Significant suppression of island growth in epitaxial (Pb,La)(Zr,Ti)O₃ thin films by two-step growth technique

Shinya KONDO, Tomoaki YAMADA,† Masahito YOSHINO, Tadashi SHIOTA,† Kazuo SHINOZAKI† and Takanori NAGASAKI

Department of Materials, Physics and Energy Engineering, Nagoya University, Furo-cho, Chikusa-ku, Nagoya 464-8603, Japan
†School of Materials and Chemical Technology, Tokyo Institute of Technology, Meguro-ku, Tokyo 152-8550, Japan

(001)-epitaxial (Pb₀.₉₁La₀.₀₉)(Zr₀.₆₅Ti₀.₃₅)O₃ (PLZT) ferroelectric thin films were fabricated on SrTiO₃ and MgO substrates, with an SrRuO₃ bottom electrode layer, using pulsed laser deposition. When films were deposited in a single step at a high temperature conventionally used for epitaxial growth, island growth was observed. To suppress the island growth, we used a two-step growth technique. First, a thin initial layer was deposited at a low temperature to promote rapid strain relaxation from the lattice mismatch. After deposition of this layer, the substrates were heated to and maintained at the higher temperature. This step leads to further crystallization of the first layer and confines dislocations to the film/substrate interface. Thus, effective strain relaxation from the lattice mismatch is achieved in the first thin layer, while realizing films with high crystallinity and flat surfaces. Finally, we performed film deposition again at the same elevated temperature until the desired film thickness was obtained. Using this technique, we suppressed island growth in epitaxial PLZT thin films.

1. Introduction

Recently, electro-optic (EO) devices using plasmonic waveguiding¹⁻³ have attracted much attention as plasmonic EO devices may offer a superior device performance over the conventional optical switches and modulators.²⁻⁵ To date, functional EO materials such as polymers⁶⁻⁸ and nematic liquid crystals have been used in waveguides because these materials allow relatively facile device fabrication. However, their EO coefficients and long-term reliability are not as good as those of oxide ferroelectrics⁹ as typified by (Pb,La)(Zr,Ti)O₃ (PLZT) and PbMg₁/₃Nb₂/₃O₃-PbTiO₃ (PMN-PT). Since such plasmonic EO devices are normally short due to the inherent metal losses, integrating oxide ferroelectrics into plasmonic EO devices requires the formation of epitaxial films with a high degree of structural perfection possessing strong EO effects. In addition, the film needs to be uniform and with a smooth surface because the highly confined optical mode in plasmonic devices is very susceptible.

Island growth often occurs in epitaxial PLZT⁵ and PMN-PT⁶ thin films, which leads to films with rough surfaces. Even with optimized growth conditions, it is not possible to avoid hillock-formation on film surfaces.⁸ Although the reasons for island growth have not been fully clarified yet, the strain relaxation process from the lattice mismatch between films and substrates would strongly correlate with island formation in PLZT and PMN-PT thin films.

In this study, we used a two-step growth technique, which was originally developed for semiconductor films.¹⁰⁻¹⁴ A very thin layer of less than 10 nm was first deposited at a temperature lower than that suitable for coherent epitaxial growth.¹³ This step yields a higher nucleation density, which promotes strain relaxation from the lattice mismatch. After deposition of the first thin layer, the substrates were heated to and maintained at the higher temperature. This step leads to further crystallization of the first layer and confines dislocations to the film/substrate interface. Thus, effective strain relaxation from the lattice mismatch is achieved in the first thin layer, while realizing films with high crystallinity and flat surfaces. Finally, we performed film deposition again at the same elevated temperature until the desired film thickness was obtained. Using this technique, we suppressed island growth in epitaxial PLZT thin films.

2. Experimental

PLZT films with thickness 170–190 nm were fabricated on 60-nm-thick SrRuO₃ (SRO)-covered SrTiO₃ (STO)(001) and MgO(001) single-crystal substrates by pulsed laser deposition (PLD) with a KrF excimer laser (λ = 248 nm), using one- and two-step growth techniques. The laser energy and repetition rate were 60 mJ and 10 Hz, respectively. A ceramic of (Pb₀.₉₁La₀.₀₉)-(Zr₀.₆₅Ti₀.₃₅)O₃ containing 5% excess PbO, which was sintered by spark-plasma sintering, was used as a target to achieve the stoichiometric lead composition in the deposited PLZT films. The conductive SRO layer served as the bottom electrode. In a plasmonic EO device, it can also serve as plasmonic waveguide cladding because the real part of its permittivity can be negative.¹⁵ After depositing the PLZT films, a circular platinum layer of diameter 100 nm and thickness 50 nm, was deposited onto the films by electron beam evaporation to serve as the upper electrode.

