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Stress Determination in Epitaxial Lead Titanate Films by Asymmetric X-ray Diffraction Method

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Residual stresses in epitaxial films were measured by X-ray diffraction method. Lattice strains of the (hkl) planes measured along particular ψ-angles were converted to the in-plane stress according to the equation of stress-strain tensor conversion. Residual tensile stresses were observed in epitaxial $PbTiO_3$ films deposited on (100) $SrTiO_3$ substrate. Tensile stresses approximately 0.9 GPa were measured in Pb-rich films, while it increased to approximately 2.0 GPa with the decreasing of Pb content in the case of Pb-poor films, which ascribed to the formation of lead and oxygen vacancies (expressed as x in $Pb_{1-x}TiO_{3-x}$).

Key words: Epitaxial thin film, Residual stress, Asymmetric x-ray diffraction, Lead titanate, MOCVD

I. Introduction

Dielectric properties of ferroelectric oxides with perovskite-like structure (*e.g.*, $BaTiO_3$, $PbTiO_3$ and PZT) can be varied by applied stress.[1-4] The stress causes ion shifts in the crystal lattice, together with the displacement of cation/anion dipole moment. That is, there are intimate relationships among applied stress, lattice strain and material properties. To understanding these relationships will be useful as a concept to control the electrical properties. Many researchers have reported about the relationship between mechanical stresses and the dielectric properties of ferroelectric bulk materials as the study of the piezoelectric materials.[5]

Recently, ferroelectric thin films have been paid great attention because of their potential applications to microelectronic and micromechanical devices. Behavior of residual stresses in thin films are quite different from those in bulk materials. Three kinds of stress are generated in the film during the film deposition process; (i) thermal stress arised from the difference in thermal expansion coefficients between the film and the substrate, (ii) intrinsic stress arised from the film itself, *e.g.*, phase transition, presence of defects and/or impurities in the crystalline lattice, and (iii) extrinsic stress arised from structural changes which produce dimensional changes.[6] Particularly, (i) is a specific nature observed only in thin film materials, that give rise to new properties which have never been observed in bulk materials.

Residual stresses of thin films are usually calculated from the lattice strain measured by X-ray diffraction. $\sin^2\psi$ method is the most famous technique for the measurement of residual stress in polycrystalline films.[7] In this technique, lattice strains of a specific (*hkl*) plane were measured at some offset angles (ψ). However, this technique can not be applied to the stress measurement of the epitaxial films since the X-ray diffraction of a (*hkl*) plane can not occur at any ψ angles. Authors investigated the other analytical technique, how lattice strains perpendicular to some (*hkl*) planes were measured by X-ray diffraction. This technique can be adopted to not only the stress measurement in epitaxial films but also that in polycrystalline films.

In present work, author investigate the residual stress in thin films using X-ray diffraction method mentioned above. The effects of some factors (substrate, film thickness and chemical composition) on the residual stress were examined. The investigation will be focused on lead titanate ($PbTiO_3$) film.

II. Experimental Procedure

2.1 Sample preparation

Epitaxial $PbTiO_3$ films were deposited on (100)$SrTiO_3$ substrates by metal-organic chemical vapor deposition (MOCVD). $Pb(C_{11}H_{19}O_2)_2$, $Ti(O{\cdot}i\text{-}C_3H_7)_4$ and O_2 were used as starting materials. The films were deposited at a rate of ~ 15 $nm{\cdot}min^{-1}$ using a chamber pressure of 1.33×10^3 Pa (=10 Torr). The substrate temperature was 650°C. $PbTiO_3$ films showed c-axis orientation perpendicular to the substrates and in-plane orientation, indicating that the films were epitaxially grown on (100) $SrTiO_3$ substrate. For reference, $PbTiO_3$ films deposited on SiO_2/(100) Si (film; polycrystalline) and (100) MgO (film; a- and c-axis orientation) substrate were also prepared. Chemical composition of the films were determined using energy dispersive X-ray analyzer (EDX; DX95T, EDAX Japan, America).

