Low-temperature growth of epitaxial PZT/LSMO/LAO film by excimer laser-assisted metal organic deposition (ELAMOD)

T. Tsuchiya, I. Yamaguchi, T. Manabe, S. Mizuta and T. Kumagai
National Institute of Advanced Industrial Science and Technology (AIST), Tsukuba Central 5, 1-1-1 Higashi, Tsukuba, 305-8565, Japan

E-mail:tetsuo-tsuchiya@aist.go.jp

Abstract. The preparation of the epitaxial Pb(Zr,Ti)O\textsubscript{3}:PZT film on SrTiO\textsubscript{3}: STO, LaAlO\textsubscript{3}: LAO, MgO and La\textsubscript{0.7}Sr\textsubscript{0.3}MnO\textsubscript{3}: LSMO / LAO substrates using the excimer laser-assisted metal organic deposition (ELAMOD) process was investigated. When using the STO substrate, the epitaxial PZT film was obtained by the ArF laser irradiation at room temperature using the 2-step irradiation method. On the other hand, when using the LAO and MgO substrates, no single phase of the PZT film was obtained by the ArF laser irradiation at room temperature. The LSMO buffer layer was prepared on the LAO substrate by thermal MOD at 1000°C, and the PZT film was then prepared on the LSMO / LAO substrate by ELAMOD at room temperature. The effects of the laser fluence, shot number and buffer layer thickness on the PZT epitaxial growth were investigated. An epitaxial PZT / LSMO / LAO film was successfully obtained by ArF laser irradiation at 80mJ/cm\textsuperscript{2} and room temperature. The formation mechanisms of the epitaxial PZT films by ELAMOD are also discussed.

1. INTRODUCTION

Since lead zirconate titanate (Pb(Zr,Ti)O\textsubscript{3}: PZT) has recently attracted a great deal of attention due to its ferroelectric properties, the processing of the PZT thin film has been investigated from various viewpoints. Among the unsolved problems for its processing, the development of the low temperature processing for the films on a silicon substrate has been increasingly recognized. To overcome these problems, we have already investigated the epitaxial growth of Pb(Zr,Ti)O\textsubscript{3} [1, 2, 3] and La\textsubscript{1-x}Sr\textsubscript{x}MnO\textsubscript{3}:LSMO [4, 5] films by excimer laser-assisted metal organic deposition (ELAMOD). However, the epitaxial growth mechanism of the oxide films by this method has not yet been clarified. In the case of the thermal MOD process, the epitaxial growth of an oxide thin film would be significantly related to the lattice mismatch between the film and substrate [6]. Therefore, the orientation or crystallinity of the produced film was expected to be dependent on the lattice mismatch using ELAMOD. In a previous paper [3], we investigated the effect of the substrate with various lattice matching and optical absorption characteristics on the epitaxial growth of the PZT film. As a result, we found that another important factor of the crystal growth of the oxide film by ELAMOD that needs to be considered is the photothermal effects due to the optical absorption of the substrate materials in the UV region. In this paper, to clarify the epitaxial growth of a PZT film using the ELAMOD process, we investigated the effect of the buffer layer on the epitaxial growth of the PZT film. In this study, we used the La\textsubscript{0.7}Sr\textsubscript{0.3}MnO\textsubscript{3}: LSMO material as a buffer layer, because it has a strong optical absorption at 193 nm and a lower lattice matching compared to the LAO substrate. In addition, oxide electrodes such as LSMO have been recently thoroughly and been studied because PZT capacitors with noble metal electrodes like Pt exhibit a significant polarization loss (fatigue) when subject to bipolar switching pulses [7, 8, 9].
2. EXPERIMENTAL

The $La_xSr_{1-x}MnO_3$: LSMO (001) film on the LAO (001) substrate was prepared by the thermal MOD. A homogeneous starting solution was prepared by mixing of the constituent metal-naphthethenate solutions (Nihon Kagaku Sangyo) and diluting with toluene to the appropriate concentration (1mol/l) and viscosity for spin coating. The molar ratios of La, Sr, and Mn in the coating solution were 0.7, 0.3 and 1.0, respectively. This solution was spin-coated onto a single-crystal LAO (001) substrate at 4000rpm. The MO coated films were dried at 200°C in air to eliminate the solvent. The films were next heated and kept at 500°C for 10 min, and then heated at 1000°C for 2h or irradiated by an ArF excimer laser (Lambda Physik, Compex110) while being heated at 500°C in air. The irradiated part was 10 mm×5 mm. The thickness of the obtained films prepared by these procedures was 40 nm. Thicker films were prepared by repetition of these procedures.

