Preparation of lanthanum strontium cobalt oxide electrode on a Si wafer for stress engineering of ferroelectric thin films

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The precursor solution for lanthanum strontium cobalt oxide (LSCO) was modified to increase the single-layer film thickness. Results show that LSCO with 170 nm thickness was deposited on a Si wafer for stress engineering of a ferroelectric thin film. The single-layer film thickness for LSCO layer increased concomitantly with increasing viscosity in LSCO precursor solution. In addition, the crystalinity and the electrical resistivity of a LSCO with lanthanum nickel oxide (LNO) seeding layers using the modified LSCO precursor solution was nearly equal to that of the reported LSCO precursor solution. The residual stress in lead zirconate titanate with Zr/Ti = 53/47 composition thin film on a LSCO(170 nm)/LNO(160 nm)/Si stacking structure was −0.9 GPa compressive stress, which enhances the ferroelectric property (2Pc = 120 μC/cm²).

1. Introduction

Ferroelectric perovskite thin films have been widely studied in recent years for their possible applications in microelectromechanical systems (MEMS),13) nonvolatile random access memory (FeRAM),14) and high-performance thermo-sensors.15) For these advanced applications, many parameters such as microstructure, orientation, and residual stress must be controlled because these parameters determine the electrical properties in a ferroelectric thin film.16–18) The residual stress is an important parameter to control the electrical properties. Therefore, many reports describe estimates of residual stress in thin films. Effects of the residual stress on the electrical properties have also been reported in the literature.7–9)

In our previous studies, we attained the stress engineering of lanthanum nitrate nitrate [La(NO3)3·6H2O], metal strontium (Sr), and cobalt acetate [Co(CH3COO)2·4H2O]. All reagents were dissolved separately to 2-methoxyethanol. Subsequently, La and Sr precursor solutions were mixed for 2 h at room temperature. Finally, the obtained La–Sr precursor solution and Co precursor solution were mixed for 2 h to obtain the LSCO precursor solution with (La0.5,Sr0.5)CoO3 composition (A-type LSCO precursor solution). In addition, 1,3 butanediol was added to Co precursor solution to increase the viscosity in the precursor solution (B-type LSCO precursor solution). The mixing ratio of 2-methoxyethanol to 1,3 butanediol in Co precursor solution was adjusted to 5:5 (B1-type) and 3:7 (B2-type).

All PZT/LSCO/LNO stacking structures were deposited on a Si wafer by spin coating with 3000 rpm. Thicknesses of the LNO and PZT layers were adjusted, respectively, to 160 and 600 nm. The viscosity for the LSCO precursor solution was estimated using a vibration type viscometer (SV-10; A&D Co. Ltd.). Each layer thickness was measured using scanning electron microscopy (FE-SEM, with Carl Zeiss Supra 35 VP, JSM 5800; JEOL). The lattice strain in PZT thin films was calculated using sin2Ψ method using X-ray diffraction (XRD, D8 advance; Bruker AXS GmbH). The ferroelectric property was evaluated using a ferroelectric test system (FCE–PZ type; Toyo Technical Co.)
3. Results and discussion

3.1 Effects of the precursor solution viscosity on film thickness

Figure 1 shows a cross sectional FE-SEM image of the obtained PZT/LSCO/LNO/Si stacking structure using B1-type LSCO precursor solution. The respective LNO, LSCO, and PZT film thicknesses were 160, 170, and 700 nm. Figure 2 shows the change in the single-layer film LSCO layer thickness with increased viscosity in the LSCO precursor solution. The respective viscosities of the 2-methoxyethanol and 1,3-butanediol are 1.2 and 154.0 cP. Therefore, the viscosity of B-type LSCO precursor solution increased concomitantly with increasing amounts of 1,3-butanediol. In addition, the homogeneous LSCO layer was obtained up to 7.0 cP (B1-type precursor solution) under the spin coating condition with 3000 rpm. The relation between the film thickness and the viscosity in the precursor solution is reported as

\[ h = \frac{h_0}{\sqrt{1 + \frac{4\rho \omega^2 h_0^3 t}{3\eta}}} \]  

(1)

here, \( \rho \), \( \omega \), and \( \eta \) respectively denote the density, the rotational speed and the viscosity. In addition, \( h_0 \) and \( t \) respectively stand for the solution thickness under the shear-stress-free condition and the spin coating time. If \( h_0 \) is constant in this spin coating condition, then the obtained results show nearly the same tendency as that of the theoretical relation.

3.2 Crystallinity and electrical resistivity

Figure 3 shows XRD patterns for the obtained LSCO thin films on a Si wafer. The LSCO layer thickness with approximately 60 nm was deposited on a Si wafer using A-type and B1-type LSCO precursor solution to estimate the effect of the precursor type on the crystallinity. For the A-type LSCO precursor solution, the LSCO thin film crystallinity was better than that of the B1-type precursor solution, which could be attributable to the difference of the single-layer thickness. Therefore, the electrical resistivity of the obtained LSCO layer using A-type precursor solution and that of the B1-type precursor solution were, respectively \( 11.2 \times 10^{-3} \) and \( 35.6 \times 10^{-3} \) \( \Omega \) cm. However, the crystallinity of the LSCO thin films using the LNO seeding layer was nearly the same. Figure 4 shows the XRD patterns for the obtained LSCO thin films with approximately 60 nm thickness on a LNO(160 nm)/Si stacking structure: (a) using A-type LSCO precursor solution and (b) using B1-type LSCO precursor solution.
films showed the $a$-axis preferred orientation because the LNO seeding layer was $a$-axis preferred orientation. In addition, the peak intensity of the LSCO/LNO was almost identical. Consequently, the electrical resistivity of the A-type and the B1-type LSCO on a LNO/Si stacking structure was also nearly the same value of $2.0 \times 10^{13} \, \Omega \, \text{cm}$.