2.2 Stress measurement

The residual stress were determined by measuring the lattice strains perpendicular to (*hkl*) planes, $\varepsilon_{(hkl\cdot\psi)}$;[8)]

$$\varepsilon_{(hkl\cdot\psi)} = \frac{d_{(hkl\cdot\psi)} - d_{0(hkl\cdot\psi)}}{d_{0(hkl\cdot\psi)}} \qquad (1)$$

where $d_{(hkl\cdot\psi)}$ is plane spacing measured in $PbTiO_3$ film and $d_{0(hkl\cdot\psi)}$ is that of $PbTiO_3$ powder.

Specimen system, S_i, crystal system, C_i, and laboratory system, L_i, are defined as shown in Fig. 1. Relationship between the lattice strain in the vertical direction to (hkl) plane, ε^L_{33}, and the strain in the crystal system, ε^C_{ij}, is described as;

$$\varepsilon^C_{ij} = \gamma_{3i}\gamma_{3j}\varepsilon^C_{ij} \qquad (2)$$

Further, the relationship between the stress and strain in crystal system are determined according to generalized Hooke's law;

$$\varepsilon^L_{33} = s^C_{ijkl}\sigma^C_{kl} \qquad (3)$$

In case of epitaxial film, the specimen system is equal to the laboratory system. Therefore, equation (2) can be described in other form;

$$\sigma^C_{kl} = \sigma^S_{kl} \qquad (4)$$

$$\varepsilon^L_{33} = \gamma_{3i}\gamma_{3j}s^C_{ijkl}\sigma^s_{kl} \qquad (5)$$

If we define $s^*_{33mn} = \gamma_i\gamma_j s^C_{ijkl}$, equation (5) is rewritten as;

$$\varepsilon^L_{33} = s^*_{33mn}\sigma^s_{mn} \qquad (6)$$

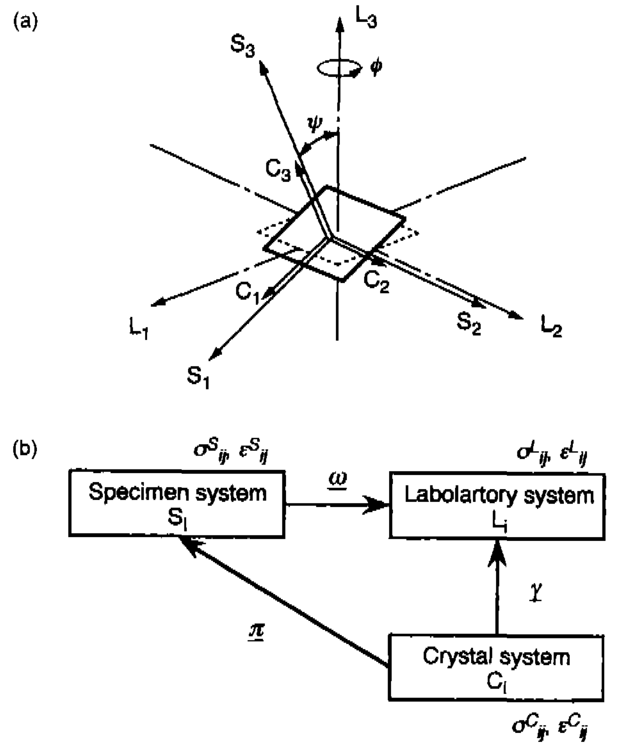

Fig. 1. Relationship among specimen system, crystal system and laboratory system. (a) Specimen configuration and (b) transformation matrices among three systems.

Table 1. Diffraction Angles and ψ-angles of Various Lattice Planes

(h k l)	2θ(°)	ψ(°)	$\sin^2\psi$
(0 0 3)	67.631	0	0
(1 0 3)	72.382	19.547	0.1119
(2 0 3)	86.071	35.378	0.3352
(3 0 3)	108.756	46.806	0.5315

This equation indicates that the stress in the crystal system, s^C_{mn}, can be calculated from the lattice strain measured by XRD, ε^L_{33}. If the residual stress in thin film is estimated to be isotropic in-planar stresses, equation (6) is furthermore rewritten as;

$$\varepsilon^L_{33} = [(s_{11} + s_{12} - 2s_{13})(\sin^2\psi + 2s_{13})]\sigma \qquad (7)$$

where s_{11}, s_{12} and s_{13} are components of elastic compliance. Consequently, value of the residual stress can be calculated from the slope of ε^L_{33}-$\sin^2\psi$ graph.[4)]

$$\sigma = \frac{\partial\varepsilon^L_{33}}{\partial\sin^2\psi}(s_{11} + s_{12} - 2s_{13})^{-1} \qquad (8)$$

Lattice strains of the (hkl) planes were measured along particular ψ-angles by asymmetric X-ray diffraction. X-ray diffractometer (XRD; X'Pert system, Phillips, Holland) was used for the measurement. Table 1 shows the lattice planes used to determine the residual stress, which exist in the same crystal zone.