The starting solution for the PZT film was prepared from a commercially available zirconium 2-ethylhexanoate oxide mineral spirits solution, titanium 2-ethyl-1-hexanolate and lead-2-ethylhexanoate. These were mixed at the molar ratio of Pb:Zr:Ti = 2.0:1.0:1.0., and homogeneously dissolved in toluene and n-butyl alcohol. The PZT films were deposited on SrTiO$_3$: STO (001), LaAlO$_3$: LAO (001), MgO (001) and $La_xSr_{1-x}MnO_3$: LSMO (001) / LAO (001) substrates. The lattice mismatch between PZT and STO, MgO, and LAO is 3.34 %, 4.45 %, and 6.65 %, respectively. This solution was spin-coated onto the substrates at 4000 rpm. The MO coated films were then dried at 200°C in air to eliminate the solvent. During the first step, the coated films were directly irradiated by the unfocused ArF laser excimer (Lambda Physik, Compex110) at a repetition rate of 25 Hz and at a fluence of 20 mJ/cm$^2$ for 1min and then irradiated by the ArF excimer laser at the repetition rate of 10 Hz and at fluences of 70 ~ 90 mJ/cm$^2$ with 600~6000 shots. To adjust the film thickness, the spin-coating and laser irradiation procedures were repeated five times. The crystallinity and epitaxy of the PZT films were examined by XRD (MAC Science, M03XHF22) 0-2θ scans (CuKα, 40 kV, 30 mA), and pole-figure analysis. In this paper, the index notation was adapted as pseudo cubic on the STO, LAO and MgO substrates.

3. RESULTS AND DISCUSSION

After the first irradiation step at the repetition rate of 25 Hz and at a fluence of 20 mJ/cm$^2$ for 1min, no peaks, except for the substrates, were observed in the XRD 0-2θ scans profiles, while the IR peaks due to the metal organic compound had completely disappeared. Therefore, the metal organic compound was decomposed, and amorphous oxide films were formed on STO, LAO and MgO substrates during the first irradiation step. Fig.1 shows XRD 0-2θ profile scans for PZT films on LAO (001), STO (001) and MgO (001) substrates after the second irradiation step at 80 mJ/cm$^2$. In the case of using the STO substrate, the peaks of PZT 002 are observed on the shoulders of the strong STO ones. When using the LAO substrate, very weak peaks of PZT 002 and the pyrochlore phase are observed. For the MgO substrate, no PZT peak was observed after the irradiation.
Based on results, the formation or crystallization of the PZT films was found to strongly depend on the substrate. It must be emphasized that with the epitaxial PZT films was not formed on the MgO substrate whereas the lattice mismatch is smaller than on the LAO substrate. Therefore, lattice matching is not the only parameter that influences to the crystal growth. For the ELAMOD process, the most plausible factor for controlling the epitaxial growth would be the photothermal effect due to the optical absorption of the substrate materials, because the absorption of LAO at 193 nm is much higher than that of the MgO substrate. Accordingly, if we used a buffer layer with a high absorbance at 193 nm and small lattice mismatching, the epitaxial PZT film would be formed on the LAO substrate, whereas it has a small optical absorption at 193 nm.

To confirm the effect of the optical absorption of the substrate on the epitaxial growth of the PZT film, we used a LSMO thin film as a buffer layer. The film was highly oriented on the LAO substrate. Also, the in-plane of the films was corroborated on the basis of the XRD pole figure analysis. Fig. 2 shows the AFM image of the LSMO film on LAO substrate. The average grain size was 30 nm. The resistivity of the LSMO film prepared by this method was $1.7 \times 10^{-3} \Omega \cdot \text{cm}$.

Fig. 3 shows the XRD patterns of the PZT films on the LSMO/LAO substrate prepared by ELAMOD using different laser fluences. At 70 mJ/cm$^2$, the PZT (002) peak is observed and the intensity increased with the increasing laser fluence to 80 mJ/cm$^2$ and decreased with the increasing laser fluence to 90 mJ/cm$^2$. Based on these results, it was found that the oriented PZT film on the LSMO / LAO substrate was successfully obtained by the ELAMOD. To examine the in-plane alignment of the films on the LSMO/LAO substrates, we performed an XRD pole-figure analysis. As a result, four sharp spots of the PZT 110/101 reflections were observed at every 90°. Therefore, the formation of the epitaxial PZT film on the LSMO / LAO substrate by the two-step irradiation method was confirmed.

