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Measurement Technique for the Evaluation of Residual Stress in Epitaxial Thin Film by Asymmetric X-Ray Diffraction

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非対称 X 線回折によるエピタキシャル薄膜の残留応力の評価手法

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An analytical technique to determine residual stress in eqitaxial thin film by asymmetric X-ray diffraction (XRD) was studied. The residual stresses of $PbTiO_3$ films were determied by XRD technique and displace measurement technique. Measurement results by these techniques were compared with each other to consider the respective advantages of each technique. The stresses measured by XRD technique were not consistent with those by displacement measurement technique, because the latter technique involves errors which origined from the shape and the size of the substrate. The stress in a polycrystalline film measured by modified $\sin^2\psi$ method was in good agreement with that measured by normal $\sin^2\psi$ method. This result suggests that modified $\sin^2\psi$ method can be applied to stress measurement not only in epitaxial thin films, but also in polycrystalline thin films. We further discuss the precision of the stress determination technique. Residual stress of epitaxial $PbTiO_3$ film on (100) $SrTiO_3$ substrate measured by modified $\sin^2\psi$ method was comparable to the theoretical stress estimated from the difference in thermal expansion coefficients between the film and the substrate. Stress values measured by modified $\sin^2\psi$ method may thus have the precision required for actual application. [Received January 12, 1999; Accepted April 22, 1999]

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

1. Introduction

Dielectric properties of ferroelectric oxide with perovskite-type structure (e.g., $BaTiO_3$, $PbTiO_3$ and PZT) can be varied by applied stress on the materials.[1)-4)] The stress causes ion shift in the crystal lattice together with the modulation of the center of cation/anion dipole moment. Many researchers have reported the relationship between mechanical stresses and dielectric properties of ferroelectric bulk materials.[5)] We focus on the application of perovskite oxide as thin film materials. In thin film materials, residual stress of $\sim 10^9$ Pa (GPa) is applied continuously because of the difference of the thermal expansion between the film and the substrate. Differences in some electrical properties between thin film and bulk material are assumed to be caused by the continuous stress indentation. However, the analysis of residual stress in thin film is quite difficult because of its unique (small and thin) microstructure.

There are two techniques to determine the film stress; displace measurement technique and X-ray diffraction (XRD) technique. The first technique was consisted of displace measurement of the substrate. Deformation of the substrate occurs during cooling-down process after film deposition at high temperatures because of mainly the thermal stress ascribed to thermal expansion coefficients between the film and the substrate. The relationships between residual stress and dielectrical properties were discussed by many researchers.[6)-8)] In another technique, XRD technique, lattice strains in crystals of thin film together with the stress indentation were measured by XRD. The residual stress was calculated from the lattice strains of crystals. Typical XRD technique (called $\sin^2\psi$ method) was presented by Sun et al.[9)] In this method, strains (ε) of a specific lattice plane (hkl) were measured at some offset angles (ψ), and then the residual stress of thin film was calculated from the relationship of ε–$\sin^2\psi$. Reliable measurement would be performed if the diffraction lines with sufficient intensity could be obtained by XRD. The $\sin^2\psi$ method was mainly used for the polycrystalline thin film with random orientation; this method can not be applied to the stress determination in the thin films which have crystals with preferred orientation because X-ray diffraction obtain only at definite ψ-angle. Therefore, this method was modified to utilize to highly-oriented thin films; some lattice planes, $(h_1k_1l_1)$, $(h_2k_2l_2)$, $(h_3k_3l_3)\cdots$, were used instead of a specific lattice plane. Lattice strains of some (hkl) planes were measured at respective ψ-angles, and then the residual stress of the film was calculated from the relationship between ε and $\sin^2\psi$. This method was first discussed on the stress determination of cold-rolled low carbon steel sheets[10),11)] and aluminum nitride (AlN) film deposited on glass substrate.[12)] These samples have preferred orientation in the direction perpendicular to substrate surface. This method was also applied to epitaxial thin films of metals and semiconductors.[13)-15)]

In present work, authors determined the residual stresses of epitaxial oxide, lead titanate ($PbTiO_3$), thin films by XRD technique and displace measurement technique. These results were compared with each other to consider the advantage of each methods. The precision of the stress determination technique was discussed.

