Stress engineering of the alkoxide derived ferroelectric thin film on Si wafer

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This paper specifically examines control of the residual stress in thin films by design of the stacking structure. For this study, we prepared highly a-, c- oriented PZT(30/70) (PZT30) thin films using chemical solution deposition (CSD). A PZT30 thin film was deposited on LaNiO3 (LNO)/Pt/Ti/SiO2/Si and LNO/SiO2/Si with different LNO layer thickness to control the thermal stress. An LNO layer was also prepared using CSD on a Pt/Ti/SiO2/Si substrate and SiO2/Si substrate. The residual stresses in the PZT30 thin films were estimated using Raman analysis. Furthermore, the dielectric property of samples was measured using an impedance analyzer. Effects of the residual stress on the dielectric behavior were demonstrated through experiment.

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1. Introduction

Ferroelectric thin films have been widely incorporated into ferroelectric random access memories and microactuators. For these applications, many researchers have reported that the microstructure,† crystal orientation,‡ electrode,¶ and residual stress‖ are important factors to improve electrical properties in thin films. Therefore, we must control many factors to attain higher electrical properties and to create high-performance devices. Previous reports show that the residual stress in thin films is an important factor that affects the thin films’ electrical properties. For example, Ito et al. reported that large compressive residual stress engenders increased dielectric properties and increased tunability.§ Ong et al. reported that the tensile residual stress decreases the piezoelectric property.‖ Therefore, control of the residual stress in thin films is an important research field to obtain ferroelectric thin films with high electrical properties.

In previous papers, we reported that control of the residual stress in thin films is possible by changing the substrate with a different thermal expansion coefficient,¶¶ changing the annealing condition,¶¶ and changing the wafer thickness.¶¶ Results of our previous studies demonstrated that changing the substrate with different thermal expansion coefficient was an effective method to control the residual stress in thin films. This method has also been reported by other researchers to control the thermal stress.¶¶ Here, single crystal substrates such as STO (11.7 × 10−6 /°C), MgO (13.5 × 10−6 /°C) are necessary to generate larger compressive residual stress, resulting in higher dielectric properties because of their higher thermal expansion coefficient than that of the film materials. However, from the viewpoint of commercial use, single crystal substrates such as STO and MgO are not reasonable substrates in terms of cost performance. Therefore, we propose a new method to control the residual stress in an alkoxide derived thin film using a commercial Si substrate.

Lanthanum nickel oxide (LaNiO3; LNO) is known as a metal oxide electrode with a larger thermal expansion coefficient (12.9 × 10−6 /°C) than that of Pt (8.8 × 10−6 /°C).¶¶ In the case of Pb(Zr0.5Ti0.5)O3 (PZT30) thin film on LNO and Pt, the thermal stress for PZT30 thin film will be compressive stress in both cases because the thermal expansion coefficient of PZT30 is reported as 9.8 × 10−6 /°C.¶¶ In addition, the thermal stress for PZT30 thin film on the LNO layer is expected to be larger compressive thermal stress than that on the Pt layer. Generally, this material is used as the seeding layer to control the crystal orientation. However, many researchers ignore the effect of this seeding layer on the residual stress in thin film, especially for chemical vapor deposition (CVD) processes, because the seeding layer is exceedingly thin.¶¶ Fujito et al. reported that the large tensile residual stress was relaxed by the buffer layer. They demonstrated this phenomenon using PZT thin film on a (La0.5Sr0.5)CoO3 (LSCO) buffer layer using pulsed laser deposition (PLD).¶¶ The residual stress in the thin film can be controlled according to the buffer layer structure design. Therefore, reasonable buffer layer thickness and stacking structure should be confirmed to generate the expected residual stress, resulting in high electrical properties.

