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Raman-spectroscopy study of $PbTiO_3$ thin films grown on Si substrates by metalorganic chemical vapor deposition

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Abstract. Raman spectra have been investigated in $PbTiO_3$ thin films grown on Si by metalorganic chemical vapor deposition. A large grazing-angle scattering technique was taken to measure the temperature dependence of Raman spectra below room temperature. All Raman modes in the thin films are assigned and compared with those in the bulk single crystal, a new A_1(TO) soft mode at 104 cm^{-1} was recorded which satisfies the Curie-Weiss relation $\omega^2 = A(T_c - T)$. Intensities of the A_1(1TO) and E(1TO) modes were anomalously strengthened with increasing temperature. Raman modes for the thin films exhibit remarkable frequency downshift and upshift which is related to the effect of internal stress.

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In recent years, ferroelectric thin films have attracted great attention due to their potential applications in microelectronic and optoelectronic devices [1]. There have been several techniques of thin-film growth including sputtering, sol-gel and MetalOrganic Chemical Vapour Deposition (MOCVD). Among them, MOCVD shows advantages over the others and can be used to prepare device-quality ferroelectric thin films including $PbTiO_3$, $Pb(Zr_xTi_{1-x})O_3$, and $BaTiO_3$ [2–4]. Perovskite lead titanate $PbTiO_3$ is an important ferroelectric material with remarkable physical properties such as a large spontaneous polarization and a high Curie temperature. Studies of $PbTiO_3$ are of considerable interest from not only practical applications but also fundamental subjects, such as the origin of ferroelectricity and the mechanism of phase transition [5].

Raman spectroscopy had been employed in studies of the soft modes and phase transition in bulk $PbTiO_3$, where Raman selection rules were rigorously obeyed in both the ferroelectric and paraelectric states [6, 7]. Recently, Raman scattering was also used to investigate the microstructures and phase transition in ferroelectric thin films. Taguchi et al. studied the Raman spectra of $PbTiO_3$ thin films prepared by rf sputtering and thermal treatment [8], where the frequency downshift of Raman modes was attributed to the pressure effect. Scott et al. studied KNO_3 thin films using Raman spectroscopy and found the effect of surface electric field on Raman modes of the thin films [9]. In the case of thin films, theoretical studies suggested that there may be some new phenomena such as the critical-thickness effect of the polar state and the change of the order of phase transitions [10]. In $PbTiO_3$, there has also been a controversy on the phase-transition behaviour at low temperatures. Kobayashi et al. [11] reported an additional phase transition at – 90 °C by X-ray and optical studies although it has long been believed to undergo only a phase transition at 490 °C. In this paper, we have successfully prepared highly (001)-oriented $PbTiO_3$ thin films on Si (001) substrates by MOCVD. We have investigated Raman spectra from the thin films and discuss the causes leading to the frequency shift of the Raman modes. We have also studied the temperature dependence of the Raman spectra and examined the behaviour of the $PbTiO_3$ thin films at low temperature.

The low-pressure MOCVD technique was described in detail elsewhere [2]. We have chosen the purified Titanium IsoPropoxide (TIP) and TetraEthylLead (TEL) as the metalorganic precursors; N_2 as the carrier gas and oxygen gas as the oxidant. The temperatures of the precursors TIP and TEL were 65 and 35 °C. The substrate temperature was kept at 650 °C. The flow rates of TIP, TEL and O_2 are 200, 250, and 250 sccm, respectively, with a total pressure of the reactor chamber at 15 Torr.

