Hydrothermally Deposited PbTiO$_3$ Epitaxial Thin Film

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A hydrothermal method is a unique method to deposit ferroelectric thin films by utilizing chemical reaction in solutions. In addition to the low reaction temperature below 200 °C, its simple process procedure, automatically aligned polarization and three-dimensional deposition are advantages. In this study, a lead titanate epitaxial thin film was obtained on a strontium ruthenate bottom electrode sputterd on strontium titanate (100). High-resolution X-ray diffraction mapping showed that the film was perfectly c-axis-oriented. Transmission electron microscope observation revealed that the film had no lattice dislocation at the interface between lead titanate and strontium ruthenate. A remanent polarization of 96.5 µC/cm$^2$ was measured with a single-crystal-like DE hysteresis curve. Observation by scanning nonlinear dielectric microscopy indicated that this film did not contain any defect such as an a-domain or a grain boundary, even on the nano scale. With various pulse parameters, nano-domain dots were patterned and the minimum dot radius of an inverted domain was 12 nm, corresponding to a data storage density of 1 Tbit/inch$^2$.

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I. INTRODUCTION

Epitaxial ferroelectric thin films, particularly lead zirconate titanate (PZT) and lead titanate (PbTiO$_3$) films, have been studied due to their large piezoelectric displacement and permanent polarization [1–3]. In an effort to obtain such a film, various film deposition processes have been explored, including sol-gel methods, sputtering methods and chemical vapor deposition methods [4–6].

A hydrothermal method [7–15] enables the deposition of a perovskite thin film in aqueous solution at very low temperatures, typically 100 – 200 °C. The high-purity film is attributed to the absence of phase changes during deposition at this low temperature of crystallization. In other deposition methods using a high-temperature process, a lead defect must be taken into consideration, because the vapor pressure of lead oxide is high; therefore, an excess of lead must be compensated. Such lead evaporation does not occur in the hydrothermal method.

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In addition to the low reaction temperature, the hydrothermal method is versatile in that it is a simple process procedure, polarization is aligned automatically, and it achieves three-dimensional deposition.

Barium titanate (BaTiO$_3$) [7], PZT [8–14], and PbTiO$_3$ [15] were previously reported to be deposited by the hydrothermal method. For epitaxial thin films, a single-crystal substrate, such as a SrTiO$_3$ substrate, is effective as reported by Chien et al [12,15]. The shortcoming of the hydrothermal method for the epitaxial film had been the peel-off morphology [12, 13, 15]; however, recently Morita et al. pointed out that the surface morphology was strongly affected by the substrate holding position [14]. By optimizing this position and using a strontium ruthenium oxide bottom electrode, the surface morphology was improved and the ferroelectric properties of the hydrothermally deposited PZT film were successfully measured for the first time. Unfortunately, the DE hysteresis curve of the PZT thin film indicated a large imprint electric field; this film could not be utilized for a data storage medium [14].

The composition ratio of Zr/Ti in the deposited PZT film was controlled in an effort to achieve the morphotropic phase boundary (MPB). The lattice-constant mismatch between the PZT and substrate was relatively large. This mismatch was thought to be responsible for the imprint property of the PZT film. The bulk a-lattice constant of lead titanate is 0.3904 nm, which is very close to that of SrTiO$_3$ (0.3905 nm). The lattice constant of a thin SrRuO$_3$ bottom electrode is considered to be almost equal to that of SrTiO$_3$. Therefore, PbTiO$_3$ has little distortion at the boundary surface with substrate; thus, superior ferroelectric performance is expected.

Lead titanate is an important perovskite-type ferroelectric material, although high-quality crystal was previously thought to be quite difficult to obtain [16–18]. A large coercive field prevented the measurement of the DE hysteresis curve of lead titanate. The remanent polarization for lead titanate was predicted to be 81

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Hydrothermally Deposited PbTiO₃ Epitaxial Thin Film – T. Morita and Y. Cho

μC/cm² [19] and thus far, very few experimental data have been provided for this fundamental value, with the exception of that reported by Tabata [20]. In this study, PbTiO₃ film was deposited on (100) SrTiO₃ and (100) SrRuO₃/SrTiO₃ substrate; then, the crystal quality and ferroelectric properties were studied.

II. DEPOSITION PROCESS

In this study, 0.5-mm-thick SrTiO₃ single-crystal substrates (100) were used. Before deposition, the substrate was treated with buffered hydrofluoric acid (BHF) and annealed at 950 °C [21] in order to obtain an atomic step surface. Atomic-force-microscope observation revealed an atomic step of 0.4 nm at the SrTiO₃ substrate surface. In this study, two kinds of PbTiO₃ thin film were prepared. First, deposition was carried out directly on this SrTiO₃ substrate and the film epitaxiality was estimated. The next one was on SrRuO₃/SrTiO₃ for the ferroelectric measurements. A 50-nm-thick epitaxial SrRuO₃ film was RF-magnetron sputtered as a bottom electrode [22] on SrTiO₃ substrate.

