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Polarized Raman scattering of epitaxial $PbTiO_3$ thin film with coexisting *c* and *a* domains

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Effects of the orientation of ferroelectric domains on the characteristics of polarized Raman spectra were studied using an epitaxially grown $PbTiO_3$ thin film in which the c-axis oriented domains coexist with the a-axis oriented domains on MgO (001). To obtain polarized spectra for both two distinctive c and a domains, we have employed scattering configurations in which the relevant phonon wave vector, $\mathbf{k}$, is perpendicular to the c axis of the tetragonal unit cell. Compared with the mode frequencies of single-crystal $PbTiO_3$, a softening of the E(TO) phonons was evident for both c and a domains, suggesting the presence of a strong tensile film stress. In addition to this, we observed a splitting of the degenerate "silent" mode into two distinctive B_1 and E modes in an epitaxially grown film on MgO (001). © *2002 American Institute of Physics.*

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Lead titanate ($PbTiO_3$) has a simple structure among many perovskite-based metal oxides and exhibits a typical displacive phase-transition character at 766 K (T_c).[1] Unlike $BaTiO_3$, in which the "soft" mode phonons are difficult to observe because of their overdamping characters,[1,2] the soft modes of $PbTiO_3$ are underdamped even at high temperatures near T_c and are known to rigorously follow the selection rules of Raman scattering.[3,4] Thus, it has been extensively studied as a model system for understanding the mechanisms of displacive ferroelectric transitions.[1,5] $PbTiO_3$ is not only important in scientific studies but also has potentials for its applications to low-voltage-driving electroluminescence devices, ultrasonic sensors, nonvolatile memory field-effect transistors (FETs), and infrared-optical FETs.[6] Furthermore, its solid solution with antiferroelectric lead zirconate [i.e., $Pb(Zr,Ti)O_3$; PZT] is one of the prime candidates for nonvolatile film capacitors in ferroelectric random access memory devices.[7,8]

A detailed study of the Raman scattering of single-crystal $PbTiO_3$ was made by Burns and Scott.[3,4] They assigned the Raman active modes of tetragonal $PbTiO_3$ and observed a softening behavior of the lowest-frequency E-symmetry transverse-optical [E(1TO)] phonon that drives a displacive ferroelectric phase transition. The first mode assignment of the A_1(1TO) phonon was suggested by Fontana and co-workers.[9] However, they did not give any explanation of the observed asymmetric line shape of the A_1(1TO) mode. The explanation of the line shape of the A_1(1TO) mode was subsequently given by Foster and co-workers.[10,11] They attributed the anomalous line shape to the anharmonicity in the effective interatomic potential. Later, Cho and Jang directly observed the softening of the A_1(1TO) phonon and the mode crossing between the A_1(1TO) phonon and the longitudinal E(1LO) phonon employing 90° scattering geometry.[12] More recently, after a detailed analysis of the A_1(1TO) phonon, they concluded that the anomalous scattering intensity of the lowest-frequency subpeak of the A_1(1TO) mode that dominated the phonon softening was not directly related to the anharmonicity in the double-well potential but originated from thermodynamically stable lattice defects.[13]

Several interesting Raman studies of $PbTiO_3$ thin films were reported recently, including epitaxially grown $PbTiO_3$ on (110) $NdGaO_3$[14] and polycrystalline $PbTiO_3$ on $Pt/Ti/SiO_2/Si$.[15] However, polarized Raman spectra that clearly separate the E-symmetry phonons from the A_1-symmetry phonons have not been obtained yet. In view of this, the main purpose of the present letter is to separately observe the two distinctive types of the soft modes, E(TO) and A_1(TO), in an epitaxial $PbTiO_3$ thin film in which the c-axis oriented domains coexist with the a-axis domains. We have obtained polarized Raman spectra for both types of domains by employing scattering configurations in which the phonon wave vector, $\mathbf{k}$, is perpendicular to the c axis of the tetragonal unit cell, irrespective of the domain configuration. Thus, we were able to separately estimate the effect of the domain orientation on the softening of E(TO) and A_1(TO) phonons.