III. Results and Discussion

3.1 Effect of the substrate species

Thermal stress, mainly ascribed to the difference in the thermal expansion coefficient between the film and the substrate, is the most important factor of the residual stress in thin films. Residual stress of $PbTiO_3$ films deposited on various substrates were shown in Table 2, together with the theoretical thermal stresses and thermal expansion coefficients of the films, α_f, and the substrate materials, α_s. Tensile stress of approximately 1.0 GPa were measured in the films on (100) $SrTiO_3$ and (100) MgO, while the compressive stress on SiO_2/(100) Si. In general, tensile stress is applied on the condition of $\alpha_f > \alpha_s$. On the other hand, compressive stress appears on the opposite condition, $\alpha_f < \alpha_s$. The results were agreed with these assumptions.

Table 2. Residual Stress of $PbTiO_3$ Films Deposited on Various Substrate

		SiO_2/Si	MgO	$SrTiO_3$	$PbTiO_3$	
					a-axis	c-axis
Residual stress (GPa)		−0.79	0.85	1.03		
Theoresical thermal stress (GPa)		−1.94	0.62	1.26		
Thermal expansion ($\times10^{-6}$°C^{-1})	[R.T.]	2.60	10.5	10.3		
	[480°C]	4.30	14.8	11.7	23.2	−74.2

Theoretical thermal stresses at room temperature were estimated as follows; Assuming the thickness of the film is much thinner than that of the substrate, thermal stress in the film can be expressed by following equation;9)

$$\sigma_{th} = \frac{E_f}{(1-v_f)}(\alpha_f-\alpha_s)(T_d-T) \tag{9}$$

where E_f and v_f are Young's module and Poisson ratio of the film, respectively (E_f=117.9 GPa, v_f=0.2). T_d is the film deposition temperature and *T* is room temperature. However, Otsu et al.[10] reported that the residual stress of $PbTiO_3$ film is relaxed at Curie temperature (T_c; ~480°C) during the cooling-down process after the film deposition. T_c can be used, therefore, instead of T_d in equation (9);

$$\sigma_{th} = \frac{E_f}{(1-v_f)}(\alpha_f-\alpha_s)(T_C-T) \tag{10}$$

In this equation, thermal stress is directly proportional to the difference of the thermal expansion coefficient, (α_f -α_s). Fig. 2 shows the theoretical thermal stress and the residual (total) stress as a function of the value of (α_f -α_s). The values of the thermal stress were quite close to those of the total stress, that proved that greater part of the total stress consists of the thermal stress.

3.2 Effect of the film thickness

Experimental data about relationship between the residual stress and the film thickness have been often provided in many researches. Changes in the residual stress accompanied with the film thickness are caused by some reasons; stress distribution which occurs in the direction to the film thickness since only one side of the film interface is fixed on the substrate, and grain growth and/or annealing proceed during the film deposition process at high temperature, etc.