Figures 1(a) and 1(b) illustrate the temperature profiles of the normal (hereafter, one-step) and two-step growth processes, respectively. For the former, the entire film was deposited at 625°C in 200 mTorr O₂. For the latter, a 6-nm-thick film was first deposited at 450°C in 200 mTorr O₂, then, the substrate was heated to 625°C and the temperature was maintained for 15 min. Finally, the second main layer was deposited onto the first layer at 625°C in 200 mTorr O₂. Both the one- and two-step grown films achieved the same total film thicknesses.
The crystal structure and the orientation of the PLZT films were determined by X-ray diffraction (XRD) using a four-axis diffractometer with Cu-Kα X-rays (Bruker, D8 DISCOVER). The microstructure and surface morphology of the fabricated PLZT films were observed using a scanning electron microscope (SEM) (Hitachi, S-4800), an atomic force microscope (AFM) (Asylum Research, MFP-3D) and reflection high-energy electron diffraction (RHEED) (ULVAC). Their ferroelectric properties were measured using a ferroelectric tester (Toyo Corporation, FCE-1). To investigate optical properties of the PLZT films, a prism coupler (Metricon Corporation, Model 2010) with a He–Ne laser (λ = 632.8 nm) through a prism was used.

3. Results and discussion

Figure 2 shows XRD θ–2θ patterns for PLZT films deposited on SRO/STO substrates by one- and two-step growth processes. Both PLZT films had a perovskite structure without any secondary phases and perfect (001)-orientation (in pseudocubic Miller index) along the substrate normal direction. XRD φ scans for PLZT (110) and STO (110) planes shown in Fig. 3 assigned the epitaxial relationship of both films to be PLZT[100]∥STO[100]. XRD patterns for PLZT films on SRO/MgO substrates (not shown) also demonstrated the same epitaxial relationship regardless of which growth process was used. Figure 4 shows XRD ω scans, i.e., rocking curves for the PLZT (002) of the films on SRO/STO substrates. The full width at half maxima (FWHM) for the one- and two-step grown films were 0.04 and 0.03, respectively, which indicates that both films have high crystallity comparable with that of reported PLZT films on similar substrates.
subsiteds.\textsuperscript{16)} Conversely, the FWHM for the one- and two-step films on MgO substrates were 1.01 and 0.95, respectively. The measured FWHM for PLZT, SRO, and substrates are listed in Table 1. PLZT films on SRO/MgO had larger FWHM caused by the large mosaicity of the SRO bottom electrode layer on the MgO substrates, which is likely caused by a geometrical mismatch of the atomic configuration at the interface between perovskite SRO and rock-salt MgO. Thus, the epitaxy of PLZT films depends on the substrate type used. It should be noticed that there was no degradation of epitaxy by employing the two-step growth process.

Fig. 5. RHEED images of PLZT films on SRO/STO along the STO[110] azimuth: (a) 60- nm-thick SRO bottom electrode layer on STO, (b) one- and (c) two-step grown PLZT films. (c-1) and (c-2) show patterns of the first 6-nm-thick layer deposited at 450°C, before and after heating to 625°C, respectively. (c-3) shows a pattern from the film after depositing the second homo-epitaxial layer at 625°C.

Table 1. FWHM of rocking curves for PLZT films deposited on SRO/STO and SRO/MgO by one- and two-step growth processes. The values for PLZT(002), SRO(002), STO(002), and MgO(002) are listed.

