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Residual stress in lead titanate thin film on different substrates

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Abstract

This paper describes the effect of thermal expansion coefficients of the substrates on the residual stress in lead titanate (PT) thin film. The residual stress in the film on the different substrates was calculated from the phonon mode shift. In addition, the dielectric constant for the film was calculated from the lattice mode frequency. As a result, the residual stress and the dielectric behavior depended upon the substrates.

Keywords: Capacitors; Dielectric properties; Perovskites; Residual stress; Sol–gel process

1. Introduction

Ferroelectric thin films have been received with great interest in many fields. The applications to memories such as ferroelectric memories (FeRAM),[1] dynamic random access memory (DRAM) and static memories (SRAM)[2] and the use of the ferroelectric films were rapidly widespread to the other types of applications such as pyroelectric detectors,[3] and micro-actuators.[4] For these applications, we should control a lot of parameters, such as microstructure,[5] orientation,[6] residual stress,[7] and so on because these parameters determine the properties of the ferroelectric thin films. The residual stress is one of the most important factors that affects the electrical properties. For example, Yanase et. al.[8] reported that the large residual stress resulted in the ferroelectricity of the epitaxial $BaTiO_3$ (BT) film with particle diameter below the critical size. If the particles were under the critical size, the resultant BT film should be paraelectric, because the crystal structure is cubic by the size effect. However, in this case, large residual stress by the lattice misfit strain stabilized the tetragonal phase. In this report, lattice misfit was measured by X-ray diffraction (XRD), while the value of the residual stress could not be calculated. On the other hand, Sun[9] calculated the residual stress in lead titanate (PT) polycrystalline film from the phonon mode shift of raman spectra. They reported that the large residual stress of 2.6 GPa existed in lead titanate film of 220 nm thickness. In the previous work,[7] we investigated thickness dependence of the residual stress and the relationship between the dielectric behavior and the residual stress.

The lattice misfit and the difference of the thermal expansion coefficient between substrate and film should lead to different residual stresses in the films. Therefore, this paper focuses on the difference of the thermal expansion coefficients of the substrates on the residual stress which was estimated by the mode shift of raman scattering.

2. Experimental procedure

A PT thin film with thickness ranging from 350 to 930 nm was deposited on $Pt/Ti/SiO_2/Si$ substrate, Si <100> substrate and MgO <100> single crystal with chemical solution deposition (CSD). The lead titanate precursor solution was prepared from lead acetate trihydrate and titanium isopropoxide. The details for the processing are described elsewhere.[10] 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 (RTA).

Film thickness was controlled by changing the number of spin coating in the range from three to eight layers and determined by scanning electron microscopy (SEM). The Raman spectra were measured using

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JASCO Corp., NR-1800, Rev. 1.00 Raman spectrometer in backscattering geometries. The 488 nm line of an argon ion laser was used as the excitation source at a power level of 10 mW. Each spectrum was the result of the addition of several scans.

3. Result and discussion

3.1. Effect of the size effect

In the case of nano particles, the soft mode or E(1TO), frequency decreases with decreasing particle size by the size effect.[11] In general, the crystal size in the thin film by RTA was smaller than that in the film by normal annealing. Therefore, the size effect should be taken into account in this study. XRD was used to calculate the crystal size in the film. The observed XRD pattern was fitted by Lorrents function to estimate the half band width and peak angle. In this paper, (112) and (211) planes for the tetragonal symmetry were used to calculate the crystal size. As a result, the crystal size of the resultant film by RTA was about 13 nm, independent of the film thickness. In the case of PT single crystal, the soft mode frequency was reported to be observed at 89 cm^{-1}.[10] However, the soft mode should shift to lower frequency by the size effect. In the previous works, the soft mode frequency with different particle diameter for PT was investigated. From the results, the E(1TO) mode frequency with 13 nm particles could be estimated at 83.1 cm^{-1}. Therefore, in this study, stress free E(1TO) mode for the PT film was presumed to be observed at 83.1 cm^{-1}. The residual stress was calculated by using this value.