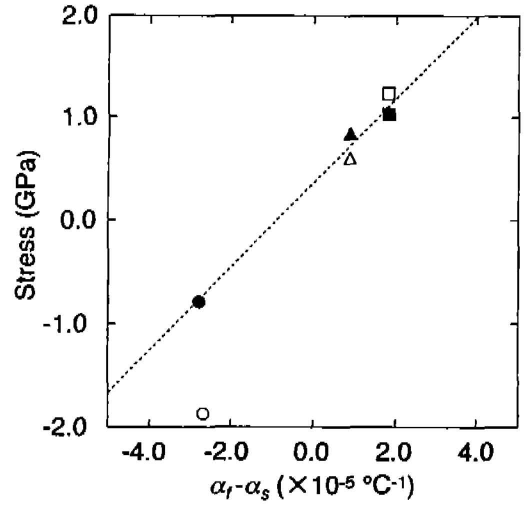

Fig. 2. Relationship among the residual stress, theoretical thermal stress and the difference of the thermal expansion coefficient, (α_f-α_s). ●▲■ : Residual stress of the film, ○△□: Theoretical thermal stress of the film, ●○: $PbTiO_3/SiO_2$/(100)Si, ▲△: $PbTiO_3$/(100)MgO, ■□: $PbTiO_3$/(100)$SrTiO_3$.

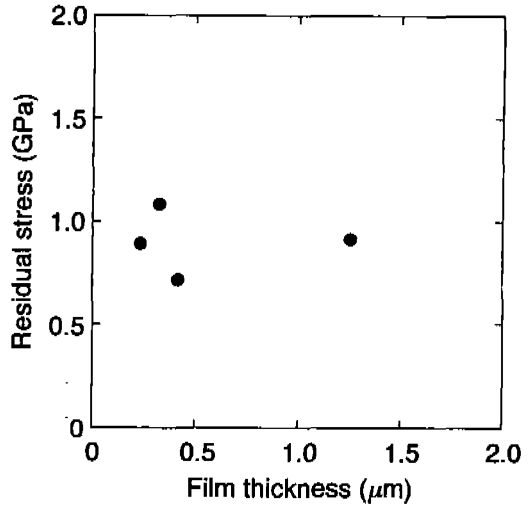

Fig. 3. Relationship between the residual stress and the film thickness.

Fig. 3 shows the result of the stress measurement in $PbTiO_3$ films deposited on (100) $SrTiO_3$ with various thicknesses. The residual stress measured in this method was the average value throughout the film thickness because X-ray penetrated through the films in this range (up to 1200 nm). Residual stress of the films were ranged from 0.7 up to 1.1 GPa; however, systematic tendency of the change could not be observed.

Stress distribution only appears at the nearest interface zone to the substrate, therefore, X-ray diffraction from the interface zone hide behind that from other zone in the case of thick film. The residual stress would change on the film with the thickness of below approximately 100 nm.

3.3 Effect of the chemical composition

We assumed that the residual stress would be varied with the chemical composition (defined as [Pb]/([Pb]+[Ti]), where [Pb] and [Ti] are the contents of Pb and Ti atoms [mol %], respectively) because of some reason; excess atoms are contained into the crystal lattice as interstitial ions, lattice defects appear in the crystal lattice, the secondary phases may appear in the film, and etc.

Fig. 4 shows the result of the stress measurement in the films with various chemical compositions, together with the crystalline phases examined by XRD. Residual stresses of approximately 1.0 GPa were measured on the films with the chemical composition between 0.44 and 0.57, while the residual stresess of approximately 2.0 GPa were measured on the film with the chemical composition below 0.40. Only a crystalline phase of $PbTiO_3$ was detected in the films with the composition of below 0.54. The films with the composition of below 0.54 were consisted of $PbTiO_3$ and α-PbO.

The residual stress did not changed at the extent of Pb excess. The excessive Pb atom do not make either the interstitial ions and the lattice defects, but creates the secondary

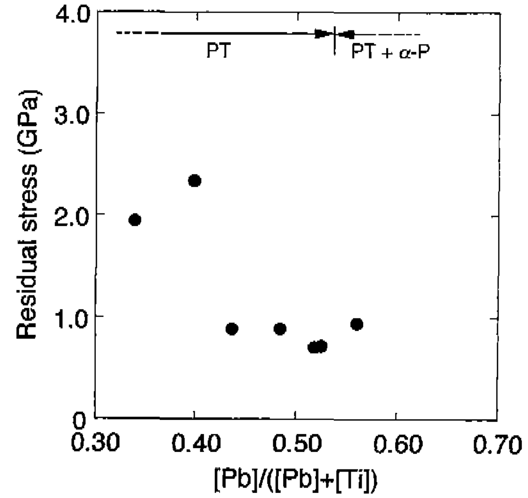

Fig. 4. Relationship between the residual stress and the chemical composition, [Pb]/([Pb]+[Ti]). PT: $PbTiO_3$ α-P: α-PbO.

