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Phonon-mode hardening in epitaxial $PbTiO_3$ ferroelectric thin films

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Using (110) $NdGaO_3$ wafers as the lattice matched substrates, $PbTiO_3$ thin films have been epitaxially grown by metal-organic chemical vapor deposition under reduced pressure. Highly resolved Raman spectra of the thin films have been recorded by a grazing-angle scattering technique. The E(1TO) mode of the epitaxial film has been observed to have a 7-cm^{-1} upward shift compared to the bulk $PbTiO_3$ single crystal, which is different from the soft-mode behavior observed in $PbTiO_3$ ultrafine powder and polycrystalline thin films. This transverse optical mode upshift phenomenon is attributable to the residual in-plane compressive stress in the epitaxial thin film caused by the film-substrate interaction. This phonon-mode-shift phenomenon provides a method to estimate the residual stresses existing in a ferroelectric thin film. [S0163-1829(97)02518-6]

Residual stresses significantly influence thin film properties.[1] Experimental observations show that even using the same film deposition technique, stresses in the films will change with specific growth conditions.[2,3] In recent years, ferroelectric thin films have been epitaxially grown on a set of lattice mismatch substrates, and obviously the understanding of stress conditions and their effects may have a direct influence on the potential use of thin films in electronic and electro-optic devices, but the existence of spontaneous polarization and domain structures makes the stress conditions complicated in ferroelectrics thin films.

For its inherent advantages such as a large spontaneous polarization, a small dielectric constants, a small coercive field, a high Curie temperature, and chemical stability, $PbTiO_3$ film has attracted much attention. With the progress in thin film preparation techniques, $PbTiO_3$ has been epitaxially deposited on $SrTiO_3$, $LaAlO_3$, $KTaO_3$, Al_2O_3, and MgO single-crystal substrates. The microstructures of these $PbTiO_3$ thin films had been extensively investigated by x-ray diffraction, scanning electron microscopy (SEM), transmission electron microscopy (TEM), Rutherford backscattering (RBS) analysis, and so on. As an important characterization method, the use of Raman scattering to investigate the phonon modes and the phase transition process of bulk $PbTiO_3$ can be dated back to the 1970s,[4–6] and recent studies on $PbTiO_3$ ultrafine powder and polycrystalline thin films added knowledge to the effect of a reduced size in ferroelectrics by the discoveries of the phase-transition temperature downshift and transverse optical (TO) mode softening.[7–9] However, Raman investigations of epitaxial $PbTiO_3$ thin film are still rare in the literature because (1) the Raman signals of the thin film are relatively low due to the transparency of $PbTiO_3$ to the laser light and (2) the relatively strong signals of the lattice-matched substrates such as $SrTiO_3$ and $KTaO_3$ have a broad dispersion and overwhelm the $PbTiO_3$ scattering signals.[10,11]

In this paper, we report the use of (110) $NdGaO_3$ substrates for the epitaxial growth and recording of Raman spectra of $PbTiO_3$ thin films. The E(1TO) mode of the $PbTiO_3$ film is found to have an upward shift which is opposite to the observation in ultrafine powder and polycrystalline thin film. When we consider the two-dimensional in-plane compressive stresses effect on the c domains of $PbTiO_3$ caused by the lattice misfit and different thermal expansion coefficients of the film and substrate, the mode upshift can be reasonably explained; in other words, the shift of the soft mode gives us a way to estimate residual stresses in epitaxial ferroelectric thin films.

$NdGaO_3$ has an orthorhombic structure (space group $Pbnm$) with the lattice constants of $a = 5.431$ Å, b=

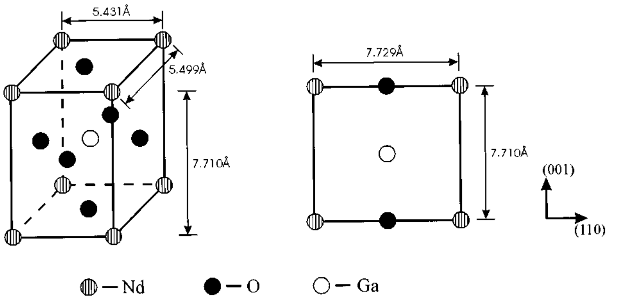

FIG. 1. Orthorhombic structure of $NdGaO_3$ (left) and the (110) surface of $NdGaO_3$.

