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Author(s)	Osada, Minoru, Nishida, Ken, Wada, Syunshuke, Okamoto, Shoji, Ueno, Risako, Funakubo, Hiroshi, Katoda, Takashi
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KOCHI UNIVERSITY OF TECHNOLOGY

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Domain distributions in tetragonal Pb(Zr,Ti)O$_3$ thin films probed by polarized Raman spectroscopy

Minoru Osada[a)]
Advanced Materials Laboratory, National Institute for Materials Science (NIMS), Tsukuba, Ibaraki 305-0044, Japan

Ken Nishida and Syunshuke Wada
Department of Electronic and Photonic Systems Engineering, Kochi University of Technology, Tosayamada-cho, Kochi 782-8502, Japan

Shoji Okamoto, Risako Ueno, and Hiroshi Funakubo
Department of Innovative and Engineered Materials, Interdisciplinary Graduate School of Science and Engineering, Tokyo Institute of Technology, Yokohama 226-8502, Japan

Takashi Katoda
Department of Electronic and Photonic Systems Engineering, Kochi University of Technology, Tosayamada-cho, Kochi 782-8502, Japan

We have investigated polarized Raman spectra of (001)/(100)-oriented tetragonal epitaxial Pb(Zr$_x$Ti$_{1-x}$)O$_3$ (PZT) thin films ($x = \sim 0.35$) in which the volume fraction of the polar c domain is systematically varied from 4% to 96%. From polarization analyses using high epitaxial quality films, we have successfully isolated the A_1 and B_1 phonons from the E phonons, thus offering a distinctive evaluation of the c domains. As increasing c-domain volume, the A_1(TO) modes linearly increase in their intensity. A remarkable correlation is found between the A_1(1TO)-mode intensity and the c-domain volume for PZT films. We suggest that this correlation as well as the A_1(1TO)-mode intensity provide a simple and useful probe for characterization of c-domain volume and ferroelectric properties in PZT-based devices. © *2005 American Institute of Physics.* [DOI: 10.1063/1.2139844]

Pb(Zr$_x$Ti$_{1-x}$)O$_3$ (PZT) systems have been extensively studied because of their overwhelming importance of ferroelectric science and technology. Due to their excellent polarization and piezoelectric properties, PZT thin films have generated a large research effort in recent years, and various applications such as nonvolatile memories, microactuators, etc., have been tested.[1,2] In the course of actual devices, it is highly important to evaluate and control the distribution of crystallographic orientation of samples in order to develop films that provide high polarizability. Such a problem is clearly exposed in memory applications. In the PZT case, since the major polarization component lies along the c axis, it is of particular importance to identify the c-domain component, which predominately contributes to polarization properties of this material. Also, considering the recent advancement in integration technology, it is desirable to employ quick, nondestructive methods that provide *in situ* measurements with submicron resolution.

Raman spectroscopy is a powerful and versatile technique for elucidating such a domain issue by monitoring Raman selection rule. It is also a nondestructive method without any contact to samples, and therefore ideal for the study of films already incorporated into devices. However, although Raman scattering has been extensively used in studies of physical properties and characterizations of PZT ceramics[3–5] and thin films,[6,7] only little has been addressed to the domain studies in PZT. We are only aware of one polar-

ized Raman study of epitaxial PZT film ($x = 0.4$),[8] which has demonstrated Raman selection rules in c and a domains. In view of the well-known difficulty in preparation of PZT single crystal, it is highly desirable to investigate polarized Raman spectra of a series of epitaxial PZT thin films with various c-domain volumes and to use these data as a hypothetical model system for PZT single crystal.

In this letter, we report on polarized Raman studies of a series of epitaxial PZT thin films with the volume fraction of the c-domain volume from 4% to 96%. By employing complete polarization analyses of A_1- and E-symmetry components, we found a remarkable correlation between the A_1(1TO)-mode intensity and the c-domain volume, thus offering a new experimental input for characterization of domain distribution in PZT.

