Thermodynamic study of c-axis-oriented epitaxial Pb(Zr,Ti)O$_3$ thin films

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Thermodynamic characteristics of single crystalline Pb(Zr$_{0.52}$Ti$_{0.48}$)O$_3$ (PZT) were investigated using c-axis oriented PZT films. The PZT films were epitaxially grown on Pt/MgO substrate and dielectric and ferroelectric properties were measured as a function of one-dimensional stress. The stress dependence of dielectric and ferroelectric properties was examined on the basis of the Landau-Devonshire’s phenomenological theory and the free energy coefficients of single crystalline PZT films were obtained. The dielectric stiffness coefficients and electrostrictive coefficient of epitaxial PZT films were obtained to be $\alpha_1 = -1.30 \times 10^9$ (m/F), $\alpha_{11} = 3.07 \times 10^8$ (m$^3$/C$^2$F), and $Q_{12} = -5.70 \times 10^{-2}$ (m$^3$/C$^2$), which are different from the values derived from the analysis of polycrystalline PZT. The temperature dependence of dielectric constant of the PZT films showed clear Curie-Weiss law and the dielectric stiffness coefficient $\alpha_1$ derived from this measurement was almost same value from the analysis of stress dependence of the dielectricity of the epitaxial PZT films.

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I. INTRODUCTION

The Pb(Zr,Ti)O$_3$ (PZT) ferroelectric materials have attracted considerable attention due to their excellent dielectric, ferroelectric, and piezoelectric properties. Ferroelectric properties of PZT can be theoretically analyzed by thermodynamic formalism on the basis of the Landau-Devonshire phenomenological theory and lots of investigations have been reported concerning electrical properties and crystalline phases of PbTiO$_3$-PbZrO$_3$ solid solution system. Haun et al. investigated PZT with a variety of Zr/Ti ratio based on the Landau-Devonshire formula in detail and derived free energy coefficients in this system. These thermodynamic coefficients of PZT have been used as the standard values to investigate thermodynamic studies of PZT in later research. In recent years, the development of the ferroelectric thin films has been significantly progressed as promising materials for use in nonvolatile memories and in microelectromechanical systems (MEMS). The characterization of the ferroelectric PZT thin films has been performed on the basis of the thermodynamic phenomenological theory using conventional free energy coefficients derived from the analysis of bulk PZT. Oh et al. have already carried out the detailed analysis of the effects of two-dimensional stress on the epitaxial PZT thin films and revealed the relationship between stress and phase diagram on the basis of thermodynamic theory. The thermodynamic equations can be expressed by spontaneous polarization and stress of single crystalline PZT. However, since it has been impossible to grow PZT single crystal with enough size for measurements of electric properties, conventional values of free energy function were derived from indirect method using polycrystalline PZT ceramics.

On the other hand, thin film deposition techniques such as rf sputtering and chemical vapor deposition enable an epitaxial growth of PZT films with single crystalline structure. In comparison with polycrystalline PZT ceramics, single crystalline epitaxial films exhibit several unique characteristics such as anomalous crystalline structure due to not only extrinsic stress from the substrate but intrinsic stress due to impinging energetic species onto the films. Therefore it is necessary to perform thermodynamic analysis and derive free energy coefficients using the epitaxial PZT films instead of the conventional bulk values. Fortunately, the crystalline structure of tetragonal PZT films with c-axis orientation is so simple that it is relatively easy to evaluate stress effects on the electric properties. In this study, we prepared c-axis oriented epitaxial PZT films with the composition near morphotropic phase boundary and measured the dielectric and ferroelectric properties as a function of one-dimensional stress along the $a$ or $b$ axis of the tetragonal unit cell. Several coefficients of free energy function of epitaxial PZT films were experimentally derived and compared with conventional values of bulk PZT derived by Haun et al. In addition, we have estimated the dielectric and ferroelectric characteristics of epitaxial PZT films under a wide range of external stress using free energy coefficients we derived through this study.