2. Experimental procedure

2.1 Sample preparation

Epitaxial $PbTiO_3$ films were deposited on (100) $SrTiO_3$ substrate 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 shape of the substrate was square board with the size of 10 mm × 10 mm × 0.1 mm. The films were deposited at a rate of approximately 15 nm·

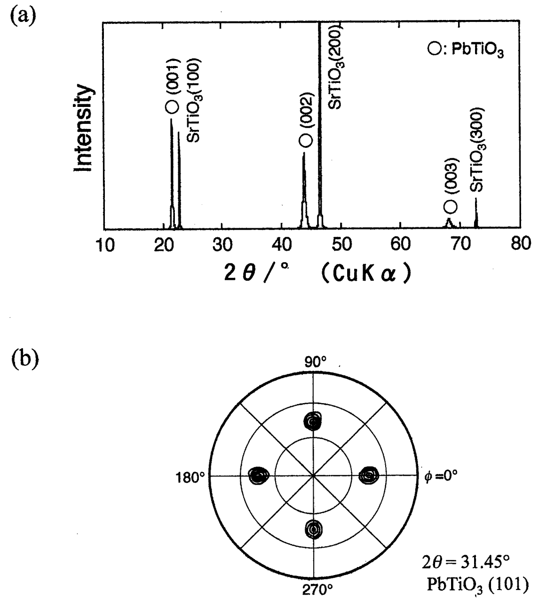

Fig. 1. XRD analytical results of $PbTiO_3$ film on (100)$SrTiO_3$ substrate.
(a) θ–2 θ scan, (b) pole figure scan.

min^{-1} under a chamber pressure of ~1.3 kPa. The substrate temperature was 650°C. Thickness of the resulting film was approximately 700 nm. Figure 1 shows the XRD analytical results of the film. The results indicated that the $PbTiO_3$ films have *c*-axis orientation perpendicular to the substrate and in-plane orientation, indicating that the films were epitaxially-grown on (100)$SrTiO_3$ substrate. As a reference sample, polycrystalline $PbTiO_3$ films were deposited on SiO_2/(100)Si substrate at the same condition.

2.2 Stress determination

Two techniques (XRD technique and displacement measurement technique) were used to determine the residual stress in this study;

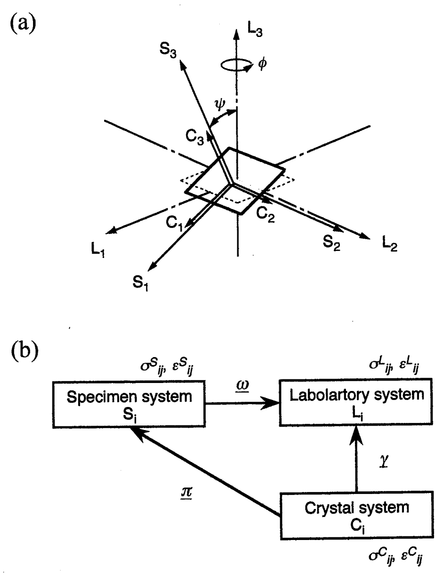

Fig. 2. Relationship among specimen system, crystal system and laboratory system.
(a) specimen configuration, (b) transformation matrices among three systems.

(a) X-ray diffraction technique ($\sin^2\psi$ method)

Residual stress of polycrystalline thin film was also determined by $\sin^2\psi$ method.[9] Specimen system (S_i), crystal system (C_i) and laboratory system (L_i) are defined as shown in Fig. 2. The film stress ($\sigma_{\sin^2\psi}$) was calculated from the relationship between the lattice strain ($\varepsilon_{(hkl\cdot\psi)}$) and offset angle ($\psi$) expressed as follows;

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

$$\sigma_{\sin^2\psi}=\frac{E}{(1+\nu)}\cdot\frac{\varepsilon_{(hkl)}}{\sin^2\psi} \quad (2)$$

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. The lattice strains of a specific (*hkl*) plane were measured with some ψ-angles by asymmetric X-ray diffraction.

In the case of epitaxial thin film, however, the film stress can not be determined by $\sin^2\psi$ method because X-ray diffraction of a specific (*hkl*) plane does not occur at any ψ-angles. Therefore, we applied modified $\sin^2\psi$ method to determine the film stress of epitaxial thin film.[10)-12)] Specimen system, S_i, crystal system, C_i, and laboratory system, L_i, are defined as shown in Fig. 2. Relationship between the lattice strain in the vertical direction to (*hkl*) plane, $\varepsilon_{33}{}^L$, and the strain in the crystal system, ε_{ij}^C, is described as;

$$\varepsilon_{33}^L=\gamma_{3i}\gamma_{3j}\varepsilon_{ij}{}^C \quad (3)$$

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

$$\varepsilon_{ij}{}^C=s_{ijkl}^C\sigma_{kl}{}^C \quad (4)$$

In case of epitaxial film, the specimen system is equal to the laboratory system. Therefore, Eq. (3) can be described in other form;

$$\sigma_{kl}{}^C=\sigma_{kl}{}^S \quad (5)$$

$$\varepsilon_{33}{}^L=\gamma_{3i}\gamma_{3j}s_{ijkl}^C\sigma_{kl}{}^S \quad (6)$$