Figure 5 shows the XRD analysis of the obtained PZT/LSCO/LNO/Si films with different LSCO layer thickness using B1-type LSCO precursor solution. The obtained PZT thin films on a LSCO/LNO/Si stacking structure were $a$- and $c$- preferred orientations independent of the LSCO layer thickness. This result was identical to that obtained for the LSCO layer using A-type precursor solution. These results show that the modified LSCO precursor solution (B1 type) was an effective precursor solution to increase the single-layer thickness for LSCO layers without reduction in quality. In addition, Fig. 6 shows the high angle XRD pattern of the PZT/LSCO/LNO/Si with LSCO = 170 nm. In the case of the bulk PZT with MPB composition, the crystal symmetry has been reported as the mixture of tetragonal and rhombohedral, and/or the monoclinic mono-phase. However, the obtained PZT thin film with MPB composition was assigned as the tetragonal mono-phase which could be due to the huge compressive residual stress. Therefore, we analyzed the residual stress condition in PZT thin film as the tetragonal symmetry.

3.3 Stress engineering

For the A-type LSCO precursor solution, the LSCO layer thickness of 80 nm was the limit without reduction in the quality of a formed film. Therefore, the largest residual stress in PZT(53/47)/LSCO/LNO/Si was approximately $-0.8 \, \text{GPa}$. However, for the PZT/LNO/Si stacking structure, LNO layer with 160 nm thickness was necessary to apply the theoretical compressive thermal stress to PZT thin film in our previous study. Therefore, we deposited the LSCO layer with 170 nm thickness using B1-type LSCO precursor solution in this study. Figure 7 shows the change in the (002) and (200) peaks positions in PZT(53/47) thin films on a LSCO(170 nm)/LNO(160 nm)/Si with increasing $\Psi$ angle. The arrows show (002) peak positions. The (002) and (200) peak positions shift to higher angles with increasing $\Psi$ angle because the compressive lattice strain exists in PZT(53/47) thin films. The residual stress in PZT thin films was calculated using sin$^2 \Psi$ method. Results show that the residual stress in PZT thin film on a LSCO(170 nm)/LNO(160 nm)/Si structure was calculated as $-0.9 \, \text{GPa}$.

In general, the total residual stress in a thin film is defined as the sum of the lattice misfit strain ($\sigma_{\text{misfit}}$), thermal stress ($\sigma_{\text{thermal}}$), and the phase transition stress ($\sigma_{\text{transition}}$). However, for alkoxide-derived thin films, the lattice misfit strain must be omitted because of the relaxation process. Therefore, the total residual stress is regarded as the sum of the thermal stress and the phase transition stress. Here, the theoretical thermal stress in PZT thin film on a LSCO layer under this annealing condition is calculated as $-0.8 \, \text{GPa}$. The phase transition stress is also a compressive stress component. From the consideration above, the theoretical total residual stress in PZT thin films is expected to be greater than $-0.8 \, \text{GPa}$. Therefore, the obtained $-0.9 \, \text{GPa}$ compressive residual stress in PZT thin film on a LSCO/LNO/Si stacking structure is concluded as the reasonable value.
Therefore, we concluded that the increase of the thermal compressive residual stress in the case of ferroelectric thin film with preferred orientation to the polarization axis. Therefore, we concluded that the increase of the thermal compressive stress engenders the enhancement of the remanent polarization. Finally the remanent polarization with 60 μC/cm² (2P_r = 120 μC/cm²) was attained under the −0.9 GPa residual stress condition.

4. Conclusions

PZT/LSCO/LNO stacking structure was deposited on a Si wafer using CSD method. For stress engineering in PZT thin film on a Si wafer, LSCO films with 170 nm was deposited on a LNO/Si stacking structure using the modified LSCO precursor solution (B1-type precursor solution). The LSCO film thickness per one process increased concomitantly with increasing viscosity in a LSCO precursor solution, and 21 nm for one spin coating process was attained. The crystallinity and the electrical resistivity of the LSCO/LNO stacking structures were nearly the same as that of the reported precursor solution (A-type precursor solution). The residual stress in PZT thin film on a LSCO(170 nm)/LNO(160 nm)Si was estimated as −0.9 GPa. The ferroelectric property was enhanced with increased compressive residual stress, and the maximum remanent polarization

Fig. 8. P–E hysteresis loops of the obtained PZT thin films: (a) −0.8 GPa residual stress and (b) −0.9 GPa residual stress.

Figure 8 shows P–E hysteresis loops for PZT thin films under −0.8 and −0.9 GPa residual stress conditions. Choi et al. reported that the remanent polarization increased concomitantly with increasing compressive residual stress in the case of ferroelectric thin film with preferred orientation to the polarization axis. Therefore, we concluded that the increase of the thermal compressive stress engenders the enhancement of the remanent polarization. Finally the remanent polarization with 60 μC/cm² (2P_r = 120 μC/cm²) was attained under the −0.9 GPa residual stress condition.

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