II. EXPERIMENTS

A. Preparation of PZT thin films

PZT thin films were deposited using rf magnetron sputtering. Pt electrodes with the thickness of 100 nm were epitaxially grown on (100)MgO substrates prior to PZT growth. The sputtering conditions of PZT films were described in previous reports. The target used was hot-pressed ceramics of which composition was near morphotropic phase boundary of Zr/Ti = 53/47 including additional PbO for the compensation of reevaporation of lead. The growth of the PZT was carried out at the substrate temperature of 550 °C. The thickness of the PZT films we prepared was 3 μm from

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the viewpoint of MEMS applications. In addition, the thin films as thick as 3 μm is desirable to eliminate the thickness dependence of the PZT films. The composition of the resulting films was evaluated by energy dispersive x-ray spectroscopy and was identified as Zr/Ti = 52/48 that was almost same ratio of target one. Figure 1 shows x-ray diffraction (XRD) pattern of the PZT thin films. Strong peaks of (001) and (002) of PZT can be observed without any other phases. We have also analyzed crystalline structure using four-circle XRD and reciprocal space maps of (004) and (204) of PZT were shown in Fig. 2. In the reciprocal space map of (004) of PZT diffraction [Fig. 2(a)], we could observe only single peak of the PZT and there were no peaks corresponding to 90° domains which appear near the side of (004) of PZT diffraction. Furthermore, in the reciprocal map of (204) diffraction [Fig. 2(b)], the peak position of (204) of PZT is located at the right side from the dotted line passing through (204) of MgO and (204) of Pt. This result indicates that the PZT films have tetragonal structure. From the peak positions of (004) and (204) of PZT, the lattice constants of a and c were calculated as 4.049 and 4.161 Å, respectively.

B. Measurement of residual stress

Epitaxial films generally have significant residual stress due to lattice mismatch as well as difference of thermal expansion coefficients between films and substrates. Particularly, PZT films were deposited at high substrate temperatures of 550 °C which induced large thermal stress during cooling down to a room temperature. In order to identify influence of internal stress on electric properties, we have to evaluate the residual stress accumulated in the PZT films prior to the evaluation of the stress effects on the electric properties. For the measurement of the residual stress, we cleaved PZT/Pt/MgO samples into strip specimens and evaluated one-dimensional residual stress of epitaxial PZT films along the length of the specimen. The width of the specimen is smaller than the length. Therefore the stress of the width direction is relaxed compared with the stress along the length and we can neglect the influence of the stress of the width direction. The curvature of the specimen was measured by surface profiler. In order to obtain adequate bending of the specimen, the thickness of the MgO substrate was reduce by wet etching from 0.3 to 0.19 mm prior to the measurement of the curvature.

Then the electric properties of the PZT films were evaluated as a function of external stress using the cantilever specimen similar with the specimen for curvature measurements. The one end of the specimen was fixed by a vise as illustrated in Fig. 3, and then one-dimensional stress was applied to the other end of the specimen.

| TABLE I. Dimension of the specimen for residual stress measurement. |
|-----------------|-----------------|
| Thickness h (m) | 0.19×10⁻³       |
| Width of the specimen b (m) | 3.03×10⁻³ |
| Young’s modulus E (Pa) | 248×10⁹       |
| Thermal expansion coefficient α (°C⁻¹) | 13.8×10⁻⁵ |
| Temperature difference ΔT (°C) | 525            |
PZT films are epitaxially grown with the perfect c-axis orientation on the MgO substrates and the specimen is cleaved out along the width of 1 mm. In this experiment, the maximum load we used was 50 gf. Stripe-shaped electrodes with the width of 1 mm were deposited on the PZT films. The residual stress was evaluated by measuring the radius of curvature $R$ of the Pt electrode due to its small thickness compared with that of MgO and PZT. The Young’s modulus of single crystal MgO is reported as 248 GPa, while the Young’s modulus of epitaxial PZT films was 92.6 GPa which we measured and reported in a previous paper. From Eq. (1), $\sigma$ becomes $-338$ MPa of compressive stress.

