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Effect of rapid thermal annealing on residual stress in lead titanate thin film by chemical solution deposition

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Abstract

The effect of annealing process on the residual stress in the lead titanate (PT) thin film was investigated in this study. The residual stress in the films with different annealing process was calculated from the phonon mode shift. As a result, the residual stress in the films deposited by the rapid thermal annealing was larger than that in the films by normal annealing process. In addition, the large residual stress in the films by the rapid thermal annealing was relaxed by the post annealing to the value in the film deposited by normal annealing. Moreover, the dielectric behavior of the films obeyed the modified Devon Shire theory which was proposed in our previous study.

Keywords: A. Sol–gel processes; C. Dielectric properties; E. Membranes; Residual stress

1. Introduction

Ferroelectric thin films have been received great interest in many fields. Memories such as dynamic random access memory (DRAM), static memory (SRAM) [1] and ferroelectric random access memory (FeRAM) [2] were proposed, and then ferroelectric films have been rapidly wide spreaded for other types of applications: FeRAM, pyroelectric detectors, and micro actuators for MEMS. However, for these applications, we should design the device structures because the electrical properties of the ferroelectric thin films depend on a lot of parameters, such as microstructure [3], orientation [4], residual stress [5], and so on.

The residual stress is one of the most important factors to control the electrical properties of the ferroelectric thin films. Yanase et al. [6] reported that the large residual stress resulted in the ferroelectricity for the epitaxially grown barium titanate film with thickness bellow the critical size. Under the critical size, the crystal structure should be a cubic symmetry by the size effect. However, large residual stress led to the tetragonal phase by lattice misfit strain to exhibit the ferroelectricity. In their report, lattice misfit was measured by XRD. However, the actual value of the residual stress could not be calculated. On the other hand, Sun et al. [7] calculated the residual stress in a lead titanate (PT) polycrystalline film from the phonon mode shift. They reported that the large residual stress of 2.6 GPa existed in a lead titanate film with 220 nm thickness. In our previous work [5], thickness dependence of the residual stress was investigated as well as the relationship between the dielectric behavior and the residual stress. Our previous work [5] also showed that the frequency of the soft mode decreased with decreasing film thickness. This suggests the residual stress in the film increased with decreasing film thickness. Moreover, the relation between the dielectric constant and the residual stress obeyed the modified Devon Shire theory. This theory indicates that the reciprocal of dielectric constant changed linearly as a function of stress [8] and the observed reciprocal of dielectric constant increased linearly with increasing film thickness. The intrinsic dielectric constant along *a*- and

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c-axes were also successfully derived by extrapolation into the ambient pressure, which was in good agreement with the values of the single crystal. This indicates that the effect of the residual stress could be appropriately estimated by the shift of the soft mode, *E*(1TO). However, the residual stress should be changed by annealing process, because the different crystallization behavior by the various annealing process should arise the different residual stresses. Therefore, we investigated the effect of annealing process on the residual stress in this paper.

2. Experimental procedure

The PT thin films with thickness ranging from 380 to 1125 nm on Pt/Ti/SiO_2/Si substrate were deposited by a chemical solution deposition (CSD). The starting reagents for the preparation of the PT precursor solution are a lead acetate trihydrate and a titanium isopropoxide. The details for the processing are described elsewhere [9]. In this study, PT precursor films with different thickness were deposited by spin coating. Each layer was dried at 110 °C for 10 min and pre-annealed at 350 °C for 10 min to pyrolyze the organic compounds. The final annealing was carried out at 650 °C for 5 min by rapid thermal annealing in each layer. Post-annealing was carried out at 600 °C for 120 min by normal annealing to discuss the effect of post annealing on residual stress.

Film thickness were varied by changing the number of spin coating in the range from four to eight layers and determined by scanning electron microscope (SEM) observations. Raman spectroscopy measurements were performed with a Jobin–Yvon RAMANOR HG-2S Raman spectrometer by back scattering geometries at room temperature. The 488 nm line of an argon ion laser was used as the excitation source at a power level of 200 W. The width of both the entrance and exist slit was set at 300 μm, corresponding to a spectral resolution of 2.7 cm^{-1}. Each spectrum was the addition of several scans.