Pulsed laser deposition (PLD) was employed to prepare an epitaxial $PbTiO_3$ film on MgO (001). The deposition conditions used in the present study are as follows: (i) laser source; KrF excimer (248 nm), (ii) fluence; 1.0 J/cm^2, (iii) oxygen pressure; 150 mTorr, (iv) laser frequency; 7 Hz, (v) deposition temperature; 660 °C. The thickness of $PbTiO_3$ film, as estimated using field-emission scanning electron microscopy, was 250 nm.

Figure 1(a) shows the θ–2θ x-ray diffraction (XRD) pattern of the PLD-grown film. As marked in the figure, (001) and (002) peaks are caused by the diffraction from the c domain in which the crystallographic c axis of the tetragonal unit cell is perpendicular to the substrate plane, MgO (001).

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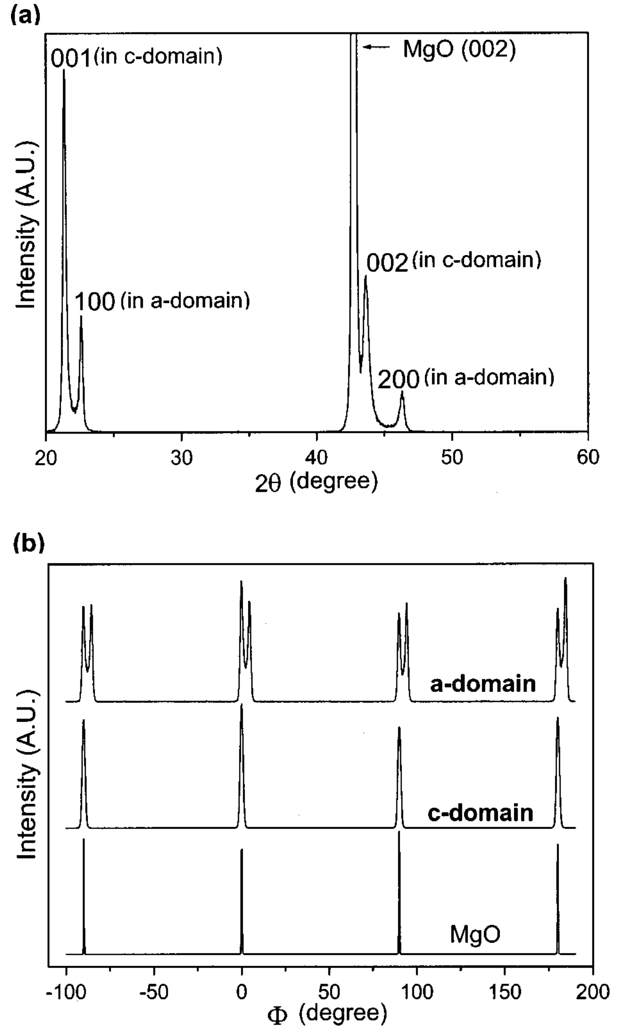

FIG. 1. XRD characterization of $PbTiO_3$ thin film grown on MgO (001). (a) XRD θ–2θ pattern, (b) x-ray Φ-scan spectra of c and a domains in $PbTiO_3$ and of MgO (001).

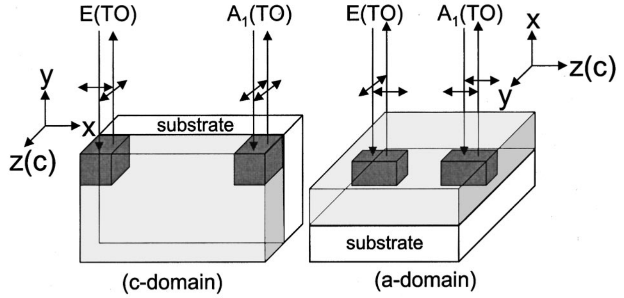

FIG. 2. Raman scattering geometries used for the study of E(TO) and A_1(TO) modes of $PbTiO_3$ thin film in which two distinctive c and a domains coexist.

