Investigation of PbTiO₃ thin films with reduced and re-oxidized treatment using Raman spectroscopy

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Investigations of the lattice dynamics of defects, such as oxygen vacancies, are important to understand the properties of PbTiO₃ and related materials. Herein polarized Raman spectra of epitaxial PbTiO₃ thin films with reduced and re-oxidized treatment were investigated. The oxygen-reduced spectrum displayed an additional mode related to oxygen vacancies, whereas the re-oxidized spectrum was the same as the initial one. The oxygen vacancy content increases as the intensity of additional mode increases, suggesting that Raman spectroscopy can be used to characterize the oxygen stoichiometry.

Raman spectroscopy is a versatile and useful technique with a high sensitivity for evaluating crystal structures. Herein we investigate the Raman spectra of PbTiO₃ thin films with reduced and re-oxidized treatment. The additional mode is related to the oxygen vacancies in oxygen reduced PbTiO₃ thin films when the wavelength of excitation laser is adjusted to a resonant condition related to oxygen vacancies. First-principles calculations of the phonon mode related to oxygen vacancies support the assignment of the additional mode.

Key-words: Raman spectroscopy, PbTiO₃ thin film, Oxygen vacancy, Additional mode, First-principles calculation, Reduced treatment, Re-oxidized treatment

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1. Introduction

Due to their excellent dielectric, pyroelectric, piezoelectric, and ferroelectric properties, Pb-based ferroelectric materials, such as PbTiO₃ and Pb(Zr,Ti)O₃ with perovskite-type structures, are one of the most successful materials for electric device applications (e.g., infrared radiation sensors, microactuators, and nonvolatile memories). However, because Pb and oxygen ions have high vapor pressures, the stoichiometry in A₂B₄+8O₉, Pb₁₋ₓTiO₂₋ₓ₋ₓ (Pb or oxygen vacancy) deviates during crystal growth or device processing. These vacancies affect the ferroelectric properties, such as degradation of the insulation property or pinning of spontaneous polarization.

To reveal the changes in the ferroelectric properties due to these vacancies, it is important to understand the lattice dynamics in the crystal because the optical phonon frequency is directly linked to the origin of the dielectric and ferroelectric properties. We reported that the phonon frequency of the B₁₁-mode is only related to the oxygen ion lattice vibration and changes upon introducing an oxygen vacancy in PbTiO₃ thin films. In case of a reduced SrTiO₃ single crystal, Tence et al. observed an additional phonon mode related to oxygen vacancies and the appearance of the symmetry forbidden phonon mode in Raman spectra. Kourouklis et al. demonstrated that in oxygen-deficient YBa₂Cu₃O₆₋ₓ samples, the A₁g axial stretching mode undergoes both softening and broadening as the oxygen deficiency increases, suggesting that Raman spectroscopy can be used to characterize the oxygen stoichiometry.

2. Experimental procedure

PbTiO₃ thin films were grown on (100) MgO substrates by metal organic chemical vapor phase deposition (MOCVD). Details of the growth conditions are described elsewhere. The film thickness was 300–400 nm. High resolution X-ray diffraction (XRD) measurement (PANalytical, X’Pert MRD) indicated that the PbTiO₃ thin films are epitaxially grown with a (001)/(100) orientation. The PbTiO₃ thin films were heat-treated at 600–800°C for 2 h under a hydrogen atmosphere in order to generate various numbers of oxygen vacancies in PbTiO₃ thin films. X-ray
fluorescence (XRF) spectroscopy (Philips, PW2404) determined the Pb/Ti ratio in the films. The non-Rutherford elastic resonance spectroscopy (NRERS) method using a Rutherford backscattering (RBS) equipment (NHV Co., NH-1700) was used to estimate the number of oxygen vacancies in the PbTiO₃ thin films (actual oxygen ion content in the PbTiO₃ thin film). NRERS utilized a nuclear reaction $^{16}\text{O}(\alpha,\alpha)\text{O}$ that occurs between an oxygen nucleus and a helium ion with a certain incident energy because this method has a relatively high-sensitivity to oxygen ions compared to the standard RBS method. Raman spectra were measured with the 520.8 nm line from an Ar + Kr mixed gas ion laser (~5 mW) for the resonant condition to oxygen vacancies when the laser probe beam was focused at a 1-µm-diameter spot on the sample surface. The backward scattering light was collected and dispersed by a spectrometer (Jobin Yvon, T64000 or Renishaw, inVia Reflex).