3. Results and discussion

In the case of nano crystals, the soft mode *E*(1TO) frequency decreases with decreasing crystal size by the size effect. Generally, the crystal size in the thin film by RTA was smaller than that of the normal annealing. Therefore, the size effect should be taken into account in this study. At first, the crystal size in the resultant thin film was calculated by the Sherrer's equation from the observed XRD pattern. The resultant XRD pattern was fitted by the Lorrents function to estimate the half bandwidth and the peak angle. In this study, tetragonal (1 1 2) and (2 1 1) peaks were used to calculate the crystal size. As a result, the crystal size in the resultant films by RTA was about 16 nm independent of the thickness. In the case of PT single crystal, the soft mode frequency was reported to be 89 cm^{-1} [10]. However, the soft mode should shift toward lower frequency by the size effect. In the previous works, the soft mode frequencies for PT nano crystals with different diameters were investigated [11], and the *E*(1TO) mode frequency for 15.9 nm crystal was estimated to be 82.8 cm^{-1}. Therefore, in this study, stress free *E*(1TO) mode for the PT film was assumed to be 82.8 cm^{-1} to calculate the residual stress in PT films. The observed spectra were fitted by simply the sum of damped harmonic oscillators and a Debye relaxation mode to determine the peak positions (Eq. (1)).

$$I(\omega) = \left(\frac{1}{e^{h\omega/kT} - 1} + 1\right) \times \left(\frac{F_r \omega \gamma_r}{\omega^2 + \gamma_r^2} + \sum_i \frac{2\Gamma_i F_i \omega \omega_i^3}{(\omega_i^2 - \omega^2)^2 + 4\Gamma_i^2 \omega_i^2 \omega^2}\right) \quad (1)$$

where the former term of Bose–Einstein factor, ω_i, Γ_i and F_i are the mode frequency, damping factor and oscillator strength, respectively, and γ_r and F_r are the inverse relaxation time and the strength associated with the relaxation mode.

In this study, the residual stress in the resultant thin films were calculated from the shift of soft mode, *E*(1TO) (Eq. (2))

$$\omega(\sigma) = \omega(0) - \frac{\partial \omega}{\partial \sigma}\sigma \quad (2)$$

where $\omega(0)$ is the frequency of the soft mode under zero stress condition.

In this study, we used 82.8 cm^{-1} as $\omega(0)$ to take into account for the size effect. $\omega(\sigma)$ is proportional to the pressure σ. $\partial\omega/\partial\sigma$ was estimated to be 5.0 cm^{-1}/GPa by the work of Sanjuro et al. [12] and of Cerdeira et al. [13].

Raman spectra for the lead titanate thin film with various thickness are shown in Fig. 1. Fig. 2 shows the thickness dependence of mode frequencies. The soft mode *E*(1TO) frequency decreases with decreasing film thickness (Fig. 2). This suggests that the residual stress in the film increased with decreasing film thickness.

Fig. 3 shows the thickness dependence of the residual stress calculated from Eq. (2). As a result, the residual stress in the films by RTA process was larger than that in the films by the normal annealing process [5]. However, the large residual stress was relaxed to the values in the films by the normal annealing after the post-annealing.

The possible origins of the residual stress in films are the difference of the thermal expansion between the bottom electrode and the materials, and the phase transition on cooling process. In this study, Pt was used in bottom electrode and the thermal expansion coefficients for the Pt and a lead titanate are 8.8×10^{-6} and 11.86×10^{-6}/°C, respectively. On the basis of these considerations, the total residual stress in films should be given as follows:

$$\sigma_{total} = \sigma_{thermal} + \sigma_{transition} \quad (3)$$

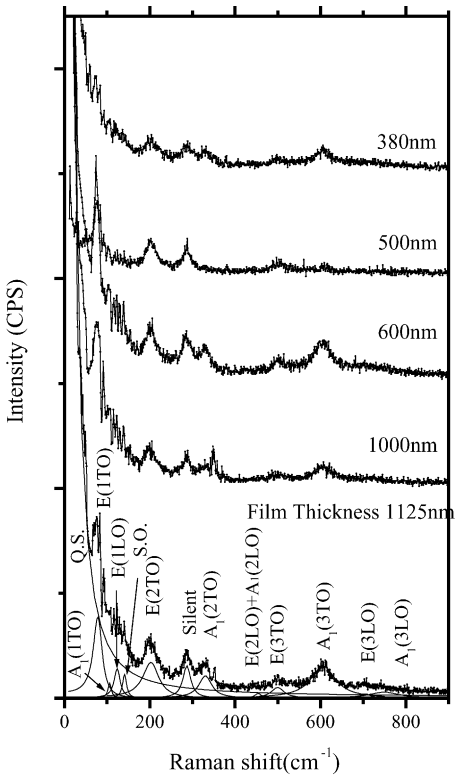

Fig. 1. The observed Raman spectra of lead titanate thin film with RTA process.