Crystal structure of the thin films was checked by a Rigaku X-ray diffractometer with nickel-filtered Cu-K_α radiation. The results showed that the films were highly [001]-oriented with a pure $PbTiO_3$ single phase. Raman-spectroscopy measurements were performed using a SPEX 1403 Raman spectrometer. The 488 nm line of an Ar^+ laser with 100 mW output power was used. The widths of both entrance and exit slits were set at 150 μm. A large grazing-angle scattering technique was taken to collect the weak Raman signals from the thin films. The geometrical arrangement is shown in Fig. 1, where the incident angle ϕ was about 70° to the normal of the film

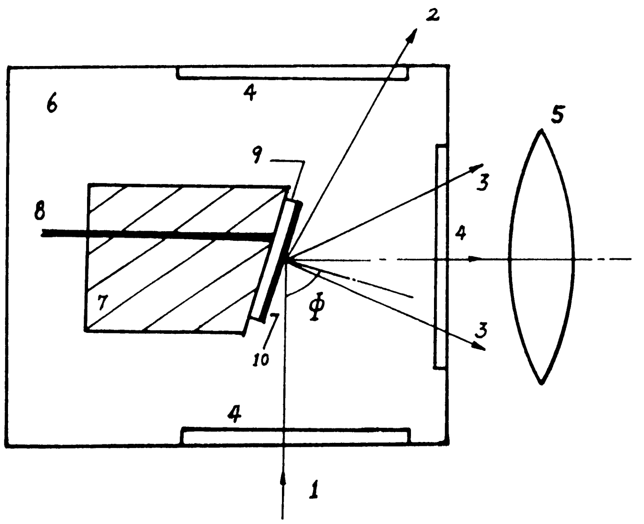

Fig. 1. Schematic diagram of the near-right-angle Raman-scattering geometry in $PbTiO_3$ thin films and the Si substrate system (*1* incident light; *2* reflected light; *3* scattered light; *4* quartz window; *5* lens; *6* cryostat; *7* copper rod; *8* thermo couple; *9* Si substrate; *10* $PbTiO_3$ thin film)

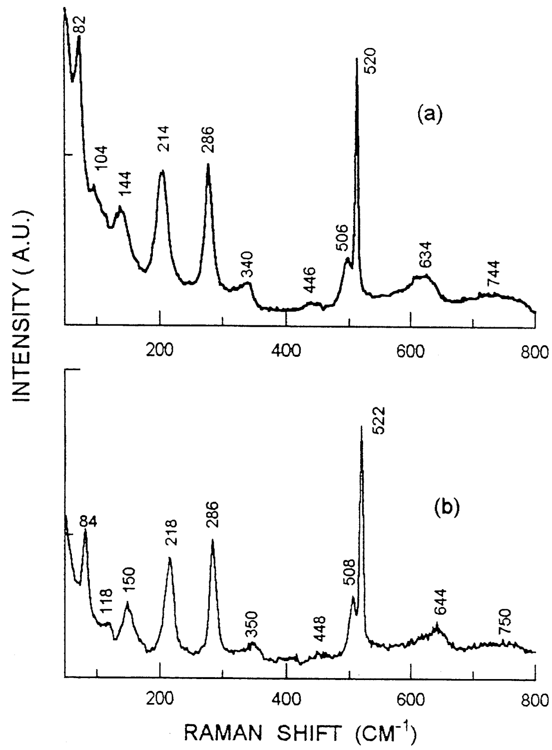

Fig. 3a,b. Raman spectra of the $PbTiO_3$ thin film on the Si substrate; (**a**) at 300 K; (**b**) at 73 K. The 488 nm line of an Ar^+ laser with 200 mW output power was used

plane; the polarisation of the incident and the scattering light are perpendicular to their respective propagating directions and lie in the plane of the paper. The samples were mounted on the wedge-shaped end of the copper rod which was placed in a liquid-nitrogen cryostat so that the sample temperature could be precisely controlled via a programming heater. Both the room-temperature and low-temperature Raman-scattering measurements were performed in a vacuum cell in order to block air spectra.

Figure 2 shows the X-ray diffraction pattern of the MOCVD-grown $PbTiO_3$ thin films. It exhibits that the $PbTiO_3$ grown on the Si(100) substrate is a highly [001]-textured polycrystalline film. The *c*-axis orientation ratio α is calculated to be 0.71. Tetragonality (c/a) of the film is calculated to be 1.063, which is almost the same as that for the bulk single crystal.