First-principles calculations were performed using the projector-augmented wave (PAW) method, as implemented in the VASP code. The exchange–correlation functional was given by the local density approximation (LDA), as presented by Ceperly and Alder parameterized by Perdew and Zunger. In the PAW potential, 5d 6s 6p for Pb, 3s 3p 3d 4s for Ti, and 2s 2p for O were explicitly treated as valence electrons. The plane wave cut-off was set to 600 eV. The k-points mesh of Brillouin zone sampling in primitive cells, which was based on the Monkhorst-Pack scheme, was $6 \times 6 \times 6$ for $P\bar{m}m$, and $P\bar{4}mm$. Under these conditions, an energy convergence less than 1 meV per PbTiO₃ was achieved. Lattice constants and internal coordinates were fully optimized until the residual Hellmann–Feynman (HF) forces were less than $1.0 \times 10^{-3}$ eV/Å, which forced the space groups of the corresponding phase and the experiment to agree. Dynamical properties were computed by interatomic force constants in the real space. The whole set of force constants was obtained from the HF forces generated by a nonequivalent atomic displacements in a supercell for a given crystal structure. The dimensions of the supercells were $3 \times 3 \times 3$ for $P\bar{4}mm$ (135 atoms). To calculate the HF forces, the k-point mesh in a supercell was selected to be $3 \times 3 \times 3$. To hold the translation invariance, phonon frequencies were calculated by solving an eigenvalue problem for the dynamical matrix that satisfied the sum rules for lattice constants. All lattice dynamics calculations were performed by employing Phonon code. In an ionic crystal, the dipole–dipole interaction affects the interatomic force constants and causes longitudinal optical/transverse optical (LO/TO) splitting at the wave vector of $k \approx 0$, namely near Γ-point. However, the present study did not consider the influence of the dipole on the interatomic force constants because we are interested in evaluating the soft-mode phonon. Inclusion of LO/TO splitting only slightly changes the soft-mode phonon because the dipole–dipole interaction is limited on the LO modes with a wave vector $k \approx 0$, leaving the frequencies of TO modes unchanged.

3. Results and discussion

PbTiO₃ belongs to the space group $C_{4v}$, which yields $3A_1 + B_1 + 4E$ phonon modes. Figure 1(a) shows that the Raman spectrum of the as-grown (before heat treatment) epitaxial thin film is a typical tetragonal PbTiO₃ without a second phase and all expected phonon modes. Based on group theory, the $E$-symmetry modes can be observed in the cross $xy$- or $yz$-polarization configuration, whereas the parallel $xx$- or $yy$-polarization configuration yields the $A_1$-symmetry and $B_1$-phonon modes.

Polarized Raman analysis was performed to identify the phonon modes of the Raman spectra. Figures 1(b) and 1(c) show the polarized Raman spectra of a PbTiO₃ thin film. The $A_1$(TO) symmetry and $B_1$-phonon modes are clearly isolated from the $E$(TO) phonon modes, indicating a high-quality epitaxial PbTiO₃ thin film. Most importantly, the $B_1$-phonon mode around 290 cm⁻¹ is separated from the $E$ mode. The $B_1$-phonon mode consists of only oxygen ions, which are nearly coplanar with the titanium ions and move in opposite directions. Therefore, the $B_1$-phonon mode can be selectively used to obtain the information about oxygen vacancies in PbTiO₃ films.