If we define $s_{33mn}{}^*=\gamma_i\gamma_j s_{ijkl}{}^C$, Eq. (6) is rewritten as;

$$\varepsilon_{33}{}^L=s_{33mn}^*\sigma_{mn}{}^S \quad (7)$$

This equation indicates that the stress in the crystal system, $s_{mn}{}^C$, can be calculated from the lattice strain measured by XRD, $\varepsilon_{33}{}^L$. If the residual stress in thin film is estimated to be isotropic in-planar stresses, Eq. (7) is furthermore rewritten as;

$$\varepsilon_{33}{}^L=[(s_{11}+s_{12}-2s_{13})\sin^2\psi+2s_{13}]\sigma \quad (8)$$

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 $\varepsilon_{33}{}^L$–$\sin^2\psi$ graph.

$$\sigma=\frac{\partial\varepsilon_{33}}{\partial\sin^2\psi}(s_{11}+s_{12}-2s_{13})^{-1} \quad (9)$$

Lattice strains of the (*hkl*) planes were measured along particular ψ-angles by asymmetric X-ray diffraction. X-ray diffractometer (XRD; X'Pert system, Philips, Holland) was used for the measurement. Iso-inclination method which us-

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

ed focusing beam irradiation was applied as an optical system of asymmetric X-ray diffraction. Table 1 shows the lattice planes used to determine the residual stress, which exist in the same crystal zone on the stereographic projection. Components of elastic compliance of $PbTiO_3$ are shown as follows; $s_{11}=7.5\times10^{-12}\,m^2\cdot N^{-1}$, $s_{12}=-1.5\times10^{-12}\,m^2\cdot N^{-1}$ and $s_{13}=-1.1\times10^{-12}\,m^2\cdot N^{-1}$.[16),17)] In these measurement, tensile stresses are shown as positive values and, on the other hand, compressive stresses are represented as negative values.

(b) Displace measurement technique (Stoney method)

Residual stress of thin film mainly occurs the difference of the thermal expansion coefficients the film and the substrate, together with the displacement of substrate. The residual stress of the thin film (σ_{Stoney}) was calculated by comparing the substrate curvatures before and after the film deposition, according to Stoney's equation (Eq. (10));[8)]

$$\sigma_{Stoney}=\frac{E}{6(1-\nu)}\frac{b^2}{d}\left(\frac{1}{R}-\frac{1}{R_0}\right) \qquad (10)$$

where R_0 and R are radii of substrate curvature before and after the film deposition, b and d are the thickness of the substrate and the film, E and ν are Young's module and Poisson's ratio of the substrate, respectively. Substrate curvatures were measured on back side of the substrate using microstylus profilometer (DEKTAK3; Sloan Technology, USA).

3. Results and discussion

3.1 Stress measurement by X-ray diffraction method

In this chapter, we mainly discuss about the stress measurement of epitaxial thin film by modified $\sin^2\psi$ method. Lattice planes exist in the same crystal zone were selected to measure the lattice strains in this technique. Figure 3 shows the XRD profiles of (003), (103), (203) and (303) planes of the $PbTiO_3$ film. Each of XRD pattern was enough intense to determine the lattice strain because the lattice plane aligns well to the same direction as for the epitaxial film. Raw diffraction peaks were divided into $K\alpha_1$ and $K\alpha_2$ components and then the peak positions were determined by full width at half maximum (FWHM) middle point method. The peak position were further converted into the lattice spacing $d_{(hkl\cdot\psi)}$ in Eq. (1). In this calculation, lattice spacing with no stress $d_{0(hkl\cdot\psi)}$ were measured on commercial $PbTiO_3$ powder.

Residual stress of the epitaxial film was determined from the relationship between the lattice strains $\varepsilon_{33}{}^L$ and offset angles ψ according to Eq. (10). $\varepsilon_3{}^L$–$\sin^2\psi$ graph of epitaxial $PbTiO_3$ film was fabricated from the result of the lattice strain measurement as shown in Fig. 4. The value of $\partial\varepsilon_{33}{}^L/\partial\sin^2\psi$ can be calculated from those relation by using least-squares method. X-ray measurement of the lattice strain was performed three times per a ψ-angle. There were some divergency among the plots of the measurement result, which may ascribed to the selection of optical system and the error of sample alignment. However, almost all plots were dispersed along the straight line calculated by the least-squared method. From those relation, the slope of the straight line, $\partial\varepsilon_{33}{}^L/\partial\sin^2\psi$, was calculated to be approximately. We can further derive the value of residual stress in epitaxial $PbTiO_3$ film from the slope, $\partial\varepsilon_{33}{}^L/\partial\sin^2\psi$, and the elastic compliance of $PbTiO_3$, s_{11}, s_{12} and s_{13}, according to Eq. (10). Finally, the residual stress of epitaxial $PbTiO_3$ film on $SrTiO_3$ was calculated to be approximately 1.6 GPa.