On the other hand, assuming the stress of the PZT films was caused by the difference of the thermal expansion coefficients with MgO substrate, the strain at the interface of PZT/MgO was written by

$$\frac{h_1/2}{R} - \frac{\alpha h_2}{E_1 h_1} \Delta T = - \frac{h_2/2}{R} + \frac{\sigma}{E_2} - \alpha_{T_2} \Delta T,$$

where $\alpha_{T_1}$ and $\alpha_{T_2}$ are the thermal expansion coefficients of MgO and PZT films, and $\Delta T$ is the difference between a deposition temperature and a room temperature. The thermal expansion coefficient of single crystal MgO is reported to be $\alpha_{T_1} = 13.8 \times 10^{-6} (^\circ$C), therefore that of the epitaxial PZT was calculated to be $\alpha_{T_2} = 6.69 \times 10^{-6} (^\circ$C). On the other hand, the radius of curvature $R_0$ of the PZT films on 0.3-mm-thick MgO was given from the Eq. (1) and (2)

$$\frac{1}{R_0} = \frac{(\alpha_{T_1} - \alpha_{T_2}) \Delta T}{(h_1 + h_2)/2 + (E_1 h_1 + E_2 h_2)/(E_1 I_1 + E_2 I_2) b (h_1 + h_2)}.$$

B. Stress dependence of electric properties

The relative dielectric constants of the PZT films were measured as a function of extrinsic one-dimensional stress. The extrinsic stress $\sigma^*$ from the load to the PZT was given as

$$\sigma^* = E_2 \frac{M y}{E_1 I_1 + E_2 I_2}.$$

From Eqs. (1) and (3), the residual stress of the as-grown PZT films on the MgO substrate with a thickness of 0.3 mm was determined as $\sigma_0 = -340$ MPa of compressive stress. The residual stress only affects the c-axis (or b axis) since the PZT films are epitaxially grown with the perfect c-axis orientation on the MgO substrates and the specimen is cleaved out along the a or b axis.
Although the obtained values were relatively scattered, we observed clear stress dependence as the remanent polarization increased with applying compressive stress, while it decreased with applying tensile stress.

C. Thermodynamic analysis

The Gibbs free energy function for PZT is expressed as

$$\Delta G = \alpha_1 (P_1^2 + P_2^2 + P_3^2) + \alpha_{11} (P_1^4 + P_2^4 + P_3^4) + \alpha_{12} (P_1^2 P_2^2 + P_2^2 P_3^2 + P_3^2 P_1^2)$$

$$+ \alpha_{111} (P_1^6 + P_2^6 + P_3^6) + \alpha_{112} (P_1^4 P_2^2 + P_2^4 P_3^2 + P_3^4 P_1^2) + \alpha_{23} P_1^2 P_2^2 P_3^2$$

$$- \frac{1}{2} s_{11} (X_1^2 + X_2^2 + X_3^2) - s_{12} (X_1 X_2 + X_2 X_3 + X_3 X_1)$$

$$- \frac{1}{2} s_{44} (X_1^2 + X_2^2 + X_3^2) - Q_{11} (X_1 P_1^2 + X_2 P_2^2 + X_3 P_3^2)$$

$$- Q_{12} (X_1 P_1^3 + P_2^3 + X_2 P_3^3 + X_3 P_1^3 + P_2^3)$$

$$- Q_{44} (X_1 P_2 P_3 + X_5 P_3 P_1 + X_6 P_1 P_2),$$

where $P_1$ and $X_i$ are the polarization and stress; $\alpha_i$, $\alpha_{ij}$, and $\alpha_{ijk}$ are the dielectric stiffness coefficients at constant stress; $s_{ij}$ are the elastic compliances at constant polarization; and $Q_{ij}$ are the electrostrictive constants. In the reduced notation, the tensile stresses are denoted by $X_1$, $X_2$, $X_3$ and shear stressed by $X_4$, $X_5$, $X_6$.

Since the PZT films we prepared showed tetragonal structure, the following conditions should be satisfied in Eq. (5): $P_1 = P_2 = 0$, $P_3 \neq 0$. In the experiments we applied one-dimensional stress along the length of the beam-shaped specimen, and we can define the following conditions of the stress: $X_1 = \sigma$, $X_2 = X_3 = X_4 = X_5 = X_6 = 0$. Therefore, Eq. (5) in the epitaxial PZT films with tetragonal phase results in the equations

$$\Delta G = \alpha_1 P_3^2 + \alpha_{11} P_3^4 + \alpha_{111} P_3^6 - \frac{1}{2} s_{11} \sigma^2 - Q_{12} \sigma P_3^2.$$  \hspace{1cm} (6)

