FULL PAPER

Evaluation of strain components in PbTiO_3 thin films by micro-Raman spectroscopyMasamichi NISHIDE¹, Takashi KATODA¹, Hiroshi FUNAKUBO² and Ken NISHIDA^{3,†}¹Leading technology laboratory, Kochi 781-8132, Japan²Department of Innovative Engineered Materials, Tokyo Institute of Technology, Yokohama 226-8502, Japan³Department of Communications Engineering, National Defense Academy, Yokosuka, Kanagawa 239-8686, Japan

We proposed a novel method to evaluate strain components in PbTiO_3 thin films using Raman spectroscopy. In this method, the strain components are calculated from peak shifts of three $E(\text{TO})$ -modes. The coefficients to calculate the strain components were decided via least square technique using experimental values for two-dimensional stress and hydrostatic pressure. The strain components that were estimated using the obtained coefficients were in good agreement with those measured by X-ray diffraction measurement (XRD). The average error between the strain components evaluated by XRD and Raman spectroscopy was about 0.05%.

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1. Introduction

Ferroelectric thin films have been used for various applications such as non-volatile memories, actuators and sensors etc.¹⁾ It is known that electrical properties and Curie temperature of ferroelectric materials are significantly affected by lattice strain.^{2)–4)} These changes depend on the direction of the strain as well as their magnitude. For example, Curie temperature of PbTiO_3 (PT) decreased when hydrostatic pressure is applied,^{5),6)} while, that increase under two-dimensional strain.^{7),8)} Recently, strain engineering of the ferroelectric thin films to enhance the ferroelectric properties has been studied. Therefore, the strain has been evaluated by various measurement methods. Since micro-Raman spectroscopy is noncontact and nondestructive measurement method and has relatively high spatial resolution (about 1 μm), this method has been extensively used for the strain (stress) measurement.^{9)–13)} However, the conventional technique using Raman spectroscopy could not separate the strain components (strains of the a - and c -axis of the films), which suggests that the strain measurement of the films by Raman spectroscopy is difficult. In this study, we propose a novel method to evaluate the strain components of PT thin films, which is based on a modified Cerdeira's model that has been used on strain measurement of cubic semiconductors.¹⁴⁾

2. Experimental procedure

The (100)/(001)-oriented epitaxial PT thin films were grown on (100) c - $\text{SrRuO}_3/\text{SrTiO}_3$, (100) MgO ,

(100) $\text{LaAlO}_3/\text{Sr}(\text{Al},\text{Ta})\text{O}_3$ and (100) $\text{SrRuO}_3/\text{LaNiO}_3/\text{CaF}_2$ substrates at 600°C by pulsed metalorganic chemical vapor deposition (pulsed MOCVD). Film thickness was about 50–400 nm. The lattice parameters of the PT thin films were characterized by X-ray diffraction measurement (XRD, PANalytical X'Pert MRD) that equipped with two-bounce Ge[220] hybrid monochromator. The in-plane lattice parameters were measured by glancing angle XRD. Detailed analysis of the crystal structure was carried out by high resolution XRD reciprocal space mapping (HRXRD-RSM). Raman spectroscopy measurement was carried out using Renishaw inVia Raman spectroscope. 514.5 nm line of an Ar+Kr mix gas laser was employed as an excitation source, and it was focused to a spot size of about 2 μm on the sample surface through a 40 $\times$ objective lens with NA = 0.46. Laser power was about 6 mW. The Raman spectra were corrected in back scattering configuration. Wavenumber calibration of the Raman spectroscope was carried out with a Ne lamp.

3. Results and discussion

The PT has symmetry of $P4mm$ and there are 12 optical Raman active modes, i.e., three A_1 -modes and a B_1 -mode vibrating along the polar axis, and four two-degenerate E -modes vibrating along the direction normal to the polar axis. Furthermore, these modes split into TO- and LO-modes due to long range Coulomb force.¹⁵⁾

3.1 Theory of the strain components measurement

In this section, we lead equation to evaluate the strain components of the PT from Raman measurement. This equation is based on Cerdeira's model,¹⁴⁾ which has been

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used for stress analysis of IV, III-V and II-VI compound semiconductors. In harmonic oscillator model, dynamical equation for the optical phonon modes under applied strain can be written as bellow

$$\ddot{m}u_i = - \sum_k K_{ik} u_k = - \left(K_{ii}^{(0)} u_i + \sum_{klm} \frac{\partial K_{ik}}{\partial \varepsilon_{lm}} \varepsilon_{lm} u_k \right) \quad (1)$$

where u_i , $\bar{m}$ and ε are i -th components of displacement of the atoms, reduced mass of the atoms and strain (strain was treated in percent unit in this study), respectively. $K_{ii}^{(0)} = \bar{m}\omega_0^2$ is effective spring constant in the absence of strain.