Figure 3a displays the Raman spectrum of the $PbTiO_3$ thin film on Si at 300 K. The 520 cm^{-1} peak stems from the first-order vibrational mode of the Si substrate, the other peaks are from the thin film and are clearly resolved

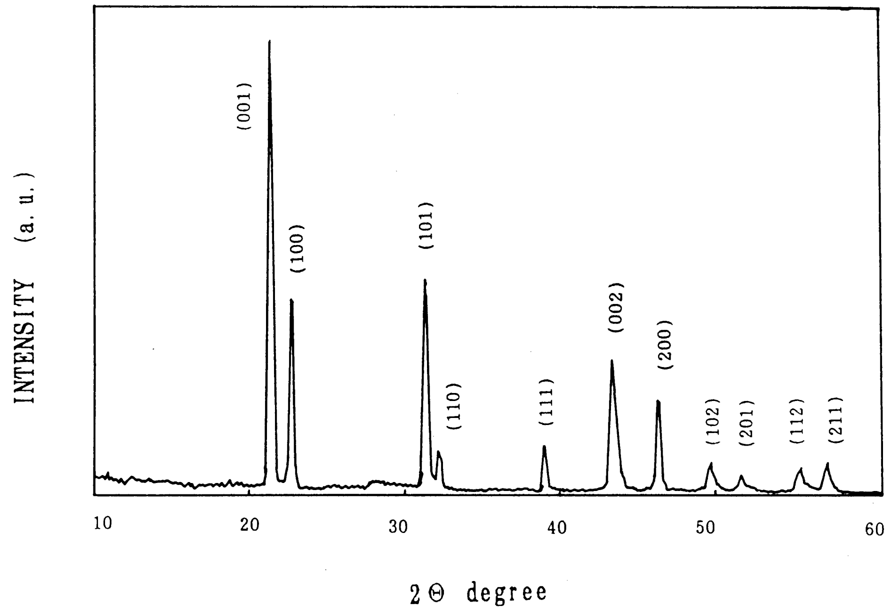

Fig. 2. X-ray diffraction pattern of the MOCVD-grown $PbTiO_3$ thin films

Table 1. Frequencies of optical phonons in $PbTiO_3$ single crystals and thin films at room temperature

Mode	Single crystal		Present work
	[6]	[7]	
E(1TO)	89	89	82
A_1(1TO)	127	148	104
E(1LO)	128	130	144
A_1(1LO)	215		
E(2TO)	221	220	214
$B_1 + E$	290	290	286
A_1(2TO)	364	362	340
E(2LO) + A_1(2LO)	445	440	446
E(3TO)	508	508	506
A_1(3TO)	651	650	634
E(3LO)	717	720	744
A_1(3LO)	797		

with quite strong intensity, which indicates that the substrate contribution is largely decreased by using the above-described scattering geometry (Fig. 1). All the phonon modes of the $PbTiO_3$ thin film are also listed in Table 1 for comparison with the Raman data of the single crystal [6, 7]. The 144 cm^{-1} mode was believed to be a second-order mode [6]. According to our measurements, the intensity attenuation of the mode exhibits a $n + 1$, not $(n + 1)^2$ temperature dependence, where

$$n = 1/[\exp(\hbar\omega/kT) - 1] \tag{1}$$

is the Boltzmann distribution factor. The result indicates that it is really a first-order mode rather than a second-order mode. It is in good agreement with that obtained by Fontana et al. [7]. The mode at 286 cm^{-1} assigned as $B_1 + E$ is a silent mode. The 634 and 734 cm^{-1} modes are two broader lines. Their linewidths are sensitive to microstructural changes, and their broadening is expected and consistent with the highly textured polycrystalline thin films with some randomly oriented grains.