On the other hand, (100) and (200) peaks correspond to the diffraction from the a domain in which the a axis is normal to the substrate plane. Figure 1(a) clearly indicates the coexistence of c and a domains. The relative fraction, α, of the c domain, as estimated using the relation

$$\alpha(\omega)=I_{\omega(001)}/\{I_{\omega(001)}+I_{\omega(100)}\},\ \text{was}\ 0.7.$$

The degree of in-plane epitaxial relationship between $PbTiO_3$ film and MgO (001) was assessed by examining XRD Φ-scan spectra. As presented in Fig. 1(b), the peaks for (101) reflection of the c domain occur at the same azimuthal Φ angles as those for MgO (202) reflection and are 90° apart. The same relationship does hold between the a-axis domain and MgO. This clearly indicates the presence of fourfold symmetry for both c and a domains and a "cube-on-cube" epitaxial growth of $PbTiO_3$ on a MgO (001) substrate. In case of the a domain, however, each peak is further split into two subpeaks, and they are 4.4° apart. This indicates the formation of a 90° twin-domain wall at the boundary between the c-axis domain and the a domain and a consequential tilting of the a-axis domain with respect to the c domain. The twin-domain boundaries form on {101} planes, and the degree of tilting ($\Delta\omega$), as estimated from the peak splitting in the θ-rocking curve, is 2.2°. The tilting is caused by the tetragonality of $PbTiO_3$, and $\Delta\omega$ is given by $[90° - 2\tan^{-1}(a/c)]$.

One can estimate the lattice parameters, c and a, for both types of domains using θ–2θ patterns and Φ-scan spectra. From $2\theta_{001}$ in Fig. 1(a), one can directly evaluate d_{001}, which is equal to the c-axis lattice parameter of the c domain. Let us call this c_c. In the Φ scanning for (101) plane, $2\theta_{101}$ should be detected first. Then, d_{101} was estimated from this value. The a-axis lattice parameter for the c domain (abbreviated as a_c) was readily computed from d_{101}. Exactly the same procedure applies to the evaluation of a_a and c_a for the a-axis domain. The estimated lattice parameters are: $a_c = 3.92$ Å, $c_c = 4.13$ Å for the c domain, and $a_a = 3.91$ Å, $c_a = 3.92$ Å for the a domain. The lattice parameters of tetragonal single-crystal $PbTiO_3$ are $a = 3.899$ Å and $c = 4.153$ Å. The decrease of the tetragonality *(c/a)* in the thin film, as compared with that of stress-free single-crystal $PbTiO_3$ ($c/a = 1.065$), can be correlated with the stress exerted on the film.[16] Since $c/a = 1.050$ for the c domain and 1.003 for the a domain, the residual film stress is expected to be more pronounced in the a domain than in the c domain.

The Raman-scattering data were obtained using a NRS-2100 spectrometer (JASCO, Japan) equipped with a triple-grating monochromator and a Coherent Innova 90C Ar laser at 5145 Å. It has a spectral resolution of 1 cm^{-1}. The measurement was performed with a micro-Raman option using a LN_2-cooled charge coupled device. Since tetragonal $PbTiO_3$ belongs to C_{4v} (4 mm) point group, the E-symmetry soft modes can be observed in the cross polarization configuration, i.e., (yz) or (xz). On the other hand, the parallel polarization configuration, $(xx+yy)$ or (zz), is needed to isolate the A_1-symmetry soft modes. For an epitaxial film with coexisting c and a domains, one has to employ two distinctive scattering geometries to obtain polarized Raman spectra. As illustrated in Fig. 2, the direction of the incident and scattered laser light in a backscattering geometry should be parallel to the substrate plane (i.e., in-plane direction) for the c domain. Contrary to this, a normal backscattering is needed to obtain both E(TO) and A_1(TO) modes for the a-axis oriented domain. As summarized in Fig. 2, the propagation direction of the relevant phonon wave vector **k** is thus perpendicular to the unique c axis, irrespective of the domain configuration.

Figure 3 presents polarized Raman spectra of both E(TO) and A_1(TO) modes for the c domain, as obtained

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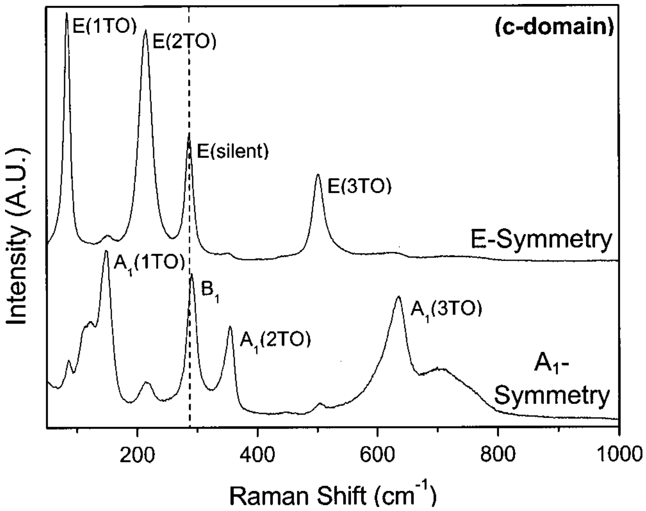