Residual stresses of thin films are consisted of (i) thermal stress arisen from the difference in thermal expansion coefficients between the film and the substrate, (ii) internal stress arisen from the film itself, e.g., phase transition, presence of defects and/or impurities in the crystal lattice and (iii) extrinsic stress arisen from structural changes which produce dimensional changes. In these factors, thermal stress is thought to be dominant factor of total stress applied in thin film. Theoretical thermal stress at room temperature $\sigma_{th.}$ was expressed by following equation;[18),19)]

$$\sigma_{th.}=\frac{E_f}{1-\nu_f}(\alpha_f-\alpha_s)(T_C-T) \qquad (11)$$

where E_f and ν_f are Young's module and Poisson's ratio of

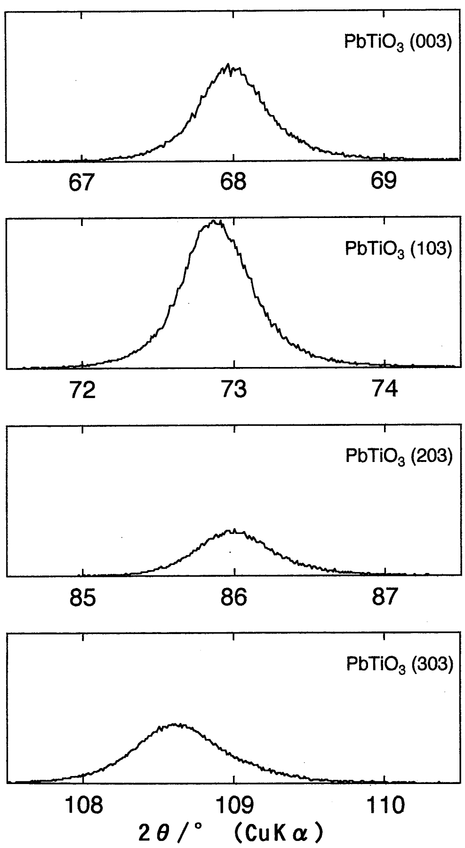

Fig. 3. Diffraction profiles of (003), (103), (203) and (303) $PbTiO_3$ planes.

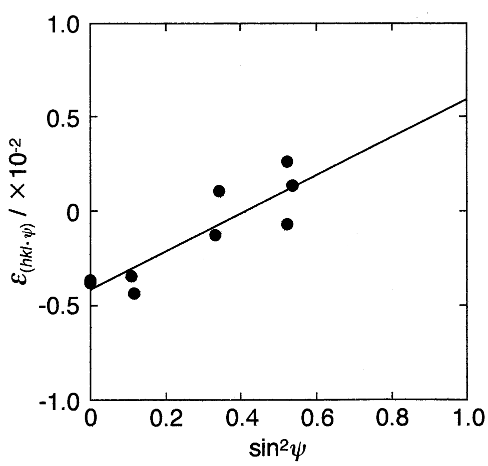

Fig. 4. Residual stress measurement of $PbTiO_3$ film on (100) $SrTiO_3$ substrate.

$PbTiO_3$ film, respectively, α_f and α_s are thermal expansion coefficients of film and substrate, T_C is the Curie temperature of $PbTiO_3$ and T is room temperature. The values of E_f and ν_f were calculated from elastic compliances as follows;[20)]

$$E_f = \frac{1}{s_{11}} \tag{12}$$

$$\nu_d = -\frac{s_{12}}{s_{11}} \tag{13}$$

Theoretical thermal stress of $PbTiO_3$ film on (100)$SrTiO_3$ substrate was estimated to be 1.5 GPa from this equation. The value of residual stress by modified $\sin^2\psi$ method was in good agreement with the theoretical value.

3.2 Comparison of the stress measurement results

The result of stress measurement by XRD technique was compared to the results by other technique to examine the precision of the result in this measurement. Values of the residual stress in an epitaxial $PbTiO_3$ film which measured by various technique were shown in Table 2, together with the results in polycrystalline film deposited on SiO_2/Si substrate. Three techniques, normal $\sin^2\psi$ method, modified $\sin^2\psi$ method (XRD technique) and Stoney method (displace measurement technique), were applied in this measurement. Modified $\sin^2\psi$ method and Stoney method can measure the film stress either in epitaxial film and in polycrystalline film, while normal $\sin^2\psi$ method can measure the stress only in polycrystalline film.