As described in this paper, we report the effect of the buffer layer structure on the residual stress in a thin film to design the buffer layer structure for larger compressive residual stress in thin films. Furthermore, effects of the residual stress on the dielectric property were demonstrated using an alkoxide-derived film.
2. Experimental procedure

The LNO and PZT30 thin films were prepared using CSD. The starting reagents for LNO precursor solution were lanthanum nitrate \([\text{La(NO}_3\text{)}_3 \cdot 6\text{H}_2\text{O}]\) and nickel acetate \([\text{Ni(CH}_3\text{COO)}_2 \cdot 4\text{H}_2\text{O}]\). The \([\text{La(NO}_3\text{)}_3 \cdot 6\text{H}_2\text{O}]\) and \([\text{Ni(CH}_3\text{COO)}_2 \cdot 4\text{H}_2\text{O}]\) were dehydrated at 150°C for 1 h. The dehydrated lanthanum nitrate was dissolved in 2-methoxy ethanol at room temperature. The dehydrated nickel acetate was dissolved in 2-methoxy ethanol and 2-amino ethanol (mixing ratio of 5/1) at 115°C for 20 min. Both the obtained solutions were mixed at room temperature for 2 h, and the precursor LNO sol was obtained. The precursor concentration was adjusted to 0.3 M.

The LNO precursor film was deposited on a Pt/Ti/SiO\(_2\)/Si substrate and a SiO\(_2\)/Si substrate by spin coating at 3500 rpm. The precursor film was dried at 150°C for 5 min, pre-annealed at 350°C for 5 min, and annealed at 700°C for 5 min using rapid thermal annealing (RTA) under an oxygen flow for every coating layer. The rate of temperature increase was adjusted to be 200°C/min. The LNO films were prepared through five repetitions of the spin-coating process.

We prepared PZT sols corresponding to the composition of \(\text{Pb(Zr}_0.3\text{Ti}_0.7\text{O}_3}\) with 10 mol% lead excess using lead acetate \([\text{Pb(CH}_3\text{COO)}_2]\), titanium isopropoxide \([\text{Ti(iso–OC}_3\text{H}_7)_4]\) and zirconium n-propoxide \([\text{Zr(OC}_3\text{H}_7)_4]\). Details of the process are described elsewhere. \(^{16},^{17}\) The precursor concentration was adjusted to be 0.3 M.

The PZT30 precursor film was deposited on LNO/Pt/Ti/SiO\(_2\)/Si substrates and LNO/SiO\(_2\)/Si substrates by spin coating at 3500 rpm. The precursor film was dried at 150°C for 5 min, pre-annealed at 420°C for 5 min, and annealed at 650°C for 5 min using rapid thermal annealing (RTA) for every coating layer. The rising temperature speed for RTA was adjusted to 200°C/min. The LNO films were prepared through five repetitions of the spin-coating process.

We prepared PZT sols corresponding to the composition of \(\text{Pb(Zr}_0.3\text{Ti}_0.7\text{O}_3}\) with 10 mol% lead excess using lead acetate \([\text{Pb(CH}_3\text{COO)}_2]\), titanium isopropoxide \([\text{Ti(iso–OC}_3\text{H}_7)_4]\) and zirconium n-propoxide \([\text{Zr(OC}_3\text{H}_7)_4]\). Details of the process are described elsewhere. \(^{16},^{17}\) The precursor concentration was adjusted to be 0.3 M.

The LNO precursor film was deposited on Pt/Ti/SiO\(_2\)/Si substrate and SiO\(_2\)/Si substrate by spin coating at 3500 rpm. The precursor film was dried at 150°C for 5 min, annealed at 700°C for 5 min using rapid thermal annealing (RTA) under an oxygen flow for every coating layer. The rate of temperature increase was adjusted to be 200°C/min. The LNO films were prepared through five repetitions of the spin-coating process.

The crystal orientation of the obtained samples was measured using an X-ray diffractometer (XRD, D4 Endeavor; Bruker AXS GmbH). The residual stress in thin films was measured using a cross section FE–SEM image (with Carl Zeiss Supra 35 VP, JSM 5800; JEOL Ltd.). The dielectric constant was estimated using an impedance analyzer (HP4192).

