuously during the synthesis. This alternative approach to single-crystal PZT growth using BZT substrates is now being investigated.

In summary, we have shown that epixial $Pb(Zr_{0.44}Ti_{0.56})O_3$ films are easily produced on a $Ba(Zr_{0.1}Ti_{0.9})O_3$ substrate by hydrothermal synthesis. Considering the lattice constants of the PZT film and the BZT substrate, the lattice misfit between them was estimated to be less than 0.1%. X-ray analyses including pole figure measurements demonstrated that the films have good crystallinity as well as excellent in-plane alignment to the BZT substrate, consistent with the appreciably low lattice mismatch. Also, the surface of the films was observed to be smooth, showing complete surface coverage. Therefore, BZT single crystals are promising substrates for the growth of heteroeptaxial thin films and also possibly for the fabrication of relatively thick PZT single crystals with little misfit strain.

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