Next, we investigated the effect of the shot number on the crystallinity of the epitaxial PZT film. Fig. 4 (a) shows the XRD patterns of the PZT films on the LSMO / LAO substrates prepared by ELAMOD using different shot number. As can be seen from the figure, a single phase epitaxial PZT film on LSMO / LAO is obtained by the ArF irradiation at 1200 shots. However, for the 600 shots and 2400 shots, the pyrochlore phase was observed. For the thermal process, it was reported that the pyrochlore phase was formed when the firing temperature was under 500°C or when lead was deficient after heat treatment at a high firing temperature[10, 11]. Based on these results, the effect of the shot number on the PZT growth by ELAMOD would be explained as follows. For 600 shots, the existence of the pyrochlore phase would be
considered to be due to the insufficient energy supply like lower temperature process. On the other hand, for the 2400 shots, the pyrochlore phase seemed to be formed due to a lead deficiency caused by the laser ablation. Similarly, we investigated the effect of the shot number on the formation of the PZT films irradiated by the ArF laser at 70 mJ/cm\(^2\) as shown in Fig. 4 (b). The crystallinity increased with the increase in the number of shots. The peak intensity of the films irradiated by the ArF laser at 70 mJ/cm\(^2\) for 6000 shots is the same as that of the film irradiated with 80 mJ/cm\(^2\) for 1200 shots. Thus, it was found that the crystallinity of the PZT film by ELAMOD depends on the combination of the laser fluence and shot number. Fig. 5 shows an AFM image of the films prepared by the ArF laser irradiation at (a) 70mJ/cm\(^2\) and 6000 shots and (b) 80mJ/cm\(^2\) for 1200 shots.

As can be seen from the figures, the surface morphology of film (a) is more uniform and the average grain size is 50nm. When using a higher fluence, the surface of the PZT film would be considered to be partially...
ablated by the laser irradiation.

Next, to clarify the effect of the LSMO buffer layer on the PZT epitaxial growth, we prepared a PZT film on the LSMO films which have different film thicknesses. Fig. 6 shows the relationship between the LSMO film thickness and the XRD intensity of the (002) PZT peak. As can be seen from figure 6, when the LSMO film thickness is 40 nm, no film is formed on the LAO substrate (Fig 1). On the other hand, when the LSMO film thickness is 80 nm, PZT (002) peak was observed. The peak intensity increased with an increasing the LSMO film thickness up to 160 nm. According to optical data, the light penetration depth into LSMO film at 193 nm is 70 nm. Based on these data, the reason why no PZT film was obtained on the LSMO (40nm) / LAO substrate would be caused by the inefficient absorption of the laser energy. Thus, it was found that the buffer layer thickness is very important to prepare the epitaxial growth of PZT film by the ELAMOD at low temperature.

Fig. 6 Relationship between LSMO film thickness and the XRD intensity of 002 PZT peak.

From these results, we proposed the formation mechanism of the PZT film by this process. When the metal organic (MO) on a substrate was irradiated by the excimer laser, the MO film was converted to an amorphous oxide film by photolysis of the MO materials during the first-step irradiation, and then the crystallization or orientation of the oxide film was considered to occur through a photo thermal reaction due to the light absorption of both the amorphous films and substrate during the second irradiation step. Therefore, it was concluded that not only a lattice mismatch, but also the photo thermal effect of the substrate material or buffer layer materials influence the epitaxial growth of the PZT film. The optimization study for the crystallinity, morphology and electrical properties are now in progress. However, the processing temperatures of the PZT/LSMO/LAO films are lower compared to the other methods, and are compatible with the integrated circuit technology. Thus, the ELAMOD method would be useful for the preparation of the PZT film at low temperatures.

4. Conclusion

The preparation of the epitaxial PZT film on the STO, LAO and LSMO/LAO substrates using the ELAMOD process was investigated. In the case of using the STO substrate, an epitaxial PZT film was
obtained by ArF laser irradiation at fluence of 80 mJ/cm$^2$ and at room temperature. On the other hand, when using the LAO and MgO substrates, no single phase of PZT film was obtained on the LAO substrate by the ArF laser irradiation. An epitaxial PZT / LSMO / LAO film was successfully obtained by ArF laser irradiation at 80 mJ/cm$^2$ and room temperature. It was found that the epitaxial growth could be controlled by a kind of buffer layer which has a strong absorption in a UV region. In addition, the buffer layer thickness was found to be important for the epitaxial growth by ELAMOD. ELAMOD can be useful for the preparation of the PZT / LSMO / LAO at low temperature.

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