<table>
<thead>
<tr>
<th>Substrate</th>
<th>FWHM (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>One-step</td>
</tr>
<tr>
<td>STO</td>
<td></td>
</tr>
<tr>
<td>SRO</td>
<td>0.02</td>
</tr>
<tr>
<td>PLZT</td>
<td>0.04</td>
</tr>
</tbody>
</table>

Fig. 6. SEM plane view images of PLZT films grown on SRO/STO by one- (a-1) and two-step growth processes (a-2) and on SRO/MgO films by one- (b-1) and two-step growth processes (b-2).

growth process was used; however, island growth was not entirely suppressed unlike the films grown on SRO/STO. The reason for residual island growth of films on SRO/MgO may be because of the larger mosaicity of SRO on MgO than that on STO, as shown in Table 1.

The XRD, RHEED, and SEM findings support the above mentioned scenario for the two-step growth process. The deposition of a defective first thin layer at low temperature followed by annealing at high temperature promotes confinement of dislocations to the film/substrate interface. This results in a significant strain relaxation from the lattice mismatch in the first thin layer while maintaining uniform film surfaces. Conversely, slow strain relaxation for the one-step growth process resulted in the Stranski-Krastanov growth mode, for which the island growth dominates above the critical thickness. However, it should be noted that, although the strain relaxation for the one-step growth process was slow, the films were also fully relaxed by the end of film deposition as can be seen in XRD reciprocal space map (Fig. 7). As a result, the both one- and two-step-grown films have almost the same lattice parameters (see Table 2).

To quantitatively discuss the effect of the two-step growth process on suppression of island growth in PLZT films, the surface roughness was measured by AFM. As shown in Fig. 8, the AFM surface morphologies of the PLZT films agreed well with the SEM observations shown in Fig. 6. Root mean square (RMS) surface roughness values estimated from $2 \times 2$-μm$^2$ AFM scans are listed in Table 3. The two-step growth process significantly reduced the surface roughness of PLZT films on both substrates. In particular, the film on SRO/STO from the two-step growth process achieved an RMS surface roughness of 0.36 nm, one of the lowest values reported among PLZT films. By comparison, a 150-nm-thick PLZT film grown on SRO/STO by RF-magnetron sputtering, one of the reported flattest films, had an RMS surface roughness of 0.9 nm.\textsuperscript{16)} It has been reported that the surface roughness of 2 nm would raise the loss of a 200-nm-thick film by 2 dB/cm or more.\textsuperscript{17)} Thus, our more uniform film will help realize light propagation in an optical waveguide with lower losses.

Fig. 9 shows typical $P-E$ loops measured at 10 kHz for PLZT films grown by one- and two-step growth processes on both substrates. The narrow hysteresis loops indicate the relaxor-type ferroelectricity, typical for the chemical composition of PLZT used in the present study. The remnant polarization $P_r$ and coercive field $E_c$ did not strongly depend on the substrate type.
Nevertheless, the two-step grown films showed a slightly larger $P_r$ compared with that of the one-step grown films. This is unlikely to be caused by the difference in residual strain between the one- and two-step grown films because the one-step grown films were also relaxed during the deposition of entire films (see Fig. 7 and Table 2). Although further investigations are needed, the larger $P_r$ observed for the two-step grown films may have arisen from the perfectly-dense and uniform film structure due to the rapid strain relaxation in the first layer.

Finally, we measured the refractive indices of the PLZT films grown in two steps using a prism coupling technique. Polarized light was coupled into the PLZT layers. The reflective indices in transverse electric mode for the films on SRO/STO and SRO/MgO were 2.5 and 2.4, respectively, which are almost the same as reported values for bulk PLZTs. Thus, applying a two-step growth process to fabricate PLZT films is a promising approach to plasmonic EO devices.

### 4. Conclusion

To fabricate epitaxial PLZT films having fairly flat surfaces for use in plasmonic EO devices, we deposited PLZT on SRO/STO and SRO/MgO by PLD using a two-step growth technique. Island growth of the films was significantly suppressed using the two-step growth process, and resulted in films with an RMS surface roughness value as low as 0.36 nm. Furthermore, the two-step growth process did not lead to any degradation of epitaxy. The PLZT films fabricated in two steps exhibited refractive indices comparable with the reported values for bulk PLZT, indicating their great potential for applications in EO devices.
Acknowledgement  This work was partly supported by Concert-Japan Project “FF-Photon” from Japan Science and Technology Agency. We thank Dr. Ping Ma at ETH-Zurich for fruitful discussions.

References