The (001)/(100)-oriented epitaxial PZT thin films were grown on MgO(100) substrate by pulsed metalorganic chemical vapor deposition at substrate temperatures of 465–540 °C.[9–11] The film thickness was changed from 150 nm to 4.7 μm by controlling the deposition time. The compositions of PZT were $x = 0.35 \pm 0.02$, which correspond to the Ti-rich tetragonal region of the morphotropic phase boundary. The x-ray reciprocal space mapping (PANalytical X'Pert MRD) was measured for estimating the volume fraction of the polar-oriented c domain in the films having the mixture orientation of (00ℓ) (c domain) and ($h00$) (a domain), followed by the same procedure as in Ref. 9. Here, we collected the reciprocal mappings of the in-plane and out-of-plane lattice parameters, and the relative volume fraction of the c domain, $V(00\ell)/[V(h00) + V(00\ell)]$, is estimated using

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[a)]Author to whom the correspondence should be addressed; electronic mail: osada.minoru@nims.go.jp
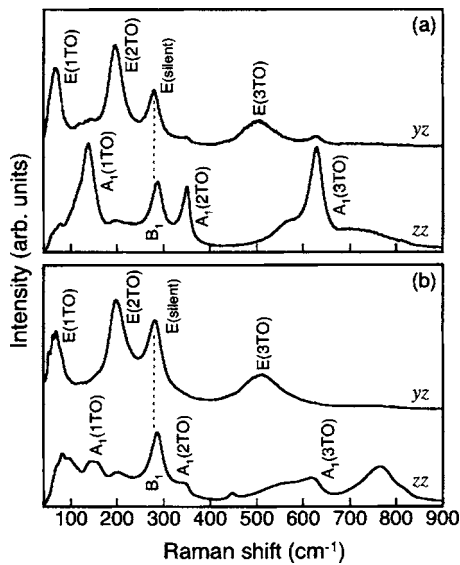
FIG. 1. Polarized Raman spectra of the E-symmetry (yz) and A_1-symmetry (zz) modes for PZT films with c-domain volume ratio of 96% (a) and 4% (b).
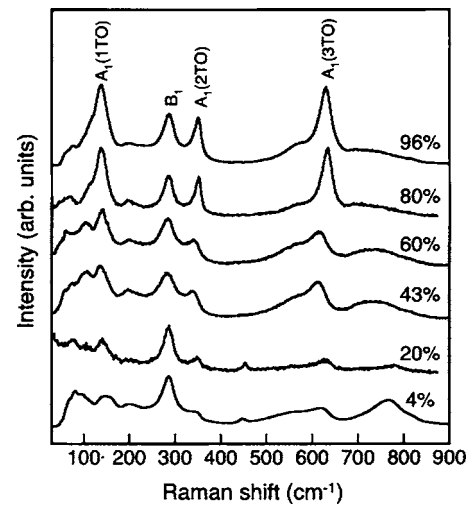

FIG. 2. The zz-polarized Raman spectra of PZT films with various volume fractions of c-domain from 4% to 96%. The A_1(TO) modes linearly increase in their intensity relative to the B_1 modes. The B_1-mode intensity is nearly the same irrespective of different c-domain volume, and thus can be used as an internal standard for evaluation of the A_1(TO)-mode intensity.

the integrated intensities of the PZT204/402 spots. In this letter, the main results were obtained from PZT thin films with the c-domain volume being 4%, 20%, 43%, 60%, 80%, and 96%. Complementary data were obtained from PZT with the c-domain volume of 10% and 90%. Details of preparation and characterization are described elsewhere.[9–12]

Raman spectra were measured with the 514.5 nm line from an Ar$^+$ laser ($\sim$1 mW) by focusing on a $1-2$-μm-diam spot on the sample surface. The backward scattering light was collected and dispersed by a subtractive triple spectrometer (Jobin-Yvon T64000) equipped with a liquid-nitrogen-cooled charge-couple-device detector. The frequency resolution was set to $\sim$1 cm^{-1} and the measurement time was typically around 1 min per spectrum.