### 3.1 Crystal orientation

Figures 1 and 2 show respective XRD patterns for the obtained PZT30 thin film on a LNO/Pt/Ti/SiO\(_2\)/Si structure and that on a LNO/SiO\(_2\)/Si structure. The LNO buffer layer was a completely (100) oriented thin film; the PZT30 layer was also a highly (100) oriented thin film in all samples. For the PZT30/Pt/Ti/SiO\(_2\)/Si stacking structure, the PZT30 thin film includes a low amount of (111) oriented grains [Fig. 1(a)]. The ratio of (111) oriented grains was less than 10%. In general, the crystal orientation degree is an important factor that affects residual stress in thin films. However, we need not consider this effect in this report because an almost identical crystal orientation degree exists in all samples.

### 3.2 Buffer layer structure

Figure 3 portrays cross section FE–SEM images of our samples. The LNO layer thickness increased concomitantly with the increasing number of the film deposition process. The LNO thickness of the 1 layer was estimated as 40 nm. On the other hand, the obtained PZT film thickness was estimated as 200 nm. The PZT30 layer was a columnar and dense structure. However, the microstructure of LNO was a granular structure; a few nanopores were confirmed in the LNO layers. In addition, the SiO\(_2\) layer thickness was determined to be about 400 nm from Fig. 3(c). The Ti layer between the Pt and SiO\(_2\) layer was about 10 nm. Therefore, the effect of Ti layer on the thermal stress can be ignored.

### 3.3 Raman analysis

Figures 4 and 5 respectively depict the Raman spectra of PZT30 thin films on the LNO/Pt/Ti/SiO\(_2\)/Si and LNO/SiO\(_2\)/Si stacking structure. All phonon modes were assigned as PZT30 lattice vibrations except for one peak at around 400 cm\(^{-1}\). The band at 400 cm\(^{-1}\) can be assigned to the phonon mode of the PZT30 lattice vibrations except for one peak at around 400 cm\(^{-1}\). The band at 400 cm\(^{-1}\) can be assigned to the phonon mode of the PZT30 lattice vibrations except for one peak at around 400 cm\(^{-1}\). The band at 400 cm\(^{-1}\) can be assigned to the phonon mode of the PZT30 lattice vibrations except for one peak at around 400 cm\(^{-1}\).

In that equation, \(\omega_0\), \(\Gamma\), and \(F\) respectively signify the mode fre-
quency, the damping factor and the oscillator strength. Furthermore, $\gamma_r$ and $F_r$ respectively represent the inverse relaxation time and the strength associated with the relaxation mode.

The residual stress in PZT30 thin film was calculated using Eq. 2. In this study, A(2TO) phonon mode shift was used to estimate the residual stress in the PZT thin film.

$$\omega(\sigma) = \omega(0) - \frac{\partial \omega}{\partial \sigma} \sigma$$  \hspace{1cm} (2)

Fig. 3. Cross section FE–SEM images of PZT30/LNO/Pt/Ti/SiO$_2$/Si. (a) LNO: 1 layer (40 nm), (b) LNO: 4 layers (160 nm), (c) the interface between Si and SiO$_2$ part, (d) the microstructure of LNO layer.

Fig. 4. Raman spectra for PZT30/LNO/Pt/Ti/SiO$_2$/Si stacking structure. (a) LNO: 0 nm (PZT/Pt/Ti/SiO$_2$/Si), (b) LNO: 40 nm, (c) LNO: 80 nm, (d) LNO: 120 nm and (e) LNO: 160 nm.

Fig. 5. Raman spectra for PZT30/LNO/SiO$_2$/Si stacking structure. (a) LNO: 40 nm, (b) LNO: 80 nm, (c) LNO: 120 nm and (d) LNO: 160 nm.

Therein, $\omega(0)$ is the frequency of the A(2TO) phonon mode under a stress-free condition. In addition, $\partial \omega/\partial \sigma$ is proportional to the pressure $\sigma$. $\partial \omega/\partial \sigma$ was reported as 13.9 cm$^{-1}$/GPa for A(2TO).$^{13}$

The LNO buffer layer thickness dependence of the residual stress in PZT30 thin film is presented in Figs. 6(a) and (b). For the PZT30/LNO/Pt stacking structure [Fig. 6(a)], the maximum residual stress was $-1.37$ GPa for LNO that was 160 nm thick. The residual stress decreased to $-0.83$ GPa for 40-nm-thick LNO; finally, the residual stress was $-0.46$ GPa for 0-nm-thick.
plane cell area by the phase transition. In this research, this factor should be almost the same in all cases because all samples have nearly the same crystal orientation degree. Although the perfect theoretical calculation for the residual stress in the resulting capacitor structure derived from hybrid integration of the CSD-derived electrode and ferroelectric thin films is impossible because of the many uncertain factors, we make effort to calculate the difference of the residual stress in PZT thin films on the different stacking structures using the reported equations, mainly taking into account the thermal stress, not the epitaxial stress and the phase transition stress.

