Switchable single c-domain formation in a heteroepitaxial PbTiO$_3$ thin film on a (001) Nb–SrTiO$_3$ substrate fabricated by means of hydrothermal epitaxy


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We used hydrothermal epitaxy to fabricate a heteroepitaxial PbTiO$_3$ (PTO) thin film on a Nb-doped (001) cubic SrTiO$_3$ (NSTO) substrate while avoiding the phase transition. By means of transmission electron microscopy and piezoresponse force microscopy analyses, it was confirmed that no a domain formed in the heteroepitaxial PTO film; the film had a single +c-domain structure at an as-synthesized state. From the measurement of the polarization-voltage hysteresis curve, large remanent polarization ($2P_r$: 144 $\mu$C/cm$^2$) resulting from the single +c-domain structure and an imprint induced by an asymmetric electrode configuration were observed. It is suggested that the single +c-domain structure was caused by the interface of the PTO film and solution rather than the interface of the PTO film and NSTO electrode under the hydrothermal conditions. This hydrothermally synthesized PTO film is anticipated to be very suitable for high-performance engineering applications. © 2005 American Institute of Physics. [DOI: 10.1063/1.1951061]

Ferroelectric thin films [BaTiO$_3$ (BTO), PbTiO$_3$ (PTO), and Pb(Zr,Ti)$_2$O$_5$ (PZT)] with a perovskite structure have offered tantalizing potential for engineering applications since their discovery. In particular, their switchable electric polarization (spontaneous polarization, $P_s$) is ideal for use in devices for nonvolatile memory. Conventionally, this polarization is obtained via the paraelectric (PE) to ferroelectric (FE) phase transition. When preparing ferroelectric thin films with a vapor phase and a chemical solution deposition method, a high processing temperature above the Curie point ($T_c$) is required to transform the unwanted intermediate pyrochlore structure to the perovskite structure. In a heteroepitaxial ferroelectric thin film, such as BTO, PTO, and PZT on a cubic oxide single-crystal substrate, a $c/a$-c-polysymmetric domain structure forms during the PE to FE phase transition to relieve the misfit strain energy between the cubic PE and the tetragonal epitaxial FE phase. In this case, the $a$ domains form through four coherent $\{011\}$ twinning, and twin planes become the $c/a$-domain boundary. Investigations have shown that $a$-domain switching is difficult even at very large external field strengths, that is, manipulating the domain structure in ferroelectric thin films is difficult. Therefore, a fabrication method using a lower processing temperature than $T_c$ is needed to restrict $a$-domain formation for high-performance engineering applications. However, it is a formidable challenge to fabricate heteroepitaxial ferroelectric thin films at lower processing temperature than $T_c$ while avoiding the phase transition.

Hydrothermal epitaxy is a technique that utilizes aqueous chemical reactions to synthesize inorganic materials in the form of epitaxial thin films on structurally similar single-crystal substrates under elevated pressure ($<15$ MPa) and at much lower temperature. Reportedly, for the first time, piezoresponse hysteresis representing polarized domain switching was obtained with a hydrothermally synthesized micron-sized PZT single crystal on a Ti substrate. Through a transmission electron microscopy (TEM) analysis, Chien et al. showed that a hydrothermally synthesized PTO film did not exhibit a $c/a$-domain boundary, whereas after heat treatment above $T_c$, the $c/a$-domain boundary in the film was revealed. Therefore, we believe that hydrothermal epitaxy, as opposed to the conventional fabrication methods, affords the possibility to fabricate a perovskite ferroelectric thin film without undergoing the phase transition. However, both the domain structure and the domain switching behaviors of the hydrothermally synthesized heteroepitaxial thin film have not been reported in detail.