From Table 1, it is found that most of the phonon frequencies for the thin film are quite lower than those for the single crystal, which is similar to that obtained by Taguchi et al. [8]. This phenomenon of frequency downshift can be attributed to compressive stress in the thin films. In $PbTiO_3$ single crystals, it was reported that phonon modes shifted to low frequency with increasing hydrostatic pressure, and the relation of the phonon frequency vs pressure could be described as

$$\omega^2 = \omega_0^2(1 - P/P_1), \tag{2}$$

where ω_0 is the frequency of the phonon mode under zero pressure and P_1 is the pressure under which the phonon frequency becomes zero [12]. The effect of compressive stress on the thin film is analagous to that of hydrostatic pressure on the single crystal. In addition to frequency downshift of most of the Raman modes, we also found upshift of E(LO) modes at 148 and 734 cm^{-1}; this is similar to the upshift of the E(LO) mode at 720 cm^{-1} in $BaTiO_3$ thin films, which was attributed to the tensile stress along the c-axis [13]. The internal stress in the thin film may be caused by different expansion coefficients between the film and substrate, or it may form when domain splitting was hindered by the adjoining grains with different orientations.

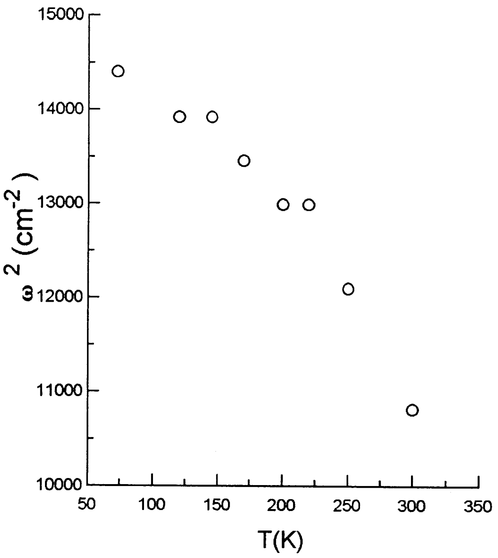

Fig. 4. Squared frequency of the A_1(1TO) phonon mode vs temperature in the $PbTiO_3$ thin film

Figure 3b shows the Raman spectrum of $PbTiO_3$ thin films taken at 73 K; all Raman features are clearly resolved. By comparing Figs. 3a and b, it is found that most of the Raman lines shift down in wave number when the sample temperature is increased from 73 to 300 K. In bulk $PbTiO_3$, the E(1TO) mode is a well-known soft mode [6, 7], while in the thin films, the A_1(1TO) mode at 104 cm^{-1} is shown to be a new soft mode. Figure 4 shows the experimental data of the squared frequency of the A_1(1TO) mode at various temperatures. It is found that this mode fits the Curie-Weiss relation [14]

$$\omega^2 = A(T_c - T) \tag{3}$$

very well, indicating a soft-mode nature. In the thin film, it is noted that the A_1(1TO) mode exhibits a more remarkable softening effect than the E(TO) mode in this temperature region. It is also found from Table 1 that the A_1(1TO) mode shows more frequency downshift under compressive stress than the E(1TO) mode.

The phonon frequencies from the thin film at various temperatures from 73 to 300 K are shown in Fig. 5. No evidence indicates that there is a phase transition at low temperature, which is consistent with the result obtained by Fontana et al. [7] in the single crystal. Theoretical studies [5] showed that in $PbTiO_3$ the lead and oxygen states hybridize leading to a large strain that stabilizes the tetragonal phase. In fact, we have found that the evidence of $-90\,^{\circ}$C phase transition found by Kobayashi et al. is the very small splitting of the a and b lattice parameters, i.e. 4.5×10^{-4} Å [11].