phase, α-PbO. The existence of α-PbO did not affect the residual stress in the $PbTiO_3$ film. On the other hand, the residual stress increased with decreasing Pb content at the extent Ti excess. If the excessive Ti atom was contained in the crystal lattice as a interstitial ion with decreasing Pb content, the residual stress would be decreased because the interstitial ion acts as the source of the compressive stress; however, this assumption opposes to the result. Lack of Pb atom causes the lattice defects (expressed as x in $Pb_{1-x}TiO_{3-x}$[11]), which act as the source of the tensile stress.

Further, to investigate the relationship between the residual stress and the lattice defects, $PbTiO_3$ films deposited by MOCVD were heat-treated in various atmospheres (oxygen, nitrogen and nitrogen/hydrogen (95/5)) at 750°C for 3 h. Table 3 show the result of stress measurement in as-deposited and heat-treated films. The residual stress of as-deposited film was 1.03 GPa. Then, the stress increased to 1.11 and 1.26 GPa during the heat-treatment in N_2 and N_2/H_2 atmosphere, respectively. On the other hand, the stress decreased to 0.55 GPa during the heat-treatment in oxygen atmosphere. Drastic change in the chemical composition was not observed after the heat-treatments.

The heat treatment in N_2 and N_2/H_2 atmospheres can create oxygen vacancies, while the treatment in oxygen atmosphere erases oxygen vacancies;[12,13)]

Table 3. Residual Stress of As-deposited and Heat-treated $PbTiO_3$ Films

	Residual stress (GPa)	[Pb]/([Pb]+[Ti])
as-deposition	1.03	0.52
heat-treatment [750°C, 3h]		
in O_2 flow	0.55	(No change)
in N_2 flow	1.11	
in N_2/H_2 flow	1.26	

$$O_O^{\times} \rightleftarrows V_O^{\cdot\cdot} + 2e + 1/2O_2 \tag{10}$$

where $O_O^{\times}$ and V_O is oxygen atom at their respective sites in the crystal lattice and doubly positive-charged oxygen vacancies, respectively. The increase of the residual stress seems to occur with increasing of oxygen vacancies. The tensile stress of 1.26 GPa decreased up to 1.17 GPa by re-heating in O_2 atmosphere at 750°C for 3 h as the reaction of oxygen vacancy generation (Eq. (10)) is reversible reaction. Also, in case of the film heated in O_2 atmosphere, the tensile stress of 0.55 GPa increased again up to 0.98 GPa by re-heating in N_2/H_2 atmosphere at 750°C for 3 h. The decrease of the residual stress by the heat treatment in O_2 atmosphere suggested that the as-deposited $PbTiO_3$ film contained oxygen vacancies.

Consequently, the residual stress of $PbTiO_3$ films were varied with the amount of the lattice defects reversibly.

IV. Conclusions

Residual stresses in epitaxial films were measured by asymmetric X-ray diffraction method. Lattice strains of the (hkl) planes measured along particular ψ-angles were converted to the in-plane stress according to the equation of stress-strain tensor conversion. The effects of some factors on the residual stress were examined. The results obtained in this experiment are summarized as follows;

1. Residual stresses of $PbTiO_3$ films deposited on (100) $SrTiO_3$ and (100) MgO are tensile stress while that on SiO_2/(100)Si is compressive stress, those were related to the difference of the thermal expansion between the film and the substrate, α_f-α_s.

2. The dependency of the residual stress on the film thickness were examined within the range from 200 nm up to 1200 nm. The stress of the films were ranged from 0.7 GPa up to 1.1 GPa; however, systematic tendency could not be observed. The change ascribed to the stress distribution would appear with the thicknesses of below 100 nm.

3. The chemical composition affected on the residual stress of the film, with decreasing the Ti content, which is ascribed to the formation of lead and oxygen vacancies (described as x in $Pb_{1-x}TiO_{3-x}$). Also, the effect of oxygen vacancies on the residual stress was examined by the heat-treatment in O_2, N_2 and N_2/H_2 atmospheres. The stress was varied with the amount of the oxygen vacancies reversibly.

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