Ferroelectric properties of an epitaxial lead zirconate titanate thin film deposited by a hydrothermal method below the Curie temperature

Takeshi Morita, a) Yasuo Wagatsuma, and Yasuo Cho
Research Institute of Electrical Communication, Tohoku University, 2-1-1 Katahira, Aoba-ku, Sendai, Miyagi 980-8577, Japan

Hitoshi Morioka and Hiroshi Funakubo
Department of Innovative and Engineered Materials, Tokyo Institute of Technology, GI-405, 4259 Nagatsuta-cho, Midori-ku, Yokohama 226-8502, Japan

Nava Setter
Ceramics Laboratory, Faculty of Engineering, Material Institute, Swiss Federal Institute of Technology (EPFL), CH-1015 Lausanne, Switzerland

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Deposition of a hydrothermal method has a number of advantages; low deposition temperature, high-purity, deposition on a three-dimensional structure, and a large thickness. The present paper investigates the improvement of an epitaxial lead zirconate titanate (PZT) thin film deposited via hydrothermal synthesis. The critical parameter contributing to the film morphology was revealed to be the holding position of the reaction solution during deposition. In addition to this improvement, the SrRuO3 bottom electrode was confirmed to be able to withstand high alkali concentrations during the hydrothermal reaction. A hydrothermal synthesis time of 24 h yielded a PZT film with a thickness of 500 nm on SrRuO3/SrTiO3 (100) at 150 °C. The remanent polarization 2Pr and coercive electric field were 38.4 μC/cm2 and 21.8 kV/cm, respectively. © 2004 American Institute of Physics. [DOI: 10.1063/1.1762973]

Epitaxial ferroelectric thin films, lead zirconate titanate (PZT) epitaxial thin films in particular, have been intensively studied for use in smart microelectrical mechanical systems and a ferroelectric random access memory due to their large piezoelectric displacement and permanent polarization.1–3 In an effort to obtain such a film, a number of film deposition processes have been explored. These processes include sol-gel methods, sputtering methods, and chemical vapor deposition methods.4–6 However, with these methods, a high-temperature crystallization process (over 600 °C) is required in order to realize a PZT film.

The advantage of the hydrothermal method is low reaction temperature (less than 200 °C). It is important to note that this temperature is below the PZT Curie temperature and more than 400 °C below the reaction temperature required of other methods. Using the hydrothermal method, the PZT thin film can be directly synthesized from an ionic reaction in solution, making it possible to obtain a high-quality ferroelectric thin film. Other superior properties of PZT films obtained using the hydrothermal method are its large thickness, its three-dimensional structure, and its self-alignment with the poling.

In 1991 Shimomura et al. reported that titanium metal is a good substrate for polycrystalline PZT thin film deposition.7 Morita et al. improved upon this hydrothermal process by achieving PZT films in a single-step process.8 These PZT films were then utilized as the drivers for microultrasonic motors and tactile sensors.9–11 Chien et al.12 adopted a SrTiO3 single crystal (100) as a substrate for epitaxial PZT deposition using the hydrothermal method. Unfortunately, electrical measurements for ferroelectric properties were unable to be conducted due to the lack of conductivity of the SrTiO3 substrate. Oledzka et al. later reported an epitaxial PZT thin film with different zirconium, and titanium ion sources at various KOH concentrations, and investigated the influence on the PZT lattice constant and the weight gain.13 While these investigations were advanced, they shared one significant shortcoming; the peeled-off morphology of the resultant epitaxial hydrothermal PZT thin film.13

In order to accurately measure the ferroelectric properties of a hydrothermal PZT thin film, a smooth surface morphology of the film is imperative. Chien’s reaction conditions12 were tested using a SrTiO3 single crystal (100) as a control. The reaction conditions are listed in Table I. The pressure vessel (Parr model 4744) consisted of an inner Teflon™ reaction vessel with a 26.4 mm diameter and maximum volume of 45 ml. After mixing the reactants, a single crystal substrate was placed directly into the reaction vessel, and the substrate was kept at the bottom of the reaction vessel. The reaction vessel was placed into a preheated 150 °C heater. After three hours, the SrTiO3 substrate was removed

| Pb(NO3)2 | 2.64 g |
| ZrOCl2 8H2O | 0.74 g |
| TiO2 | 0.20 g |
| KOH | 10N 15 ml |
| Temp | 150 °C |

TABLE I. Reaction conditions for an epitaxial PZT thin film.


aAuthor to whom correspondence should be addressed; electronic mail: tmorita@ieee.org
and carefully washed with distilled water. Oledzka et al. reported that the deposited film contained cracks and had a peeled-off morphology after the substrate had been reacted for 24 h.\textsuperscript{13} Similarly, here, the substrate was observed to contain cracks and have a peeled-off morphology after only 3 hours. A smooth surface morphology of the film was not achieved by modifying reaction conditions such as the reaction temperature and the concentration of the reactants in solution. Thus, the position at which the substrate was held in the reaction vessel was considered to be the critical condition.