Figure 2 shows the $yy$-polarized Raman spectra of PbTiO₃ thin films, which were before heat treatment and heat-treated for 2 h at 600–800°C in a hydrogen atmosphere. The novel phonon mode occurs at the lower wavelength of $B_1$-mode after heat treatment. The intensity of this novel additional mode increases as the heat treatment temperature increases. (The $B_1$-phonon mode and the
additional phonon mode are shown in Fig. 2 as Lorentz function shapes to guide the eye.) This additional mode is considered to be the oxygen vacancy related mode.

To confirm the origin of the additional mode, we performed first-principles calculations. An oxygen vacancy changes the local potential for the configuration of the neighboring atoms in the PbTiO\textsubscript{3} lattice, leading to a different local phonon that is an additional mode compare to a perfect PbTiO\textsubscript{3} crystal. This additional mode was found that the phonon dispersion was very small.

The open diamond and closed square in Fig. 2 denote the calculated phonon frequencies of PbTiO\textsubscript{3} with an introduced oxygen vacancy and stoichiometric PbTiO\textsubscript{3}, respectively. The additional mode occurs at a lower frequency than the $B_1$-phonon mode when an oxygen vacancy is introduced into PbTiO\textsubscript{3}. Therefore, the novel additional peak in the Raman spectrum is attributed to be local vibration mode related to the oxygen vacancy.

**Figure 3(a)** plots the Raman peak intensity of the $B_1$-phonon mode and the additional phonon mode related to oxygen vacancy as functions of the heat treatment temperature. Figure 3(b) shows the oxygen ion content of PbTiO\textsubscript{3} estimated by NRERS as a function of the heat treatment temperature in a hydrogen atmosphere.

**4. Summary**

In summary, Raman spectroscopy was used to evaluate the oxygen vacancies in PbTiO\textsubscript{3} thin films. As oxygen vacancies are generated, the additional mode, which is related to these vacancies, appears. The intensity of the additional mode increases while that of the $B_1$-phonon mode drastically decreases. The oxygen ion content decreases as the heat treatment temperature increases up to 700°C, while the intensity of the additional mode increases slightly, but that of the $B_1$ mode slightly decreases. However, when the heat treatment temperature exceeds 750°C, the intensity of the additional mode markedly increases, while that of the $B_1$ mode drastically decreases. The results suggest that the oxygen ions are sparse until 700°C but are abundant in films above 750°C.

An optical photograph of PbTiO\textsubscript{3} thin films, which are (a) before heat treatment, (b) heat-treated in a reduced atmosphere, and subsequently (c) heat-treated in air for 2 h (re-oxidized) is shown in **Fig. 4**. The PbTiO\textsubscript{3} thin film before heat treatment is transparent. On the other hand, the one of heat-treated in a reduced atmosphere is a black translucent. The PbTiO\textsubscript{3} thin film return to be transparent after re-oxidized.

**Figure 5** shows the Raman spectra of PbTiO\textsubscript{3} thin films before heat treatment, heat-treated in a reduced atmosphere, and re-oxidized as shown in Fig. 4. The re-oxidized and initial PbTiO\textsubscript{3} films have similar Raman spectral features. Because the oxygen vacancies in the PbTiO\textsubscript{3} thin film are retorted by re-oxidizing, the additional mode, which is related to oxygen vacancies, decreases.

In summary, Raman spectroscopy was used to evaluate the oxygen vacancies in PbTiO\textsubscript{3} thin films. As oxygen vacancies are generated, the additional mode, which is related to these vacancies, appears. The intensity of the additional mode increases while that of the $B_1$-phonon mode decreases as the number of oxygens in the PbTiO\textsubscript{3} thin film decreases, even when the amount of oxygen vacancies is small. However, re-oxidizing causes the additional mode to decrease and return to the initial level. In addition to being a versatile, highly sensitive tool to evaluate crystal structures, the findings herein clearly demonstrate that Raman spectroscopy provides useful information about the lattice dynamics related to oxygen vacancies.
References