Using the free energy equation, the spontaneous polarization $P_3$ can be derived from the condition

$$\frac{\partial \Delta G}{\partial P_3} = 0,$$

$$P_3 = \sqrt{-\frac{\alpha_1 + \sqrt{\alpha_{11}^2 - 3 \alpha_{11} (\alpha_1 - Q_{12} \sigma)}}{3 \alpha_{111}}}.$$  \hspace{1cm} (7)

In addition, dielectric constant $\varepsilon_{33}$ is also derived from the second partial derivative stability condition

$$\frac{\partial^2 \Delta G}{\partial P_3^2} = \frac{1}{\varepsilon_{33}},$$

$$\varepsilon_{33} = \left\{2 \alpha_1 + 12 \alpha_{11} P_3^2 + 30 \alpha_{111} P_3^4 - 2 Q_{12} \sigma\right\}^{-1}.$$  \hspace{1cm} (8)

In the case of epitaxial PZT films with c-axis orientation, the electric properties can be determined using four free energy coefficients of $\alpha_1$, $\alpha_{11}$, $\alpha_{111}$, and $Q_{12}$. However it has been difficult to determine the free energy coefficients since bulk PZT is a polycrystalline structure and the spontaneous polarization $P_3$ cannot be measured without single crystal.

FIG. 5. $P$-$E$ hysteresis loops of the PZT films with different external one-dimensional stress of $-50$, $0$, and $+50$ MPa.

FIG. 6. Remanent polarization of the epitaxial PZT films as a function of the one-dimensional stress.
samples. Haun et al. derived these coefficients of PZT by the indirect method from the combination of spontaneous strain and electrostrictive constants. In this study, we prepared single-crystalline PZT in a thin film form and could measure the actual spontaneous polarization \( P_s \) which is equal to the remanent polarization because the PZT films were epitaxially grown with the \( c \)-axis orientation. Therefore, we could determine the free energy coefficients directly from the experimental data.

D. Calculation of the dielectric stiffness coefficients \( \alpha_1, \alpha_{11}, \alpha_{111} \), and the electrostrictive coefficient \( Q_{12} \)

We determined free energy coefficients from the experimental data of dielectric constant and spontaneous polarization. From Eqs. (7) and (8), the dielectric constant and the spontaneous polarization are expressed as a function of the one-dimensional internal stress along the \( a \)-axis:

\[
3\alpha_{111}P_3^2 + 2\alpha_{11}P_3^2 + (\alpha_1 - Q_{12}\sigma) = 0, \tag{9}
\]

\[
15\alpha_{111}P_3^4 + 6\alpha_{11}P_3^4 + (\alpha_1 - Q_{12}\sigma) = \frac{1}{2}\varepsilon_{33} . \tag{10}
\]

We determined free energy coefficients applying stress dependences of dielectric and ferroelectric properties to the above equations. Although the dielectric constants showed clear dependence on stress, the values of remanent polarization showed significant variation, and it is difficult to determine the reliable constant of proportionality. On the other hand, the proportional ratio between polarization and stress \((dP_3/d\sigma_1)\) represents the piezoelectric coefficient \(d_{31}\) and we have estimated the stable piezoelectric coefficient \(d_{31}\) of \(-100\times10^{-12}\) mV for the \( c \)-axis-oriented epitaxial PZT films with the same composition.\(^{23}\) Therefore, we used the piezoelectric coefficient \(d_{31}\) to determine polarization dependence on the stress instead of the experimental results as shown in Fig. 6.

The piezoelectric coefficient \(d_{31}\) is expressed using the electrostrictive coefficients \(Q_{12}\) as

\[
d_{31} = \frac{dP_3}{d\sigma_1} = \frac{\delta^2 \Delta G}{\delta \sigma_1 \delta P_3} \cdot \frac{\delta^2 P_3}{\delta \Delta G^2} = \varepsilon_{33} Q_{12} P_3 . \tag{11}
\]

Using the dielectric constant and spontaneous polarization in the neutral stress, the electrostrictive coefficients \(Q_{12}\) can be obtained to be \(-5.70\times10^{-2}\) (m\(^4\)/C\(^2\)).