In an effort to confirm this hypothesis a SrTiO\textsubscript{3} substrate, 5.0 mm wide 0.5 mm thick, and 15 mm long, was fixed perpendicular to the bottom of a Teflon plate with a groove to place the substrate in. The SrTiO\textsubscript{3} was clamped to the Teflon plate and placed into the Teflon reaction vessel. All of the other reaction conditions, with the exception of the holding position, were held constant with respect to the verified experiments. After the deposition process, the substrate was observed using both an optical and a scanning electron microscope. These observations clarified that when reacted in the region from the bottom of the vessel to 6 mm above the bottom of the vessel, the surface morphology of the film was observed to peel-off. Figure 1 depicts the optical microscopic observation results for PZT thin films deposited at a depth of 3 and 9 mm. This peel-off surface morphology ob-served at 3 mm was consistent with that of both the control and 9 mm. This peel-off surface morphology obtained at 3 mm was consistent with that of both the control experiment and Oledzka’s report.\textsuperscript{13} Thus, this finding verified the possibility of obtaining a smooth surface morphology by controlling the holding position in the solutions.

When the substrate was held at a depth of 6 to 11 mm during deposition, the resultant film surface was smooth, and SEM images verified that there were no micrometer scale cracks on the surface. At deposition heights greater than 11 mm, the surface was not peeled-off, but was observed to have an uneven morphology. The deposition boundary between a peeling and smooth surface morphology was evident; therefore the origin of the peeling could be determined.

PZT powder is synthesized as a side-product of the hydrothermal method for thin film deposition. If the substrate is placed at the bottom of the reaction vessel, as was done in the previous study, the PZT thin film makes contact with the PZT powder during the reaction. This contact is thought to cause an uneven concentration around the substrate; resulting in an uneven and peeling morphology of the deposited PZT thin film. The uneven surface on the upper layer of the PZT thin film indicated that the chemical concentration was not uniform. This weak chemical concentration resulted in a decreased deposition force. These findings revealed that the optimum depth for obtaining a film with a smooth surface is from 6 to 11 mm.

In order to measure the ferroelectric properties, the bottom electrode is necessary in order to apply the electrical field. SrRuO\textsubscript{3} is a good candidate for the bottom electrode because it had good conductivity and its lattice constant is in close correspondence with that of PZT. The hydrothermal method utilizes KOH, thus it is necessary to confirm that SrRuO\textsubscript{3} electrode can withstand such a high alkali concentration. A SrRuO\textsubscript{3} film was rf sputtered on the SrTiO\textsubscript{3} substrate based on the conditions reported by Takahashi et al.\textsuperscript{14} X-ray diffraction (XRD) measurement indicated that the SrRuO\textsubscript{3} film was epitaxially deposited on the SrTiO\textsubscript{3} at a thickness of 200 nm.

The SrTiO\textsubscript{3} substrate with a SrRuO\textsubscript{3} bottom electrode was used for the hydrothermal deposition. The crystal orientations of the SrTiO\textsubscript{3} were (100). The reaction conditions were identical to those previously reported\textsuperscript{13,12} with the exception of the holding position. The holding apparatus was made of Teflon, and the substrate was maintained horizontally with the SrRuO\textsubscript{3} polished surface facing downward, 8.6 mm above the bottom in the Teflon reaction vessel. The obtained PZT thin film was transparent, and some interference fringes were observed outside the substrate. As depicted in Fig. 2, XRD measurements indicated that the PZT thin film was epitaxially oriented to the SrTiO\textsubscript{3} substrate and only one phase existed without a pyrochlore. The lattice constant tangential to the substrate was calculated to be 0.4134 nm for (001).

When the chemical reaction was complete, the precipitation and dissolution were counterbalanced. Hence, after a certain period of time, the film thickness was saturated in a similar manner to a polycrystalline PZT deposited on a titanium substrate. The saturation time was approximately 9 h for our epitaxial PZT thin film. The SEM cross section of the film deposited after 9 h is shown in Fig. 3. The thickness was 500 nm. This image confirms a high-purity PZT thin film. The obtained film had a fully dense structure. In the deposition of the film shown in Fig. 3, a Nb doped SrTiO\textsubscript{3} substrate was used for SEM observation, although even with non-doped SrTiO\textsubscript{3}, the thickness was confirmed to be same.

The obtained crystal orientations were (100) with a reaction time of 24 h, after which the film thickness was 500 nm. After the hydrothermal reaction, the substrate was dried.
at 200 °C for 1 h under atmospheric pressure conditions. The platinum top electrode was deposited by vacuum evaporation using a metal mask. The hysteresis curve shown in Fig. 4 is the first result of a hydrothermally deposited epitaxial PZT thin film. The remanent polarization $2P_r$ and coercive electric field were 38.4 $\mu$C/cm$^2$ and 21.8 kV/cm, respectively. In this graph, the positive electrical field and positive polarization are oriented in the direction from the bottom to the top electrode. These findings indicate that the PZT thin film has an imprinted electrical field and that the remanent polarization value was not large compared to an epitaxial PZT film deposited by other method, for example, metalorganic chemical vapor deposition. The self-alignment of the polings from the surface to the bottom electrode matched that of polycrystalline PZT deposited a titanium substrate. This automatic polarization is thought to be related to the mechanism of hydrothermal PZT deposition. The obtained values for remnant polarization were not sufficient; however this research has facilitated the pursuit of optimum reaction conditions.