In general, the thermal stress can be estimated as shown in Eq. (3)\(^{23}\)

\[
\sigma_{\text{thermal}} = \frac{E_f}{(1-\nu_f)} \int_0^T \left( \alpha_f - \alpha_s \right) dt ,
\]

where \(E_f\) and \(\nu_f\) respectively represent the Young’s module and Poisson’s ratio. Also, \(\alpha_f\) and \(\alpha_s\) respectively signify the thermal expansion coefficient of the film and substrate; \(T_f\) and \(T_0\) respectively denote the annealing temperature and room temperature (30°C). In addition, \(E_f\) and \(\nu_f\) respectively signify 100 GPa and 0.27 for PZT30, 180 GPa and 0.30 for LNO, and 168 GPa and 0.38 for Pt. The thermal expansion coefficient of the Si was reported as \(2.6 \times 10^{-6}\) (24).

From the constants presented above, thermal stress of PZT30 thin film on Si, Pt, and LNO, were estimated, respectively, as 0.61 GPa, 0.08 GPa, and –0.26 GPa. The minus sign in the figure means that the residual stress is compressive. Each values were calculated using Eq. (3). From the theoretical calculation, the residual stress in the PZT30 thin film on the LNO layer is expected to increase compared to that of PZT30/Pt. However, if the LNO layer thickness was less than 120 nm, the LNO layer also has large tensile stress, as reported by Zhao et al., thereby decreasing the residual compressive stress in PZT30 thin film. Zhao et al. described the thickness dependence of the residual stress in an LNO layer on a Si wafer. In their report, the residual stress in the LNO layer relaxed at 100 nm film thickness. In our study, we also estimated the change in the residual stress in LNO with thickness. Figure 7 portrays the change in the residual stress in LNO on Si and PZT on LNO/Si as a function of the LNO thickness. The residual stress in LNO was calculated from XRD analysis. Results show that the obtained values from Raman analysis were nearly identical to those of the XRD analysis. Raman and XRD analyses provide an almost identical stress value and the same stress direction.

In general, the total residual stress in a thin film is reported as the sum of the lattice misfit strain (\(\sigma_{\text{misl}}\)), thermal stress (\(\sigma_{\text{thermal}}\)), and the phase transition stress (\(\sigma_{\text{transition}}\)).\(^{19}\) In this research, the alkoxide derived PZT film was deposited on LNO layers. Namely, the (100)-oriented LNO layer effectively acts as the seeding layer to obtain the (100)-oriented PZT layer by the local epitaxy. However, the lattice misfit strain should be omitted in the case of alkoxide-derived films, because this factor acts only for epitaxial film with bellow 10 nm thick.\(^{20,21}\) In addition, the phase transition stress changes depend on the crystal orientation degree, because this factor is determined by the change in the in-plane cell area by the phase transition.\(^{22}\) In this research, this factor should be almost the same in all cases because all samples

LNO (PZT30/Pt). We observed a strong increase of the compressive residual stress in PZT30 thin film at the LNO thickness less than 120 nm, which might result from the relaxation of the residual tensile stress in LNO layer on a Si wafer. In addition, the residual stress in PZT film on LNO/SiO\(_2\)/Si structure was estimated using the XRD technique to demonstrate that Raman analysis is a powerful tool for residual stress measurement in a ferroelectric thin film. The residual stress from XRD analysis was estimated by \(\sin^2\Psi\) method. Figure 6(b) portrays a comparison of the residual stress from Raman and the XRD analysis. Results show that the obtained values from Raman analysis were nearly identical to those of the XRD analysis. Raman and XRD analyses provide an almost identical stress value and the same stress direction.