All results showed that tensile stress was applied in epitaxial $PbTiO_3$ film deposited on (100)$SrTiO_3$ substrate, while that compressive stress was applied in polycrystalline $PbTiO_3$ film on SiO_2/(100)Si substrate. We thought that value measured by modified $\sin^2\psi$ method have the precision to some extent because all results were in the same order. However, the stresses measured by XRD technique did not agree with those by displace measurement technique. The difference in these measurement results would be mainly come from the definitions of stress determination techniques. In the case of displace measurement technique, uniform stress gradient is assumed throughout film/substrate.[6),7)] When the appearance of tensile stress on the thin film is estimated, compressive stress appears on one side of the film nearby deposition surface. The compressive stress decreases linearly with the depth from the surface, b', and it change zero to tensile stress at neutral axis. Total film stress is calculated from the integral of tensile and compressive stresses in the film/substrate. In Stoney's equation, neutral axis is assumed to be present in the location at $b' = (2/3)d$; However, as steep stress gradient appears only nearby the film/substrate boundary in actual thin film, the resulting value from Stoney's equation would contain essential errors. On the other hand, residual stress calculated by XRD technique contain less error factors because the resulting value means average of stress dispersion. As steep stress gradient mainly appears nearby the film/substrate boundary closer than 100 nm (estimated

Table 2. Comparison of the Stress Measurement Results by Various Techniques

	Residual stress / GPa	
	(100)$SrTiO_3$	SiO_2/(100)Si
normal $\sin^2\psi$ method	———	-1.27
modified $\sin^2\psi$ method	1.58	-1.55
Stoney method	0.44	-0.58

from, e.g., the change of lattice parameters), error factors would contribute in a large part to the measurement result of thinner film (present work; thickness = ~700 nm); Therefore, the difference would appear between the values by XRD and displace measurement techniques. If these techniques are applied in the case of thick film (thickness > 1 mm), we might obtain the same results from two methods because the contribution of steep stress gradient becomes minor factor. Also, the difference in the measurement results may be ascribed to the precision of those techniques. The results of displace measurement technique contains some error factors; the precision of the measurement have lowered because curvature of the substrates were measured indirectly on back side of the substrate, ununiform curvature might generate on the substrate with the shape of square board, etc. As mentioned before, stress measurement of the displace measurement technique was limited by the shape and the size of the substrate.

We particularly note that the residual stress of polycrystalline film measured by modified $\sin^2\psi$ method was in relatively good agreement with the stress measured by normal $\sin^2\psi$ method. There is a similarity between normal and modified $\sin^2\psi$ methods that the stress measurements by these methods are not limited by the shape and the size of the substrate as these method are based on XRD technique. In the case of the stress measurement on polycrystalline $PbTiO_3$ thin film, X-ray diffraction could be received from all crystallites which oriented to any directions in normal $\sin^2\psi$ method, while crystallites whose (001) planes oriented perpendicular to the substrate surface were only related to the measurement by modified $\sin^2\psi$ method. If the residual stress was applied to all crystallites, we can obtain the same results from these methods theoretically. These results indicate that modified $\sin^2\psi$ method have precision to some extent which is similar to the results from normal $\sin^2\psi$ method. Also, the results suggest that modified $\sin^2\psi$ method can be applied to the stress measurement not only in epitaxial thin films, but also in polycrystalline thin films.

4. Conclusion

Analytical technique of residual stress in epitaxial thin film by X-ray diffraction was studied. Measurement results of three techniques were compared with each other to consider the advantage of each technique. The result of stresses measured by XRD technique did not agree with those by displace measurement technique because the latter technique contains some error factors which ascribe to the shape and the size of the substrate. The result on polycrystalline film measured by modified $\sin^2\psi$ method was in good agreement with the result measured by normal $\sin^2\psi$ method. These results suggest that modified $\sin^2\psi$ method can be applied to the stress measurement not only in epitaxial thin films, but also in polycrystalline thin films.

We further discussed on the precision of the stress determination technique. Residual stress of epitaxial $PbTiO_3$ film on (100)$SrTiO_3$ substrate measured by modified $\sin^2\psi$ method was comparable to the theoretical stress which estimated from the difference in thermal expansion coefficients between the film and the substrate. We thought that value measured by modified $\sin^2\psi$ method have the precision to some extent.

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