The dielectric stiffness coefficients \(\alpha_1, \alpha_{11}, \alpha_{111}\) was determined using the data of dielectric constants at representative stress states of \(-380, -340, \) and \(-260\) MPa. Spontaneous polarization at any stress can be obtained by

\[
P_3(\sigma) = P_3(-340) + \frac{dP_3(\sigma)}{d\sigma_1} \Delta \sigma
\]

\[
= P_3(-340) + d_{31}(\sigma + 340) \times 10^6 , \tag{12}
\]

where \(P_3(\sigma)\) is the spontaneous polarization at the stress of \(\sigma\) MPa. From Eqs. (9) and (10), the dielectric stiffness coefficients \(\alpha_1, \alpha_{11}, \alpha_{111}\) should satisfy the equation

\[
\begin{bmatrix}
1 & 6P_{s\sigma_1}^2 & 15P_{s\sigma_1}^4 \\
1 & 6P_{s\sigma_2}^2 & 15P_{s\sigma_2}^4 \\
1 & 2P_{s\sigma_0}^2 & 3P_{s\sigma_0}^4
\end{bmatrix}
\begin{bmatrix}
\alpha_1 \\
\alpha_{11} \\
\alpha_{111}
\end{bmatrix}
= \begin{bmatrix}
Q_{12\sigma_1} + 1/\varepsilon_{s\sigma_1} \\
Q_{12\sigma_2} + 1/\varepsilon_{s\sigma_2} \\
Q_{12\sigma_0}
\end{bmatrix},
\]

where \(\sigma_0, \sigma_1, \) and \(\sigma_2\) are \(-340, -380,\) and \(-260\) MPa, respectively. The subscripts of \(\sigma_0, \sigma_1, \) and \(\sigma_2\) in \( P \) and \( e \) represent the stress states of spontaneous polarization \( P_s \) and dielectric constant \( \varepsilon_{33} \). The spontaneous polarization and dielectric constant can be determined from Eq. (12) and Fig. 4. Then, the dielectric stiffness coefficients \(\alpha_1, \alpha_{11}, \) and \(\alpha_{111}\) were calculated to be, \(\alpha_1 = -1.30\times10^{9}\) (m/F), \(\alpha_{11} = 3.07\times10^{8}\) (m\(^5\)/C\(^2\)F), \(\alpha_{111} = -3.11\times10^{7}\) (m\(^7\)/C\(^4\)F).

The comparison of the electric properties and the free energy coefficients between bulk Pb(Zr\(_{0.5}\)Ti\(_{0.5}\))O\(_3\) by Haun et al.\(^2\) and epitaxial Pb(Zr\(_{0.52}\)Ti\(_{0.48}\))O\(_3\) films of our experiments were listed in Table II. Although spontaneous polarization and electrostrictive coefficients were almost the same as Haun’s results, the dielectric constant and dielectric stiffness coefficients of our results were significantly different. These results suggest that it is necessary to use the data of the PZT films instead of the previous bulk values for the estimation of the thermodynamic characteristics of the epitaxial PZT films.

The electric properties of the PZT films could be estimated as a function of the stress using the values listed in Table II. Figure 7 shows the relationship between relative dielectric constant and one-dimensional stress on the PZT films. The dielectric properties obtained from Haun’s data of Pb(Zr\(_{0.5}\)Ti\(_{0.5}\))O\(_3\) are also plotted in Fig. 7. This figure represents that the dielectric constant of the epitaxial films increases with one-dimensional stress, but the increase ratio is significantly smaller than that from bulk PZT, suggesting that epitaxial PZT films have relatively stable dielectric dependence on stress. On the other hand, Fig. 8 shows spontaneous polarization of the epitaxial PZT films as a function of one-dimensional stress. The spontaneous polarization shows almost same dependence as conventional data and it gradually decreases with stress.