FIG. 3. Polarized Raman spectra of the E and A_1-symmetry modes for the c axis oriented domain in $PbTiO_3$ thin film.

using the cross and parallel configurations, respectively (Fig. 2). The result shows that the polarized spectra closely follow the Raman selection rule for the zone-center phonon ($\mathbf{k}=0$).[11,12] As shown in Fig. 3, the $A_1(1TO)$ phonon has a subpeak structure. Considering the origin of anomalous line shape of the $A_1(1TO)$ mode in a single-crystalline $PbTiO_3$,[13] one can attribute this observation to the anharmonicity of the $A_1(TO)$ phonon and to the existence of thermodynamically stable defects.

It is interesting to notice the appearance of a new peak at 290 cm^{-1} in the A_1-symmetry spectrum of Fig. 3. According to the factor group analysis of $PbTiO_3$-type simple perovskites, the conversion of the Raman inactive paraelectric T_{2u} mode into the Raman active B_1 (parallel polarization configuration) and E modes is expected upon the transition to ferroelectric C_{4v} symmetry.[11] Contrary to the theoretical prediction, this type of mode splitting has not been observed until now, and among these two only a peak with the E symmetry has appeared in the polarized spectrum ("silent" mode).[11,12] However, as shown in Fig. 3, the splitting of the degenerate silent mode into the E-symmetry mode and the B_1 mode is evident now. A careful examination of the polarized spectra indicates the mode separation of 5 cm^{-1} for the c-axis oriented domain, suggesting the important role of the in-plane film stress in the shift of the mode frequency (stress-induced mode splitting).

Figure 4 compares the E-symmetry phonon spectra for three different types of $PbTiO_3$: epitaxially grown c and a domains, and single crystal. Compared with the E-mode frequencies of single-crystal $PbTiO_3$, both domains exhibit a downward shift of the mode frequencies. For example, the downward shift of the $E(2TO)$ phonon with respect to the frequency of single crystal is 6.3 cm^{-1} for the c domain and 11.7 cm^{-1} for the a domain, clearly indicating the presence of a strong tensile film stress for both types of domains. The in-plane tensile stress can be quantitatively correlated with the degree of "softening" in the mode frequency using the method outlined by Sun *et al.*[14] It is +2.11 GPa for the c domain and is +2.45 GPa for the a domain. The estimated large tensile stress seems to be closely related to the reduced tetragonality[16] in the a or c domain, as discussed previously.

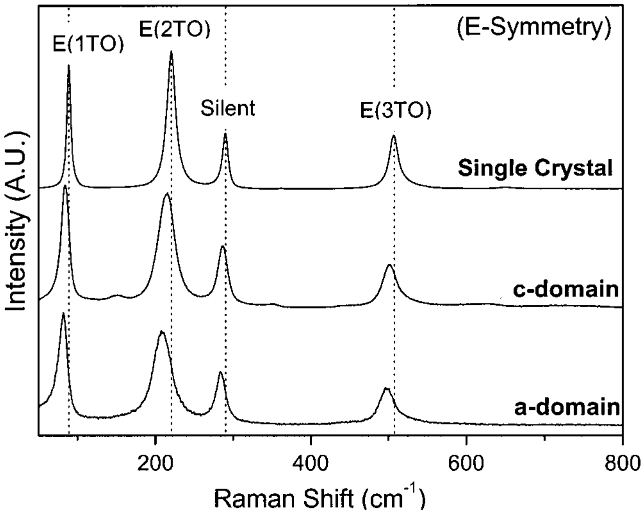

FIG. 4. Polarized Raman spectra of the E-symmetry modes for three different types of configurations: a domain, c domain, and single-crystal $PbTiO_3$.

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