5.499 Å, and $c = 7.710$ Å.[12] The axis lengths of the (110) plane are 7.729 Å (110) and 7.710 Å (001), respectively (Fig. 1). The lattice mismatch with the a-axis length of $PbTiO_3$ ($a_{PbTiO_3} = 3.904$ Å) is about 1%. Therefore, the small lattice mismatch [$LaAlO_3$ (2.7%), MgO(7.9%), and $KTaO_3$ (2.1%)] and a similar atomic arrangement of the (110) plane of $NdGaO_3$ will favor the epitaxial growth of (001)-oriented $PbTiO_3$ thin film.

The deposition took place in a horizontal low-pressure metal-organic chemical vapor deposition (MOCVD) apparatus.[13] Purified titanium-iso-propoxide (TIP) and tetraethyl-lead (TEL) were used as metal-organic precursors. Under typical growth conditions,[13] $PbTiO_3$ thin film was deposited with the thickness of 2200 Å.

The chemical composition of the film studied by Rutherford backscattering and electron microprobe and x-ray photoelectron spectroscopy (XPS) revealed that $PbTiO_3$ was stoichiometric without lead deficiency.

The as-grown $PbTiO_3$ thin film as featureless under optical microscopy and scanning electron microscopy. Figure 2 displays a typical atomic force microscope (AFM) surface image of the $PbTiO_3$ film taken on a Nanoscope III atomic force microscope at room temperature in air. In a studied area of 275×275 nm^2, the surface roughness was determined to be smaller than 20 Å, which was comparable to the $PbTiO_3$ thin film deposited on a (001) $SrTiO_3$ substrate.[14] Growth steps can also be observed in Fig. 2, which provide evidence of the layer-by-layer epitaxy of perovskite $PbTiO_3$ on (110) $NdGaO_3$ during the MOCVD process.

The microstructures and phases of the film were investigated by x-ray diffraction on a Rigaku D/MAX-RA powder diffractometer. Figure 3 is a broad angular range θ-2θ scan pattern of the specimen. Only (l00) and (00l) diffraction of the film and (ll0) diffraction of the substrate can be observed, no pyrochlore or polycrystalline phases indicating impurity or other orientations in the film have been detected even in the logarithmic scale. Because the relative x-ray diffraction intensity of (100) and (001) of $PbTiO_3$ powder is 2:1,[15] and when we neglect the difference of the angle-dependent factors of x-ray diffraction for powder and single crystal, the c-domain ratio α can be defined as

$$\alpha = I(001)/\{I(100)/2 + I(001)\}, \tag{1}$$

where $I(100)$ and $I(001)$ represent the intensity of (001) and (100) reflections, respectively. In our measurement, after the overlapping of the substrate signal on the (100) diffraction of $PbTiO_3$ film had been taken off, α was calculated to be 90.0% of the sample.

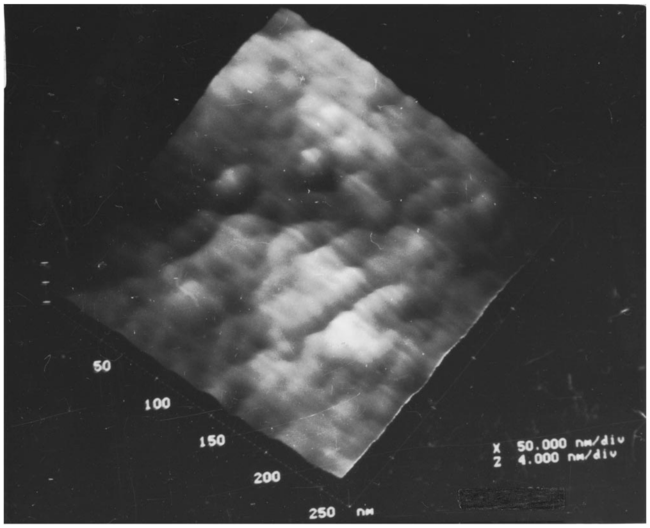

FIG. 2. AFM surface morphology of the $PbTiO_3$ thin film deposited on (110) $NdGaO_3$. The surface roughness of the film surface is smaller than 20 Å.