In the $PbTiO_3$ thin films, we have found that the intensities of the A_1(1TO) and E(1TO) soft modes increased anomalously with increasing temperature, which is clearly shown in Fig. 6. $PbTiO_3$ is a well-known pyroelectric material. In the highly [001]-oriented $PbTiO_3$

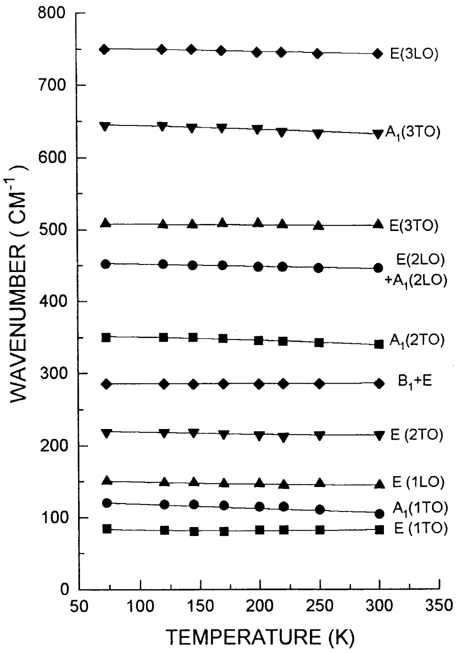

Fig. 5. Temperature dependence of all Raman modes in the PbTiO$_3$ thin films from 73 to 300 K

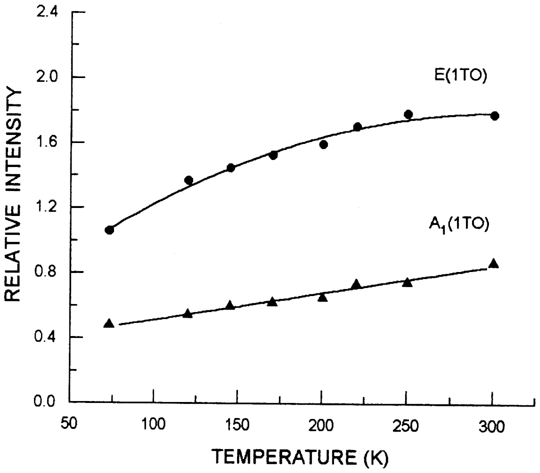

Fig. 6. Intensities of the two soft modes A_1(1TO) and E(1TO) as a function of temperature

thin film, if the charge compensation is not sufficient, the electric field will be induced on the film surface due to the decrease of the spontaneous polarization with increasing temperature. The electric field can play an important role in affecting the Raman spectra. Fluery and Worlock [15] demonstrated that the first-order Raman effect could be induced in the cubic perovskite KTaO$_3$ by application of an external electric field. Recently, Scott et al. [9] investigated experimentally the electric field on the surface of other ABO$_3$-type KNO$_3$ thin films. They found that the surface electric field can enhance the intensities of the LO phonons through the electrooptic contribution to the Raman tensor. In bulk PbTiO$_3$ single crystals, the intensities of the LO phonons are too small to be easily detected [6], while in the Raman spectra of the thin films one can observe them clearly. Enhancement of the intensities of the LO phonons clearly shows that the electric field exists in the film. In addition to the enhancement of the intensities of LO phonon modes, it is also found that in the PbTiO$_3$ thin films, the A_1(1TO) and E(1TO) modes were anomalously strengthened under the surface electric field. More studies are still needed to further investigate the effect of surface electric field on the phonon modes.

In conclusion, Raman spectra of MOCVD-grown PbTiO$_3$ thin films have been investigated by using the large-grazing-angle scattering technique from 73 to 300 K. There was no evidence of a phase transition at low temperature. A new A_1(TO) soft mode at 104 cm^{-1} was investigated and a softening effect was observed. Anomalously intensity strengthening of the A_1(1TO) and E(1TO) modes was found in the thin film. The 148 and 734 cm^{-1} E(LO) modes show a frequency upshift and the other Raman modes exhibit a downward frequency shift. We attribute them to tensile stress and compressive stress in the as-grown thin films, respectively.

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