At the starting point of domain studies, we tried to identify Raman selection rule in PZT films. Figure 1(a) compares polarized Raman spectra of PZT film with the c-domain volume of 96%. Since tetragonal PZT belongs to C_{4v} ($P4mm$) point group, the E-symmetry modes can be observed in the cross polarization configuration [(yz) or (xz)]. Under the parallel polarization configuration [(zz) or ($xx+yy$)], on the other hand, we can isolate the A_1-symmetry modes. As is shown in Fig. 1(a), the polarized spectra clearly isolate the A_1(TO)-symmetry modes from E(TO) modes, and thus closely follow Raman selection rules for zone-center phonon. Most importantly, the A_1(1TO) soft mode is clearly separated from the lowest-frequency E(TO) soft mode. We also note the appearance of the B_1 mode in the (zz) parallel configuration. According to group theoretical analysis, the Raman-inactive paraelectric T_{2u} mode transforms into the Raman-active B_1 and E modes upon the transition to ferroelectric $4mm$ symmetry.[13,14] Moreover, since the B_1 mode is connected to the *out-of-phase* vibration of TiO$_6$ octahedra along the c axis,[13] the B_1 mode should appear in the parallel polarization configuration [(zz) or ($xx+yy$)]. Contrary to theoretical prediction, this type of mode splitting is generally weak in PZT films, and only E mode has appeared in the polarized spectra. However, recent results of c-axis oriented eptaixial PT films clearly resolved the B_1 and E mode: the B_1 mode at 290 cm^{-1} appears in the (zz) parallel configuration

versus E(TO) at 285 cm^{-1} in the (yz) cross configuration.[15] In our case, the situation indeed resembles those in eptaixial PT films, and the Raman spectra in Fig. 1 reflect all Raman-active modes based on ferroelectric $4mm$ symmetry. The observed polarization dependencies, including the B_1+E(TO) splitting, indicate high epitaxial quality of our PZT films.

These polarization dependencies are not unique for the c-domain dominant film (96%), but common to other PZT with different c-domain volume. Figure 1(b) shows polarized Raman spectra of the a-domain dominant PZT film with the c-domain volume of 4%. Comparing between (zy) and (zz) spectra, the A_1- and B_1-symmetry modes are clearly distinct from the E modes. The identical polarization dependence was found in all investigated samples with different c-domain volume of 20%, 43%, 60%, and 80% (not shown here),[11] and thus a common feature to tetragonal PZT.

Here we notice that the A_1(TO) modes are highly sensitive to the c-domain volume. As is shown in Fig. 1, the general feature of the E-symmetry spectra is almost identical, irrespective of different c-domain volumes. On the contrary, the A_1-symmetry modes (1TO, 2TO, and 3TO) have much reduced intensity in PZT film with 4% c-domain volume. This effect is most probably a direct manifestation of domain distribution. Since these A_1-symmetry modes have c-polarized character linked to the spontaneous polarization,[13] the decreased c-domain volume leads to reduced A_1 phonon polarizabilities and thereby A_1 phonon intensities.

More quantitative characterization is made using a series of PZT films with various c-domain volumes. Figure 2 compares zz-polarized Raman spectra of PZT films with the volume fraction of the c-domain volume from 4% to 96%. When comparing the spectra from bottom (4%) to top (96%), the A_1(TO) modes linearly increase in their intensity, which is consistent with an increased c-domain volume. This behavior shares with all A_1-symmetry modes (1TO, 2TO, and 3TO), whereas the intensity of the B_1 mode is almost identical. We note that this intensity change in the A_1 modes is not due to the variation in the macroscopic optical properties or thickness in different films, because these cases may
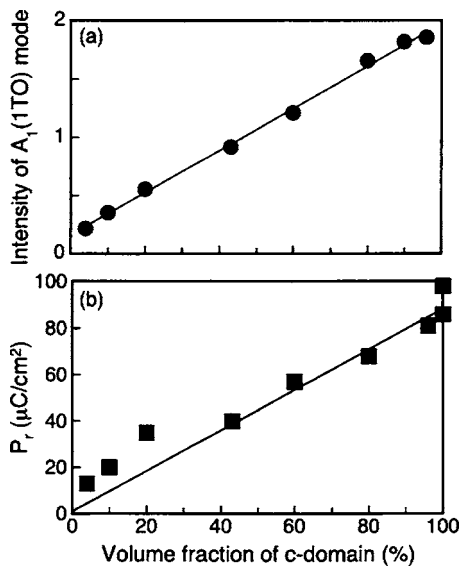
FIG. 3. (a) A_1(1TO)-mode intensity vs the c-domain volume for a series of tetragonal PZT films with the c-domain volume, ranging from 4% to 96%. (b) Variation of P_r value as a function of the c-domain volume [Refs. 10 and 11].