Also, on a Rigaku D/MAX-RA powder diffractometer, the relationship between the in-plane lattice vectors of the film and substrate was determined by a Φ scan. The (100) and (010) vectors in the c domain of $PbTiO_3$ were proved to

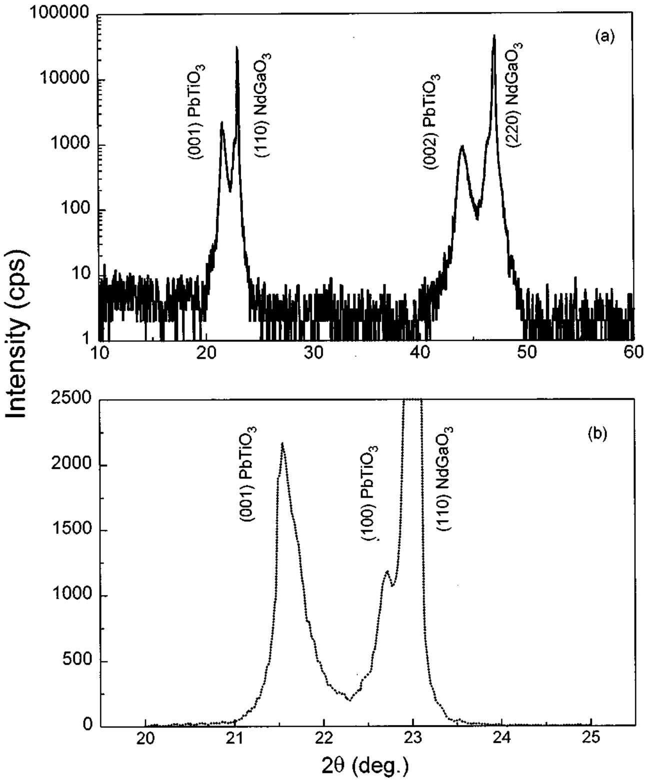

FIG. 3. XRD θ-2θ scan pattern of $PbTiO_3$ thin film deposited on the (110) $NdGaO_3$ substrate. (a) Broad θ-2θ scan pattern in a logarithmic scale. (b) Enlarged pattern shows the film is a and c domains coexisting.

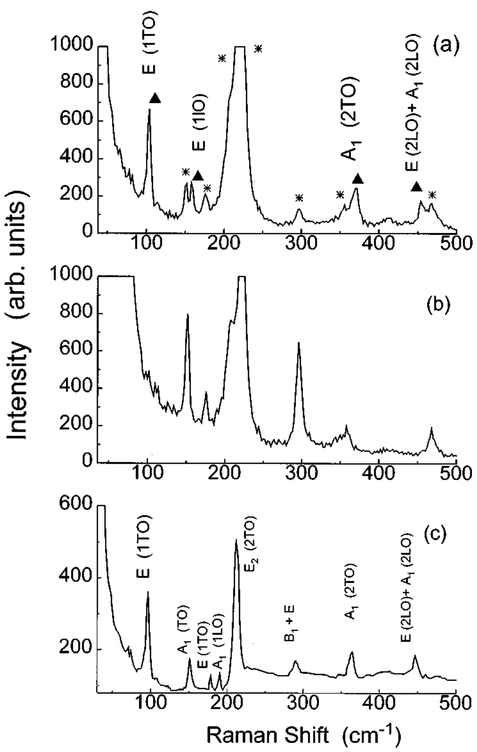

FIG. 4. Raman spectra of (a) the $PbTiO_3/NdGaO_3$ heterostructure, (b) $NdGaO_3$ substrate (the peaks marked with * correspond to the substrate signals), and (c) film signals obtained from the difference spectrum method.

be aligned exactly with the (110) and (001) vectors of the $NdGaO_3$ substrate, and so the epitaxial nature of the film was confirmed.

In the Raman scattering measurements taken on a SPEX 1403 Raman spectrometer, a grazing-angle scattering technique[16] has been employed to enhance the film signal. The 488-nm line of an Ar^+ laser was used as the excited light with an output power of 100 mmW. The resolution of the spectrum was set at 2 cm^{-1}.

The Raman spectra from the $PbTiO_3$-coated region and the masked substrate of the same specimen are illustrated in Figs. 4(a) and 4(b). Four highly resolved $PbTiO_3$ peaks can be discerned in Fig. 4(a). More precise film signals were achieved by using the Raman difference spectroscopy technique.[17] The band [in Fig. 4(c)] of the epitaxial thin film featured the previous results of bulk $PbTiO_3$ single crystal. All frequencies of the detected peaks are listed in Table I, together with the reported data of $PbTiO_3$ single-crystal[6,18] and polycrystalline films.[8,16,19]

The $E(1\text{TO})$ and $A_1(1\text{TO})$ modes of ferroelectric $PbTiO_3$ connect to the soft $T_{1u}(1\text{TO})$ mode of the paraelectric phase and are discerned as ''soft modes'' in that they tend to zero frequency as T_c or P_c is approached from below.[20] So these two modes are temperature and pressure sensitive. In our epitaxial $PbTiO_3$ thin film, these two modes were found to have upward shifts and were opposite to the observations in polycrystalline $PbTiO_3$ thin film and ultrafine particles.