E. Dependence of dielectric constant on temperature

It is known that the dielectric properties of ferroelectric materials strongly depend on temperature in accordance with

<table>
<thead>
<tr>
<th></th>
<th>bulk PZT (Ref. 5)</th>
<th>epitaxial PZT film</th>
</tr>
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<tbody>
<tr>
<td>Dielectric constant</td>
<td>(\varepsilon) (F/m)</td>
<td>(3.38\times10^{-9})</td>
</tr>
<tr>
<td>Spontaneous polarization</td>
<td>(P_s) ((\mu)C/cm(^2))</td>
<td>50</td>
</tr>
<tr>
<td>(\alpha_1) (m/F)</td>
<td>(-4.887\times10^7)</td>
<td>(-1.30\times10^8)</td>
</tr>
<tr>
<td>(\alpha_{11}) (m(^3)/C(^2)F)</td>
<td>(4.764\times10^7)</td>
<td>(3.07\times10^8)</td>
</tr>
<tr>
<td>(\alpha_{111}) (m(^3)/C(^2)F)</td>
<td>(1.336\times10^8)</td>
<td>(-3.11\times10^7)</td>
</tr>
<tr>
<td>(Q_{12}) (m(^3)/C(^2))</td>
<td>(-4.6\times10^{-2})</td>
<td>(-5.7\times10^{-2})</td>
</tr>
</tbody>
</table>
the Curie-Weiss law. In the dielectric stiffness coefficients, \( a_1 \) depends on temperature and can be defined as

\[
a_1 = \frac{(T-T_0)}{2\varepsilon_0 C},
\]

where \( C \) is Curie constant, \( \varepsilon_0 \) is dielectric constant of free space, and \( T_0 \) is the Curie-Weiss temperature. Therefore dielectric constants in paraelectric and ferroelectric phases are expressed as

\[
\frac{1}{\varepsilon} = \frac{(T-T_0)}{\varepsilon_0 C} (T> T_0),
\]

\[
\frac{1}{\varepsilon} = -2 \frac{(T-T_0)}{\varepsilon_0 C} (T\leq T_0).
\]

In this experiment, we observed the dielectric constant as a function of temperature, and evaluated the dielectric stiffness coefficient of \( a_1 \) in order to confirm the validity of the free energy coefficient obtained by stress dependence. Figure 9 shows the relationship between dielectric constants of the PZT films and temperature. The dielectric constant gradually increased and exhibited the maximum at the ferroelectric-paraelectric phase transition temperature. The reciprocal plot of dielectric constant is good agreement with the Curie-Weiss law as shown in Fig. 9. The Curie-Weiss temperature was determined as 384 °C, which is almost the same as bulk Pb\((\text{Zr}_{0.5}\text{Ti}_{0.5})\text{O}_3\) of 392.6 °C.\(^5\) The Curie constant of epitaxial PZT films was obtained from Fig. 9 as \( C = 1.44 \times 10^5 \) °C, which was smaller than that of bulk PZT (4.247 \times 10^5 °C). On the other hand, the dielectric stiffness coefficients \( a_1 \) at a room temperature is also determined from Eq. (12) as \(-1.37 \times 10^{8} \text{ m/F}\), which is almost the same as the value derived in the previous section \((-1.30 \times 10^{8} \text{ m/F})\). This result indicates that the dielectric dependence on temperature has proved the validity of dielectric stiffness coefficients of single crystalline and single domain PZT films obtained by the estimation of electric dependence on one-dimensional stress.

### IV. CONCLUSIONS

We prepared \( c \)-axis-oriented epitaxial PZT films with the composition of \( \text{Zr/Ti}=52/48 \) and investigated thermodynamic characteristics. The dielectric and ferroelectric properties of epitaxial films depend on external stress and their characteristics were examined on the basis of the Landau-Devonshire’s phenomenological theory. The dielectric stiffness coefficients and the electrostrictive coefficient of epitaxial PZT films were obtained as \( a_1 = -1.30 \times 10^8 \) (m/F), \( a_{11} = 3.07 \times 10^8 \) (m\(^2\)/C\(^2\)) and \( \alpha_{111} = -3.11 \times 10^7 \) (m\(^2\)/C\(^2\)), and \( Q_{12} = -5.70 \times 10^{-2} \) (m\(^2\)/C\(^2\)), which are different than the values derived from the analysis of polycrystalline PZT. The temperature dependence of dielectric constant demonstrated that the dielectric properties obeyed Curie-Weiss law. The dielectric stiffness coefficient of \( a_1 \) calculated from the temperature dependence was almost the same as the value obtained from the analysis of the stress dependence of the PZT films.

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