$$\begin{vmatrix} p_1 \varepsilon_{11} + q_1 \varepsilon_{22} + q_2 \varepsilon_{33} - \lambda & 2r_1 \varepsilon_{12} & 2r_2 \varepsilon_{13} \\ 2r_1 \varepsilon_{12} & p_1 \varepsilon_{22} + q_1 \varepsilon_{11} + q_2 \varepsilon_{33} - \lambda & 2r_2 \varepsilon_{23} \\ 2r_3 \varepsilon_{13} & 2r_3 \varepsilon_{23} & p_2 \varepsilon_{33} + q_3 (\varepsilon_{11} + \varepsilon_{22}) - \lambda \end{vmatrix} \equiv 0$$

$$\lambda = \omega^2 - \omega_0^2$$

where ω and ω_0 are phonon frequency for the strained and the non-strained PT crystal. Here we restrict attention to main strain and then obtain the following equation for the $E(\text{TO})$ -modes vibrating along the x -direction of the unit cell

$$p_1 \varepsilon_{11} + q_1 \varepsilon_{22} + q_2 \varepsilon_{33} - \lambda_{E(\text{TO})} = 0 \quad (2)$$

Above equation can be written in matrix notation as $\boldsymbol{\varepsilon} \cdot \mathbf{p} = \lambda$. To calculate the strain components from the peak shifts, Eq. (2) for $E(1\text{TO})$, $E(2\text{TO})$ and $E(3\text{TO})$ -modes are combined as bellow $[\varepsilon_{11} \ \varepsilon_{22} \ \varepsilon_{33}] [\mathbf{p}_1 \ \mathbf{p}_2 \ \mathbf{p}_3] = [\lambda_{E(1\text{TO})} \ \lambda_{E(2\text{TO})} \ \lambda_{E(3\text{TO})}]$ and above equation is multiplied on the right by inverse matrix of $[\mathbf{p}_1 \ \mathbf{p}_2 \ \mathbf{p}_3]$, then following equation is derived

$$\begin{aligned} \varepsilon_{ii} &= [\lambda_{E(1\text{TO})} \ \lambda_{E(2\text{TO})} \ \lambda_{E(3\text{TO})}] [\bar{\mathbf{p}}_i] \\ \varepsilon_{ii} &= \bar{p}_{i1} \lambda_{E(1\text{TO})} + \bar{p}_{i2} \lambda_{E(2\text{TO})} + \bar{p}_{i3} \lambda_{E(3\text{TO})} \end{aligned} \quad (3)$$

where $\bar{\mathbf{p}}_i$ is i -th column vector of the inverse matrix of $[\mathbf{p}_1 \ \mathbf{p}_2 \ \mathbf{p}_3]$. If $\bar{\mathbf{p}}_i$ is determined, one can calculate the strain components from the peak shifts of the $E(\text{TO})$ -modes. Here, the $E(\text{TO})$ -modes were chosen by reason that these modes have no overlap with additional modes as seen in the $A_1(\text{TO})$ -modes, therefore, determination of the peak top positions is facile. $\bar{\mathbf{p}}_i$ can be determined by simultaneous equation with three equations, which is constructed by the experimental value for three samples with different strain condition. However, it sometimes is singular. In this study, therefore, $\bar{\mathbf{p}}_i$ was determined via least square solution of over-determined system that is constructed by experimental values for the PT thin films with various strain conditions (two-dimensional stress) and hydrostatic pressure data.¹⁶⁾ The over-determined system has following form,

$$\begin{bmatrix} \lambda_{E(1\text{TO})} & \lambda_{E(2\text{TO})} & \lambda_{E(3\text{TO})} \\ \lambda'_{E(1\text{TO})} & \lambda'_{E(2\text{TO})} & \lambda'_{E(3\text{TO})} \\ \lambda''_{E(1\text{TO})} & \lambda''_{E(2\text{TO})} & \lambda''_{E(3\text{TO})} \\ \vdots & \vdots & \vdots \end{bmatrix} [\bar{\mathbf{p}}_i] = \begin{bmatrix} \varepsilon_i \\ \varepsilon'_i \\ \varepsilon''_i \\ \vdots \end{bmatrix} \quad (4)$$