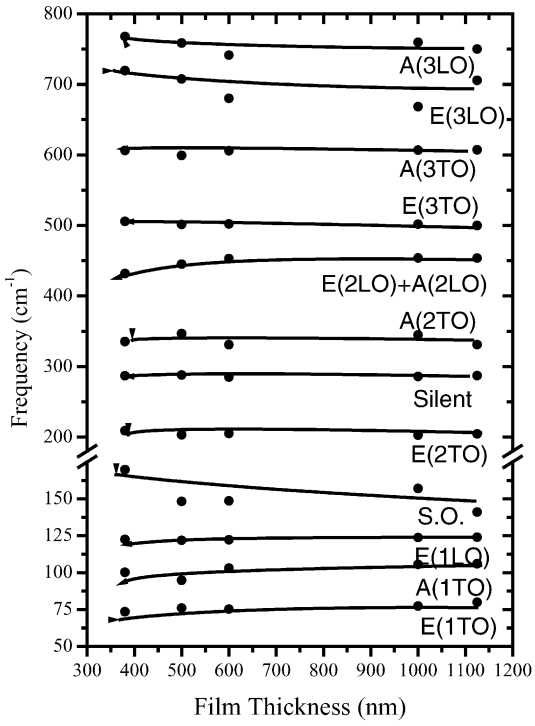

Fig. 2. The thickness dependent of the mode frequency.

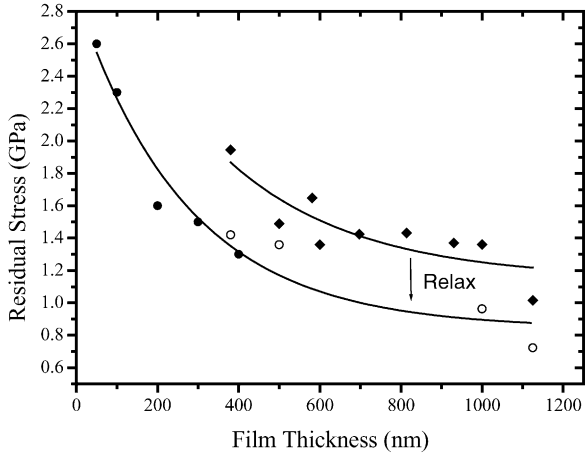

Fig. 3. The thickness dependent of the residual stress for lead titanate film ((●) normal annealing process (Fu et al. [3]), (◆) RTA process, (○) after post annealing).

Eq. (3) indicates that the total residual stress could be expressed by the sum of the stress from the difference of the thermally induced stress (σ_{thermal}), and the stress by the phase transition on cooling process ($\sigma_{\text{transition}}$). In our previous work [14], the stress by the phase transition is larger than that by the difference in the thermal expansion coefficient. For the thermal stress, the compressive stress from the bottom electrode (Pt) should be arise on the way of heating process, because of the difference in the thermal expansion coefficient between film and bottom electrode. In contrast, it leads to the tensile stress on cooling. On the other hand, the phase transition gives the compressive stress in the film on cooling. In the case of a lead titanate, the tensile stress should be arise in the films by the phase transition from tetragonal phase to cubic phase, because of the changing in the cell volume. In contrast, the phase transition from cubic to tetragonal phase should give rise to the compressive stress in the film after cooling. The crystallization temperature for a lead titanate by CSD was reported to be 450 °C [9], and the curie temperature is 490 °C [8]. However, the heating rate was 200 °C/min in a RTA process. Therefore, the crystallization state will be different from that of the film by the normal annealing (10 °C/min). The thin film by the RTA process should maintain the high temperature condition, leading to the smaller thermal stress. By this reasons, the residual stress in the films by a RTA process was larger than that in the films by the normal process.