3.2. Residual stress in film

In order to calculate the residual stress in PT films, the soft mode or (E(1TO)) frequency should be determined. Therefore, the observed spectrum was fitted by simply the sum of damped harmonic oscillators and a Debye relaxation mode to determine the phonon modes (Eq. 1).

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

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 strength associated with the relaxation mode. In this study, the residual stress in the films were calculated from the amount of the soft mode shift. [Eq. (2)]

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

where $\omega(0)(=89cm^{-1})$ is the frequency of the soft mode for particles without size effect under stress free condition. $\omega(\sigma)$ is proportional to the pressure σ. $\delta\omega/\delta\sigma$ was estimated to be 5.0 cm^{-1}/GPa from the work of Sanjuro et al[12] and Cerdeira et al.[13] On the other hand, we used 83.14 cm^{-1} to take the size effect into account in this study.

Fig. 1 exhibits the raman spectra below 900 cm^{-1} for the lead titanate thin film with various thickness. As a result, the soft mode or E(1TO) frequency decreased with decreasing film thickness. This suggests that the residual stress for the film increased with decreasing film thickness. Fig. 2 shows the thickness dependence of the residual stress in the film on different substrates. The coefficient of thermal expansion for Pt, Si, MgO and lead titanate is 8.8×10^{-6}/°C, 2.8×10^{-6}/°C, 13.5×10^{-6}/°C and 11.86×10^{-6}/°C, respectively. From this figure, the residual stress in the film on the substrate that have larger thermal expansion coefficients was larger than that in the film with the smaller thermal expansion coefficient. These results indicated that the residual stress in the film arose not only from the difference of the thermal expansion coefficient between the electrode and the film but also from the other factors such as the volume change in the transformation from cubic to tetragonal phase. Thus, the compressive stress by the

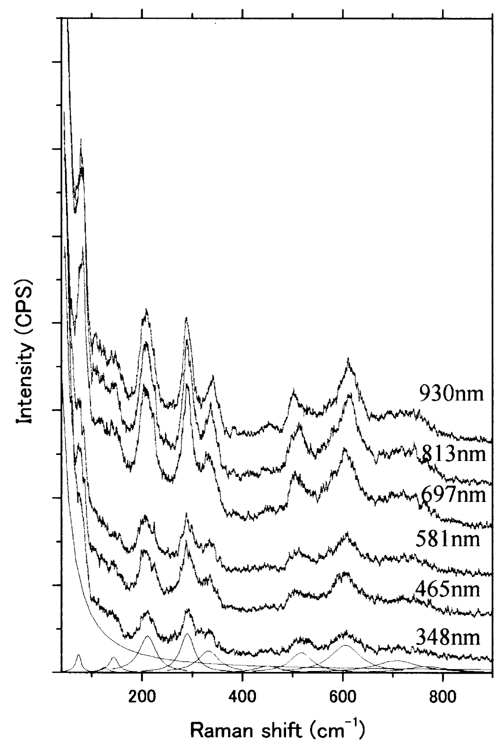

Fig. 1. The observed raman spectra of lead titanate thin film on Si < 100 > with different thickness.

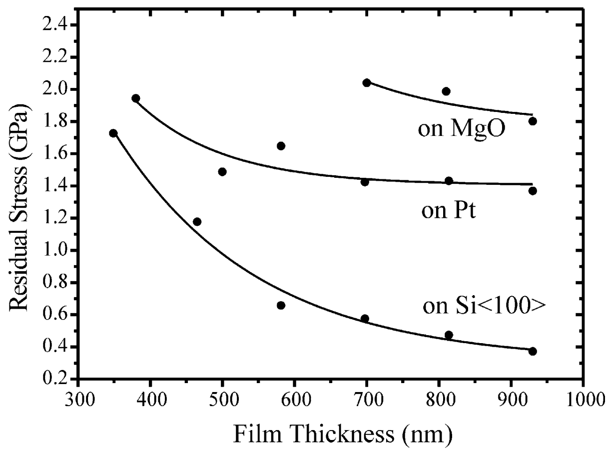

Fig. 2. The thickness dependent of the residual stress.