FIG. 4. Relation between P_r and A_1(1TO)-mode intensity.

change the overall Raman scattering intensity. Thus, these results clearly indicate that the intensity of the A_1(TO) modes is directly correlated with the change in the c-domain volume.

Figure 3(a) shows the A_1(1TO)-mode intensity plotted against the c-domain volume for PZT films. Here we plotted the variation of the A_1(1TO) mode, since this mode consists of the displacements of the B-site ions (Ti, Zr) relative to A-site ions (Pb), which is closely linked to spontaneous polarization of PZT material.[13] Also, the polarized character of this mode allows one to selectively monitor the changes in A_1(TO) mode. It is obvious that there is a correlation between the A_1(1TO)-mode intensity and c-domain volume. As is evident from Fig. 3(a), the intensity of this mode is proportional to the c-domain volume. We therefore suggest that this correlation as well as the observation of the A_1(1TO) mode can be used as a simple and convenient means to evaluate c-domain volumes in PZT films.

We should now emphasize that the experimental input of Fig. 3(a) is quite important from the viewpoints of practical applications, because the c-domain volume has strong impacts on ferroelectric properties. In Fig. 3(b), we have replotted the reported variation in polarization properties against the c-domain volume for the same films used in this study.[10,11] As with the A_1(1TO)-mode intensity [Fig. 3(a)], the remanent polarization value (P_r) also shows a similar linear increase with the c-domain volume in the c-domain dominant region. We note that the P_r value shows some anomalous behavior in the a-domain dominant region, which indicates a possible contribution of a-to-c domain switching to polarization properties in this region.[11] Thus, a full correlation between Figs. 3(a) and 3(b) in the whole region awaits further studies in the a-domain dominant region. Neverthe-
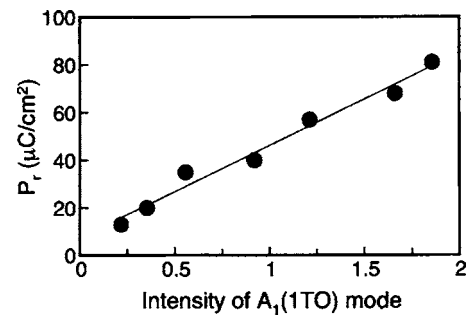
less, since the c-domain volume has a major contribution to polarization properties, the A_1(1TO)-mode intensity [Fig. 3(a)] should provide a useful probe for ferroelectric properties in PZT. In this context, we plotted the relation between P_r and A_1(1TO)-mode intensity in Fig. 4. Clearly, the P_r value can be rescaled with the A_1(1TO)-mode intensity, which again demonstrates the importance of Fig. 3(a) for useful guidelines of designing properties in practical devices.

In summary, we have utilized polarized Raman spectroscopy for characterization of tetragonal epitaxial PZT thin films with various c-domain volumes. From polarized spectra, we found a remarkable correlation between the A_1(1TO)-mode intensity and the c-domain volume, thus offering a simple probe of domain distributions in PZT films. Together with the nondestructive characteristics and high-spatial sensitivity of Raman spectroscopy, our results clearly indicate the feasibility of Raman spectroscopy in addressing some fundamental issues on the relation between domain dynamics and ferroelectric properties in PZT, as well as constitute a quick, nondestructive method for characterization in the practical devices.

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