Next, in order to demonstrate the relationship between the dielectric behavior and the residual stress, the intrinsic dielectric constant for a PT thin films were calculated from Lyddane–Sachs–Teller (LST) relation (Eq. (4)).

$$\frac{\varepsilon}{\varepsilon_\infty} = \frac{\omega_{1\text{LO}}^2}{\omega_{1\text{TO}}^2} \times \frac{\omega_{2\text{LO}}^2}{\omega_{2\text{TO}}^2} \times \frac{\omega_{3\text{LO}}^2}{\omega_{3\text{TO}}^2} \tag{4}$$

The intrinsic dielectric constant was calculated from the phonon mode frequencies. LST relation shows that the dielectric constant can calculate from the ratio between the

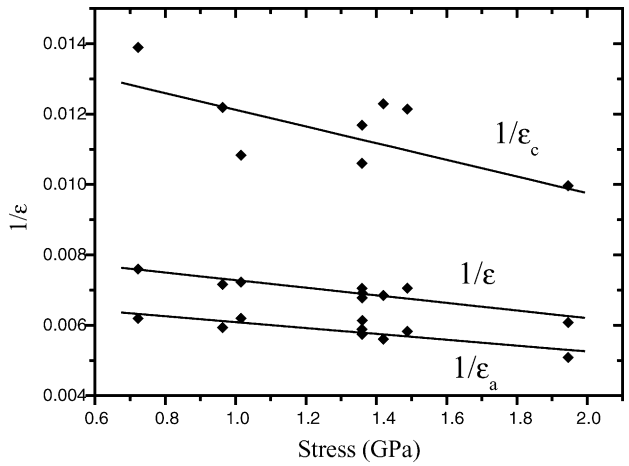

Fig. 4. The reciprocal of the dielectric constant with changing stress according to the modified Devon Shire theory.

Transverse mode frequency and the Longitudinal mode frequency. The observed phonon mode frequencies were substituted in the LST relation. The epsilon infinite, ε_∞ indicates the dielectric constant at ultimately high frequency where lattice vibration is not able to follow. The square of the refractive index was used for ε_∞ in this study ($\varepsilon_\infty = 2.66^2 = 7.08$) [15]. The dielectric constant along the *c*-axis was determined by the frequencies of the A_1 modes, because, A_1 modes indicate the phonon mode along *c*-axis. The dielectric constant along the *a*-axis was determined by the frequency of the E modes, because E modes indicate the phonon mode along *a*-axis. According to the modified Devon Shire theory under the assumption that the stress component perpendicular to the surface of the film is relaxed, the Eq. (5) was given [8].

$$\frac{\partial \varepsilon^{-1}}{\partial \sigma} = \text{const.} \tag{5}$$

Fig. 4 illustrates the reciprocal of the intrinsic dielectric constant as a function of the stress σ. The reciprocal of dielectric constant linearly increased with decreasing stress. This suggests the dielectric behavior changed according to the modified Devon Shire theory. Next equations were obtained from modified Devon Shire theory.

$$\frac{1}{\varepsilon_a(\sigma)} = 0.019 - 0.0029\,|\sigma|$$

$$\frac{1}{\varepsilon_c(\sigma)} = 0.0078 - 0.0007\,|\sigma|$$

$\varepsilon_c(0)$ and $\varepsilon_a(0)$ under zero stress were estimated to be 53 and 128, respectively. On the other hand, the dielectric constant for a PT single crystal, along *a*- and *c*-axes, ε_a and ε_c were 111 and 55, respectively [10]. These values were good agreement with the values for the single crystal. This indicates that the effect of the residual stress could be appropriately estimated by the shift of the soft mode *E*(1TO).

4. Conclusions

The PT thin films with different thickness were deposited by a CSD. The residual stress evaluated by the Raman scattering was increased with decreasing film thickness. In addition, the residual stress in the films by the rapid thermal annealing was larger than that in the films by the normal annealing. However, the large residual stress was relaxed by the post annealing to the values in the films deposited by the normal annealing. In addition, the values of the dielectric constant were calculated by the LST relation. As a result, dielectric behavior for PT thin films could be successfully expressed by the theoretical equation. The inverse of the dielectric constant changed according to the modified Devon Shire theory. The intrinsic dielectric constant in *a*- and *c*-axes derived by the extrapolation into the ambient pressure in Eq. (2) were in good agreement with the values of a single crystal, showing the accuracy of the experimental results.

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