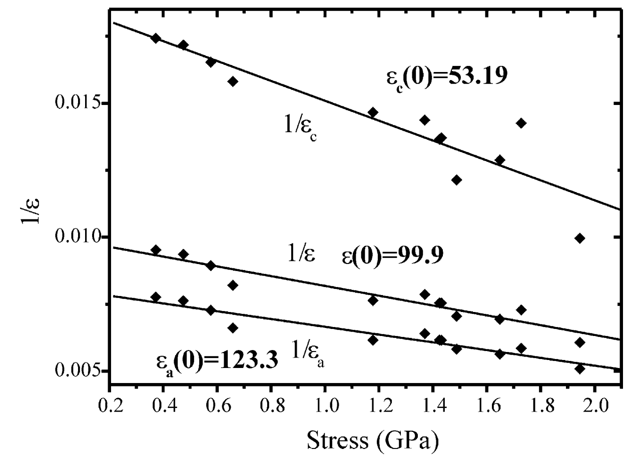

Fig. 3. The reciprocal of the dielectric constant with changing stress according to the modified Devonshire theory.

phase transition during crystallization process is very important factor for the residual stress or the ferroelectricity of the resultant film.

3.3. Dielectric behavior

In order to estimate the relationship between the dielectric behavior and the residual stress, the intrinsic dielectric constant of PT thin film was calculated from Lyddane-Sachs-Teller (LST) relation [Eq. (3)].

$$\frac{\varepsilon}{\varepsilon_\infty} = \frac{\omega_{1LO}^2}{\omega_{1TO}^2} \cdot \frac{\omega_{2LO}^2}{\omega_{2TO}^2} \cdot \frac{\omega_{3LO}^2}{\omega_{3TO}^2} \quad (3)$$

Conventionally, dielectric constants are determined by impedance analyzer. However, in the case of the measurement by impedance analyzer, those values include the extrinsic effects such as space charge and pores as well as the other factors related to the grain boundaries. From this reason, we cannot discuss the effect of the residual stress on dielectric constant by the impedance analyzer. In this study, the intrinsic dielectric constant was calculated from the phonon mode frequency of the raman spectrum. The observed phonon mode frequency was interpolated in the LST relation. The ϵ_∞ indicates the dielectric constant at high frequency where lattice vibration is not able to follow. The square of the refractive index is used as the ϵ_∞ in this study. The dielectric constant along the *c*-axis was determined by the frequencies of the A_1 modes and the dielectric constant along the *a*-axes was determined by the frequency of the E modes.

In the previous work, we discussed the relationship between the residual stress and the intrinsic dielectric constant, and concluded that the Eq. 4 was given from the modified Devonshire theory under the assumption that the stress component perpendicular to the surface of the film is relaxed;

$$\frac{\partial \varepsilon^{-1}}{\partial \sigma} = constant \quad (4)$$

As a result, the reciprocal of dielectric constant linearly increased with decreasing stress. Fig. 3 shows the change in the reciprocal of dielectric constant with stress. This figure suggests the dielectric behavior obeyed the modified Devonshire theory which was proposed in the previous paper.[14] The next two equations were obtained from modified Devonshire theory.

$$\frac{1}{\varepsilon_c(\sigma)} = 0.0188 - 0.0037|\sigma|$$

$$\frac{1}{\varepsilon_a(\sigma)} = 0.0081 - 0.0015|\sigma|$$

From the above equations, $\epsilon_c(0)$ and $\epsilon_a(0)$ were estimated to be 53 and 123, respectively. On the other hand, the dielectric constants of PT single crystal along *a*- and *c*- axes are 55 and 111, respectively.[15] This indicated that the effect of the residual stress could be appropriately estimated by the shift of the soft mode or E(1TO).

4. Conclusion

The PT thin films with different thickness were deposited by a CSD. The residual stress in the PT thin films increased with decreasing film thickness. In addition, the residual stress in the film was affected by the thermal expansion coefficients of the substrates. The residual stress in the film on the substrate that has larger thermal expansion coefficients was larger than that in the film with the smaller thermal expansion coefficient. Moreover, the reciprocal of the dielectric constant obeyed the modified Devonshire theory. The intrinsic dielectric constant along *a*- and *c*- axes derived by extrapolating the ambient pressure in Eq. 4 was in good agreement with the values of a single crystal.

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