where the prime marks of the variables show difference

The subscripts of i, k, l and m take the number of 1, 2 and 3, each number represents x, y and z direction in the unit cell. $\partial K_{ik} / \partial \varepsilon_{lm} = K_{iklm}^{(1)}$ is change in spring constants for applied strain ε_{lm} . Considering symmetry of the tetragonal phase, following relation can be obtained, $K_{1111}^{(1)} = K_{2222}^{(1)} = \bar{m}p_1$, $K_{3333}^{(1)} = \bar{m}p_2$, $K_{1122}^{(1)} = K_{2211}^{(1)} = \bar{m}q_1$, $K_{2233}^{(1)} = K_{1133}^{(1)} = \bar{m}q_2$, $K_{3311}^{(1)} = K_{3322}^{(1)} = \bar{m}q_3$, $K_{1212}^{(1)} = K_{2121}^{(1)} = K_{1221}^{(1)} = K_{2112}^{(1)} = \bar{m}r_1$, $K_{2323}^{(1)} = K_{1313}^{(1)} = K_{3113}^{(1)} = K_{3223}^{(1)} = \bar{m}r_2$, $K_{3131}^{(1)} = K_{3232}^{(1)} = K_{2332}^{(1)} = K_{1331}^{(1)} = \bar{m}r_3$.

From Eq. (1) and above considerations we obtain the following secular equation

of the samples. Least square solution can be obtained by normal equation $\bar{\mathbf{p}}_i = \boldsymbol{\varepsilon}_i (\boldsymbol{\lambda}^T \boldsymbol{\lambda})^{-1}$. Pseudo-inverse matrix $(\boldsymbol{\lambda}^T \boldsymbol{\lambda})^{-1}$ is calculated via singular decomposition.

3.2 Crystal structure and measurements by XRD and Raman spectroscopy

In this section, we consider crystal structure of the PT thin films used in this study, and explain about the way to obtain experimentally the parameters $\boldsymbol{\lambda}$ and $\boldsymbol{\varepsilon}$. **Figure 1** shows HRXRD-RSM pattern of the 300 nm thick PT thin film grown on $\text{SrRuO}_3/\text{SrTiO}_3$ substrate measured around 200 SrTiO_3 diffract peak. The separated spots of 200 diffract peak are found, indicating twin structure in the PT thin film. Tilt angle of the spots from center position was about 2.8° . φ -scan spectra of the 204 diffract peaks for the PT thin film and the $\text{SrRuO}_3/\text{SrTiO}_3$ substrate are shown in **Fig. 2**. As shown in Fig. 2, the diffract peaks for the PT thin film and the substrate show same peak position. It indicates that the PT thin film has epitaxially grown on the substrate. We confirmed that the all samples also had epitaxially grown on the substrates. The strain is defined as $\varepsilon = (d - d_0)/d_0$, where d and d_0 are lattice parameters of

Fig. 1. HRXRD-RSM around SrTiO_3 200 for the 300 nm thick PT thin film grown on the $\text{SrRuO}_3/\text{SrTiO}_3$ substrate.

the PT thin films and single crystal, respectively. We used the lattice parameters of the PT single crystal ($a = 3.900$ and $c = 4.148 \text{ \AA}^{17}$) as d_0 . The out-of-plane and in-plane lattice parameters of the PT thin films were measured by 2θ - θ scan along the directions normal and parallel to the film surface.

Figure 3 shows cross-polarized Raman spectra of the 300 nm thick PT thin films deposited on various substrate. As shown in this figure, only E -modes can be found according to Raman selection rule.^{18),19)} This fact leads to facility of determination of the peak top position. It is important to note that the obtained $E(\text{TO})$ -modes is vibration parallel to the sample surface and only contain the information about (100)-oriented unit cell (a -domain) due to above-mentioned momentum conservation law and Raman selection rule. Therefore, the observed peak shifts can be associated with the strain components of the (100)-oriented unit cell, i.e., the strains of the in-plane and out-of-plane a -axes ($\varepsilon_{a//} \approx \varepsilon_{11}$ and $\varepsilon_{a\perp} \approx \varepsilon_{22}$) and in-plane c -axis ($\varepsilon_{c//} \approx \varepsilon_{33}$). λ can be obtained by these Raman measurements. We used the peak top positions of the single crystal [$E(1\text{TO}) = 89.72$, $E(2\text{TO}) = 218.07$ and $E(3\text{TO}) = 505.57 \text{ cm}^{-1}$] as ω_0 . The peak top positions

Fig. 2. ϕ -scan spectra of the 204 diffract peaks for (a) the PT thin film and (b) the SrRuO₃/SrTiO₃ substrate.