In this letter, we used hydrothermal epitaxy to fabricate a heteroepitaxial PTO thin film on a Nb-doped (001) cubic SrTiO$_3$ substrate at lower temperature than $T_c$. Both TEM and piezoresponse force microscopy (PFM) observations clearly indicated that the hydrothermally synthesized heteroepitaxial PTO thin films did not undergo phase transition. Furthermore, a single +c-domain structure in the heteroepitaxial PTO thin film was observed by means of the PFM and this unique domain structure was stable during the hydrothermal epitaxy process.

Heteroepitaxial PTO thin films were fabricated by means of hydrothermal epitaxy on a Nb (0.5 wt %)-doped (001) single-crystal SrTiO$_3$ wafer (NSTO) used as both a substrate and a n-type semiconductor bottom electrode. PTO film with a thickness of approximately 1.2 $\mu$m was synthesized by reacting 0.2 g anatase TiO$_2$ powder with 1 g Pb(NO$_3$)$_2$ in 20 mL of 8 M KOH solution at 160 °C under a compressive hydrostatic pressure of below 15 MPa (maximum operating pressure for a reactor) for 16 h. For a comparison, as-synthesized films were also annealed in air ambient at 600 °C above $T_d$ (490 °C). The heteroepitaxial growth of PTO film on the NSTO substrate was confirmed by x-ray diffraction (XRD). Both TEM and PFM (Seiko SPA 400) were used to observe the domain patterns of the as-synthesized and 600 °C annealed PTO films. During the imaging, the film was scanned with an oscillating tip bias of 5 V$_{pp}$ (peak to peak) at 8 kHz to the bottom electrode. The
ferroelectric hysteresis curve in the hydrothermally synthesized PTO thin film was measured with RT66A ferroelectric tester (Radiant Technologies Co.).

Figure 1 and the inset show the XRD θ–2θ profile and the (101) pole figure of the PTO thin films, respectively. These experimental results clearly show that our PTO thin films were heteroepitaxially grown by means of hydrothermal epitaxy on a NSTO substrate. In addition, no peak from the intermediate pyrochlore structure was found, even though the PTO films were fabricated at very low temperature. With the theoretical approach, it was assumed that the PTO thin film produced at 160 °C did not undergo the phase transition. However, with only TEM results, it is difficult to determine whether a phase transition has occurred during the hydrothermal process while avoiding the phase transition. We can conclude that our PTO thin film has only a single +c-domain structure at the as-synthesized state.

The PFM image (16 μm² area) of an as-synthesized PTO thin film displays only a dark color, which represents the polarization vector directing toward the film surface (+c domain) as shown in Fig. 3(a). PFM images on other areas of one sample and of another batch sample also showed only the dark color at the as-synthesized state. This result indicates that our PTO film has only a single +c domain at the as-synthesized state. On the other hand, as anticipated from the TEM results, the PFM image of 600 °C annealed PTO film in the inset to Fig. 3(a) clearly shows the c/a/-polydomain structure typically observed in a heteroepitaxial ferroelectric thin film on a cubic oxide substrate that has undergone the phase transition. The cross-strips are the {101} twinned a domains on the (001) plane in the tetragonal phase. From TEM and PFM observations, we can conclude that our PTO thin film has only a single +c-domain structure at the as-synthesized state.