Before applying SrRuO₃/SrTiO₃, we used Nb-doped SrTiO₃ substrate to provide conductivity as a bottom electrode for PZT deposition, although the measured DE hysteresis curve had been strongly distorted. This phenomenon must be related to the conductive mechanism of Nb-doped SrTiO₃, and some research has already been reported [23,24]. When the metal-coated AFM cantilever is used to measure the ferroelectric properties, information just below the probe tip is detected, and the incomprehensible conductive mechanism between ferroelectric film and the bottom electrode can be neglected. However, to study the fundamental properties of deposited ferroelectric films, this strange conductivity with Nb-doped SrTiO₃ bottom electrode must be considered. Therefore, the Nb-doped SrTiO₃ substrate was rejected and the SrRuO₃ bottom electrode on SrTiO₃ was utilized for lead titanate deposition in this study.

The hydrothermal reaction conditions for the epitaxial lead titanate thin film are listed in Table 1. After adding the reagents (Table 1) to the pressure vessel (Parr Model 4744), the substrate was placed in the reaction vessel by using a Teflon holder in the same manner as that for PZT deposition [14]. The substrate was maintained horizontal, 8.6 mm above the bottom of the pressure vessel, facing the polished bottom surface. After either 24 hours or 3 hours of deposition, the substrate was removed, cleaned ultrasonically with distilled water, and dried for 1 hour at 200 °C under atmospheric conditions. It is important to note that the highest temperature achieved in this study was 200 °C, which is far below the Curie temperature of lead titanate (490 °C).

III. CRYSTAL QUALITY AND FERROELECTRIC PROPERTIES

The in-plane lattice constants of SrTiO₃, SrRuO₃ and PbTiO₃ are 0.3905, 0.3930 and 0.3904 nm, respectively [25,26]. The out-of-plane lattice constant of PbTiO₃ is 0.4150 nm. In-plane lattice constants of PbTiO₃ and SrTiO₃ are so close that the PbTiO₃ film was deposited on this SrTiO₃ to examine the crystal quality before using SrRuO₃/SrTiO₃ substrates.

After PbTiO₃ deposition, crystal orientation was estimated by using a high-resolution X-ray diffraction mapping system (X’Pert PRO MPD, Panalytical Co. Ltd.). The full width at half maximum (FWHM) of the rocking curve of (002) PbTiO₃ on SrTiO₃ was 0.060°, indicating that the hydrothermal method has superior potential for high-quality crystal film. For reference, the FWHM of SrTiO₃ (100) single crystal was 0.010°. Such a high-quality crystal ferroelectric film is useful for ultra-high-density data storage media, because such systems require uniform ferroelectric crystal in nano-meter scale.

To apply the conductive bottom electrode, a 50-nm-thick epitaxial SrRuO₃ film was RF-magnetron sputtered on SrTiO₃ that had an atomic step surface. The hydrothermal process to deposit PbTiO₃ was the same as that of PbTiO₃/SrTiO₃. The sample was 3-hour PbTiO₃ deposition type corresponding to 50 nm thickness. The X-ray diffraction mapping at the (103) peak verified the epitaxial deposition and there were no peaks from a domain of PbTiO₃ as shown in Figure 1. As can be seen from Figure 1, in-plane lattice constants for all components, PbTiO₃, SrRuO₃ and SrTiO₃ were very close and the maximum distribution was 0.8 %.

Compared to PbTiO₃/SrTiO₃ film, the PbTiO₃ peak became broad for PbTiO₃/SrRuO₃/SrTiO₃ film. The rocking curve for the PbTiO₃/SrRuO₃/SrTiO₃ was composed of two types of crystals, a good epitaxial film and a broadened one. The former film had almost the same FWHM as PbTiO₃/SrTiO₃, and the latter had about 0.8°. Detailed study of this configuration will reveal the hydrothermal deposition process, and this is under investigation. The FWHM of PbTiO₃/SrRuO₃/SrTiO₃ deteriorated to 0.43° with SrRuO₃ bottom electrode, although this value is good for ferroelectric thin films.

In addition to the X-ray diffraction mapping, an interface between PbTiO₃ and SrRuO₃ was observed with

| Pb(NO₃)₂      | 2.26 g  |
| TiO₂         | 0.393 g |  |
| KOH          | 10N 15 ml |
| Substrate    | SrRuO₃/50 nm/SrTiO₃(100) |
| Temp.        | 150 °C |
| Time         | 3 h or 24 h |