Fig. 4. Relationship between the strain components evaluated from XRD and Raman spectroscopy for (a) two-dimensional stress (thin films) and (b) hydrostatic pressure. The symbols $\varepsilon_{a//}$, $\varepsilon_{a\perp}$ and $\varepsilon_{c//}$ denote the strains of in-plane and out-of-plane a -axis, and in-plane c -axis for a -domain unit cell, respectively.

were determined by non-linear peak fit. Since the observed peak top positions were different by the measurement points, we measured the Raman spectra at 25 points on the samples and used the average value of these. At the calculation of the coefficients $\bar{p}$, we used the experimental values for seven PT thin films with different substrates and film-thickness, and hydrostatic pressure data that was extracted from Refs. (5) and (16).

3.3 Strain components measurement by Raman spectroscopy

The calculated values of $\bar{p}$ are shown in **Table 1** (strain was treated in percent unit at the calculation). Relationship between the strain components evaluated by XRD and Raman spectroscopy for two-dimensional stress (thin films) and hydrostatic pressure are shown in **Figs. 4(a)** and **4(b)**. It can be seen that there are linear relationship. Average errors between the strain components evaluated

Fig. 3. Cross-polarized Raman spectra obtained from the PT thin films grown on various substrates. (a) SrRuO₃/SrTiO₃, (b) MgO, (c) LaAlO₃/Sr(Al,Ta)O₃ and (d) SrRuO₃/LaNiO₃/CaF₂ substrate. The symbols * indicate the peaks of the substrates.

Table 1. Coefficients $\bar{p}$ calculated from Eq. (4)

$\bar{p}_{11}$	-6.48 E-5	$\bar{p}_{12}$	-1.99 E-5	$\bar{p}_{13}$	-2.19 E-5
$\bar{p}_{21}$	-1.82 E-4	$\bar{p}_{22}$	-5.63 E-6	$\bar{p}_{23}$	-2.96 E-5
$\bar{p}_{31}$	-3.31 E-4	$\bar{p}_{32}$	3.03 E-4	$\bar{p}_{33}$	-6.81 E-5

Fig. 5. Thickness dependence of the strain components for the PT thin films grown on the MgO substrates. The solid and open symbols denote the strain components evaluated by XRD and Raman spectroscopy, respectively.

by XRD and Raman spectroscopy were 0.046 ($\varepsilon_{a||}$), 0.072 ($\varepsilon_{a\perp}$) and 0.066% ($\varepsilon_{c||}$) for two-dimensional stress (thin films), and 0.102 (ε_{11}), 0.099 (ε_{22}) and 1.372% (ε_{33}) for hydrostatic pressure. From this result, it is considered that the strain components can sufficiently be estimated using the three Raman modes. Here, it is important to note that the Raman peak positions are affected by other factors such as elemental substitution and defect. Therefore, this method could not put correct values for significantly deformed and damaged samples. To confirm availability of this method, we investigated thickness dependence of the strain components for the PT thin films grown on the MgO substrates and compare the evaluated values obtained by XRD and Raman spectroscopy. These samples have not been involved to the samples used at the calculation of the coefficients $\bar{p}$. The results are shown in Fig. 5. There are reasonable agreements between these values. This result indicates that our novel method is useful for measurement of the strain components in the PT thin films. Using this method, in-plane and out-of-plane strains can easily be measured. And the approach we used in this study could be diverted to other tetragonal ferroelectrics. It is hoped that application range of Raman spectroscopy will expand in combination with some advantages of Raman spectroscopy such as high spatial resolution and ease of in-situ measurement. Future task is to investigate effects of shear strain and of crystal orientation because these effects were not considered in this study.

4. Conclusion

We proposed the novel method to evaluate the strain components in the PT thin films using Raman spectroscopy. In this method, the strain components are calculated from the peak shifts of the three $E(\text{TO})$ -mode. The coefficients to calculate the strain components were decided via least square technique of over-determined system which

was constructed by the experimental values for the seven PT thin films grown on the various substrates and the hydrostatic pressure data. The strain components that were estimated using the obtained coefficients were in good agreement with those measured by XRD. The average error between the strain components evaluated by XRD and Raman spectroscopy was about 0.05%.

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