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![Fig. 6. (a) Change in the residual stress in PZT30 film on LNO/Pt/SiO\(_2\)/Si as a function of the LNO buffer layer thickness. (b) Change in the residual stress in PZT30 film on LNO/SiO\(_2\)/Si as a function of the LNO buffer layer thickness.](image)

![Fig. 7. Change in the residual stress in PZT30 and LNO as a function of the LNO thickness.](image)
PZT30 thin film was independent of the LNO thickness because the residual stress in the LNO layer was independent of the thickness. The LNO layer also receives thermal stress from the under-layer. For LNO/Pt and LNO/Si, the thermal stresses in the LNO layer are calculated respectively as 0.71 GPa and 1.77 GPa [Fig. 8]. Namely, the LNO layer acts as the relaxation layer for the constrain stress from Si wafer which leads to the compressive stress in PZT layers. Therefore, the residual compressive stress in PZT gradually increased with increasing relaxation layer in the range up to 120 nm thick.

Here, the difference of the residual stress in PZT30 thin film between PZT30/LNO/Pt/Ti/SiO2 and PZT30/LNO/SiO2 stacking structure is about 0.6 GPa for all cases [Figs. 6(a) and 6(b)], although the difference of the theoretical calculation of the residual stress in LNO layer was about 1.0 GPa. This value is almost half. From Fig. 3(d), the obtained LNO layer has a few nanopores in the LNO layer. Therefore, the residual stress in LNO layer relaxed because of the nanopores in the LNO layer, engendering a small difference of the residual stress in PZT30 thin film compared to that of the theoretical value.

### 3.4 Dielectric Property

Figure 9 presents the frequency dependence of the dielectric constant of PZT30/LNO/Pt/Ti/SiO2 and PZT30/LNO/SiO2 stacking structure with different LNO thickness. Consequently, the dielectric constant increased concomitantly with increasing LNO thickness. Ito et al. reported that the dielectric constant of BaTiO3 thin film increased concomitantly with increasing compressive thermal stress.8) Therefore, the tendency shown here is a very reasonable result. Figure 10 portrays the change in the reciprocal of the dielectric constant at 1 kHz as a function of the residual stress. Fu et al. reported the relation between the residual stress and the dielectric constant. According to the modified Devonshire’s theory, under the assumption that only a 2D stress acts in the plane of the film, Eq. 4 can be given as:26)

$$\frac{\partial \varepsilon^{-1}}{\partial \sigma} = \text{const.}$$

(4)

If the reciprocal of the dielectric constant (1/ε) is proportional to the residual stress, then it can be said that the dielectric constant behavior changes according to Devonshire’s theory. In addition, they also showed the change in the 1/ε along α-axis as a function of the residual stress in lead titanate thin film was 0.0013 /GPa.27)

In contrast, that of the (100)-oriented PZT(30/70) thin film was estimated to be 0.0015/GPa in this study. Therefore, the obtained change in the 1/ε with stress is considered to reasonable value. Consequently, the difference of the dielectric constant of these samples was affected by the difference of the residual stress because the 1/ε is proportional to the residual stress and change in the 1/ε with the residual stress was also reasonable value. The residual stress was controlled by the design of the stacking structure, bringing improvement of the dielectric behavior using the stress control method described herein.

### 4. Conclusions

Highly α- c-oriented PZT30 thin films was prepared using CSD on a different stacking structure. All thin films have almost identical film thickness, microstructure, and crystal orientation, but different residual stress conditions. The residual stress in thin film was controlled by the stacking structure design. The compressive residual stress increased concomitantly with increasing LNO buffer layer thickness, and the residual stress in PZT30 thin film also increased as a result of the relaxation of the residual stress in LNO layer. Therefore, the residual stress in the under-layer (buffer layer, electrode, etc.) strongly affects the residual stress in thin films. The dielectric constant was changed according to the modified Devonshire’s theory, meaning that the dielectric constant was also controlled by control of the residual stress in thin films.
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References