Figure 3(b) illustrates the polarization-voltage (P–V) hysteresis curve obtained from the PTO capacitor. In this capacitor, the hydrothermally as-synthesized PTO film was placed between the Pt top electrode and NSTO bottom electrode. The voltage was applied to the top electrode while plotting the P–V hysteresis curve. Compared to the spontaneous polarization (Pₛ; 57 μC/cm²) of PTO crystals fabricated by the conventional high-temperature method, the PTO thin film has large remanent polarization (2Pₛ; 144 μC/cm²) resulting from the single +c-domain structure. However, our PTO capacitors show an imprint phenomena; a negatively biased hysteresis curve is observed, as shown in this figure. It appears that this imprint phenomenon is related to the single +c-domain structure in the PFM image of the PTO film. On the contrary, in the imprint phenomenon, a polarization vector directing toward the PTO film/NSTO substrate is preferable. In the literature, the preference of the polarization direction is explained by a process-induced accumulation of oxygen vacancies at one interface between the film and the substrate. However, oxygen vacancy formation is not possible in our sample, because under the hydrothermal conditions the oxygen is continuously supplied to the growing surface of the tetragonal PTO thin film. Accordingly, we can exclude this intrinsic effect as a cause of the imprint. Reportedly, asymmetric electrode configurations, such as, a metal top electrode and semiconductor bottom electrode, have an influence on which polarization direction is more stable upon application of voltage. When the polarization vectors direct toward the film surface, the negative polarization charges accumulate along the interface of a ferroelectric film and a n-type semiconductor, which induce a large depolarization field. To reduce this depolarization field, the n-type semiconductor should provide sufficient holes equivalent to accumulated negative polariza-
ferroelectric film.4–7,15,22–24 In this study, as shown in Figs.

It is well known that these boundary conditions have a large influence on the kinds of domain structures that form in a hydrothermally synthesized PTO capacitor. The capacitor structure is composed of top and bottom electrodes and PbTiO$_3$ film between the Pt top electrode and Nb-SrTiO$_3$ (n-type semiconductor) bottom electrode (PbTiO$_3$ film thickness: 1.2 µm. Top electrode area: 3.14 × 10$^{-4}$ cm$^2$).

Generally, in a ferroelectric system, to reduce the electrostatic energy associated with the depolarization field, a c/c-polydomain structure is established when no electrical or mechanical boundary conditions exist.24 However, this constitutes an ideal case. Under real circumstances, an epitaxial ferroelectric film should have both electrical boundary conditions such as electrodes and an outer charged atmosphere in the growing state and mechanical boundary conditions such as epitaxial, thermal, and phase transformation strains. It is well known that these boundary conditions have a large influence on the kinds of domain structures that form in a ferroelectric film.4–7,15,22–24 In this study, as shown in Figs. 2(a) and 3(a), a single +c-domain structure formed in the PTO film during the hydrothermal epitaxy process. The effect of the mechanical boundary conditions on domain structure formation is negligible because the phase transition is avoided and very small thermal and epitaxial strains occur at the synthesis temperature.15 Accordingly, it is suspected that the electrical boundary conditions can contribute to the single +c-domain structure formation. If the interface between the PTO film and NSTO electrode is responsible for the domain structure formation during the hydrothermal epitaxy process, the stable polarization direction in the PFM image of the as-synthesized state should be directed toward the interference of the film and substrate. It is assumed that, above room temperature, the electron mobility in the NSTO decreases because polar optical-mode scattering is dominant25 while the mobility of OH$^-$ ions in the KOH solution increase at elevated temperature.26 It is suggested that, under the hydrothermal condition, the high mobility OH$^-$ ions in the solution can screen the positive polarization charges in the ferroelectric PTO film; the interface of PTO film and the KOH solution have a greater effect on the domain structure formation than that of PTO film and a NSTO electrode. Therefore, the single +c-domain structure formed in the as-synthesized state. However, after hydrothermal epitaxy process, the interface between the PTO film and NSTO electrode should be in an unstable state because of incomplete compensation of the negative polarization charge. Further experimental and theoretical analyses on this phenomenon are in progress.

In summary, on the basis of TEM and PFM analyses, it was confirmed that a heteroepitaxial PTO film on a cubic NSTO substrate could be fabricated by means of hydrothermal epitaxy while avoiding phase transition. Furthermore, it was observed by means of PFM that the single +c-domain structure formed in the PTO film. The imprint in the PTO capacitor can be explained by the asymmetric electrode configuration rather than the formation of oxygen vacancies at the interface. It is suggested that, during the hydrothermal epitaxy process, high mobility OH$^-$ ions play a critical role in the single +c-domain formation in the film.

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