Table 1. Reaction conditions for an epitaxial PbTiO₃ thin film.
a transmission electron microscope (TEM). As shown in Figure 2, each atom, which was impossible to identify as a Pb or Ti ion, was clearly aligned to [001] direction in PbTiO$_3$. This perovskite structure had a lattice constant of 0.4 nm, matching PbTiO$_3$. Surprisingly, there was no lattice dislocation within the observation range of more than 150 nm, corresponding to 600 perovskite structures. Furthermore, no domain wall was found, showing a single-domain structure. This result was in accordance with the X-ray diffraction mapping indicating no a-domain. Perfectly c-axis-aligned epitaxiality was revealed; however, at the interface, the indistinct part was confirmed. Because the position of each atom was disperse, this part was observed as white colored, whose thickness was about 20 nm. This part seems to be related to the broadened rocking curve of 0.8° FWHM with X-ray diffraction. From the point of view of the hydrothermal deposition process, the PbTiO$_3$ film is synthesized through the repeated melting and crystallization processes. The chemically stable condition is the crystal rather than the solution; then, the final state becomes the film structure. At the initial condition the high alkali concentration was thought to corrode the SrRuO$_3$. This consideration suggests that the SrTiO$_3$ has better resistance to alkali solution than SrRuO$_3$, due to the superior FWHM value of PbTiO$_3$ deposited on SrTiO$_3$ without SrRuO$_3$.

IV. FERROELECTRIC PROPERTIES AND NANO-DOMAIN PATTERNINGS

To measure the DE hysteresis curve, a platinum top electrode (0.083 mm$^2$) was evaporated on the PbTiO$_3$ by a shadow-masked metal process, and the DE hysteresis property was subsequently measured. The thickness of the lead titanate film was 100 nm. As shown in Figure 3, a single-crystal-like DE hysteresis curve with well-saturated polarization was obtained. The remanent polarization value was 96.5 µC/cm$^2$ and the coercive electric field was 290 kV/cm. The remanent polarization for lead titanate was predicted to be 81 µC/cm$^2$ [20] and thus far, very few experimental data have been provided for this fundamental value, with the exception of those reported by Tabata [23]. In our case, a relatively superior lattice constant matching the substrate, the low-temperature deposition and the direct deposition with ionic reaction contribute to the high purity and low conductivity of the crystal. The initial imprint direction of the film was from the bottom electrode to the surface, which was in agreement with that observed in scanning nonlinear dielectric microscopy (SNDM) observation as shown later. The imprint must be related to the deposition mechanism of the hydrothermal method, and this subject is under investigation.

By using the epitaxial PbTiO$_3$ thin film deposited for 3 hours (50-nm thickness), the inverse domain was patterned by using a platinum-iridium-coated atomic force probe. The curvature radius of the probe was 25 nm and the electrical potential of the probe was grounded. The domain pattern was drawn by applying a DC plus or minus voltage with an amplitude of 5 volts to the SrRuO$_3$ bottom electrode, in three successive scanning processes. The scanned areas were 800 nm, 400 nm and 200 nm square, respectively. After three scanning procedures, the domain pattern was observed by SNDM [27–29]. As shown in Figure 4, the expected domain pattern was obtained; however, the area was about 50-nm larger than that expected. This was due to the spread of the electric field below the scanned probe tip. As seen in the figure, the polarization direction was aligned during deposition process and the poling treatment was not re-
A pulse voltage was subsequently applied to pattern domain dots with various pulse parameters, as shown in Figure 5. The minimum dot radius of 12 nm was achieved under the trial parameters with –5 V and a 40-µsec pulse. This size corresponds to a data size of 1 Tbit/inch², and is a match for the data storage density by using a congruent lithium tantalate (CLT) medium [27, 29]. The high crystal quality of a CLT single crystal was suitable for an ultra-high-density medium, although the process to reduce the thickness to less than 100 nm was complicated. Recently, a smart film fabrication process using a polarization controlled wet etching process for CLT [30]. The simple process of the hydrothermal method and the large permittivity of PbTiO₃ are additional advantages from the point of view of higher resolution of SNDM measurements. However, the poling reversal response of lead titanate to the short pulse was relatively inferior. At a voltage of –5 V, the 40-µsec pulse was the limitation for the reversal of poling. To date, CLT has been confirmed to respond to a 4-nsec pulse [29]. This property determines the writing speed for the data storage system; thus, it is required in order to investigate which material parameter is related to the fast response against the electric field.

V. SUMMARY

An epitaxial lead titanate thin film was successfully deposited on SrRuO₃/SrTiO₃ substrates. The crystal quality was estimated with the high resolution X-ray diffraction mapping and the transmission electron microscope observation. The results indicated that the film was composed of a perfectly c-axis-oriented structure, and there was no lattice dislocation at the interface. The distinct part at the interface was thought to be made at the initial state of the hydrothermal synthesis.

A single-crystal-like DE hysteresis curve indicated that a high quality single crystal film. The polarization direction was aligned from the bottom to the surface during deposition, and uniform ferroelectricity was confirmed with SNDM observation. With the DE hysteresis curve, the remanent polarization was 96.5 µC/cm² and coercive electric field was 290 kV/cm. Using the PbTiO₃ film the domain direction was controlled with conductive cantilever and detected with SNDM. The obtained
nano-dot pattern verified the suitability of lead titanate film as an ultra-high-density data storage medium. At present, the pulse parameter is being optimized in order to obtain a smaller dot radius.

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