Investigations on $PbTiO_3$ ultrafine particles revealed that a size effect causes a lot of property changes in ferroelectrics. This size influence becomes significant under a critical size. Studies of Chattopadhyay *et al.*[2] showed that the c/a ratio starts showing a strong dependence on the particle size below 60 nm. Raman scattering research by Ishikawa *et al.*[7] pointed out that the $E(1\text{TO})$ mode has a downward shift and the phase transition temperature decreased when the particle size is less than 50 nm. This effect of a reduced size can well explain the ferroelectricity weakening phenomenon in polycrystalline film,[20] where the grain size is around the scale of 100 nm and most of the strain should be released by the grain boundary and formation of domains. However, in the epitaxial $PbTiO_3$ film, the influence of the surface layer can be neglected because the film thickness is much larger than the size of powder particles and polycrystalline grains. It is realized that in the epitaxial thin film, the film-substrate interaction is only partly released through domain formation, and due to the difference stress relaxation mechanisms,[21] the exact stresses in the epitaxial film are hard to determine. We

TABLE I. Comparison of the frequencies of optical phonon modes in $PbTiO_3$ single-crystal and polycrystalline thin films with the epitaxial $PbTiO_3$ film grown on $NdGaO_3$ substrates in this study.

	Single crystal		Polycrystalline film			
	a	b	c	d	e	Present work
$E(1\text{TO})$	89	89	80	82	86.4	96
$A_1(1\text{TO})$	127	148	116	104	161	150
$E(1\text{LO})$	128	130		144		170
$A_1(2\text{LO})$	215					190
$E(2\text{TO})$	221	220	206	214	210	215
B_1+E	290	290	287	286		290
$A_1(2\text{TO})$	364	362	341	340		364
$E(2\text{LO})+A_1(2\text{LO})$	445	440	443	446		447
$E(3\text{TO})$	508	508	501			

[a] Reference 6.
[b] Reference 18.
[c] Reference 8.
[d] Reference 16.
[e] Reference 19.

TABLE II. Constants used in the calculations.

P_c (10^9 N m^{-2})	12.1
ω_0 (cm^{-1})	89
d_{31} (10^{-12} C N^{-1})	−2.5
d_{33} (10^{-12} C N^{-1})	11.7
s_{11} (10^{-12} m^2 N^{-1})	7.2
s_{12} (10^{-12} m^2 N^{-1})	−2.1

noticed that the in-plane stresses will influence the spontaneous polarization of ferroelectric thin films through the piezoelectric effect and result in the shift of the E(1TO) mode. Therefore, the phonon mode shift gives information on the stresses the film suffer, and thus provides us a way to estimate the remnant stresses existing in the epitaxial thin film.

Studies on the hydrostatic pressure effect on $PbTiO_3$ single crystals revealed that transverse phonon modes shifted to low frequency with increasing hydrostatic pressure, and the relation between them can be expressed as[20]

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

where ω_0 is frequency is phonon mode under zero pressure and P_c is the critical pressure above which the phonon frequency becomes zero.

The piezoelectric equation tells us that external stresses will change the polarization of ferroelectric materials. When considering the lattice symmetry of tetragonal $PbTiO_3$, the relationship between the external stresses and the change of polarization (Δp) is

$$\Delta p=d_{31}T_1+d_{31}T_2+d_{33}T_3, \tag{3}$$

where d_{ij} are the piezoelectric coefficients and T_i are the stresses along the lattice vector directions.

In the hydrostatic case, the material suffers an external pressure which can also be regarded as a three-dimensional (3D) compressive stress consider, and so we have $T_1=T_2=T_3=P$; then, Eq. (3) can be simplified as

$$\Delta p=(2d_{31}+d_{33})P. \tag{4}$$

From Eqs. (1) and (3), we obtain the following expression of the relationship between the phonon mode frequency and change of spontaneous polarization:

$$\omega^2=\omega_0^2\{1-\Delta p/[(2d_{31}+d_{33})P_c]\}. \tag{5}$$

In the polycrystalline thin films where the grains have different orientations, it is reasonable to consider that there exists an effective hydrostatic pressure in the film, but the epitaxial thin film has a preferential orientation, and so the unit cells in the film only suffer 2D in-plane stresses caused by a film-substrate interaction. So Eq. (3) can be simplified as

$$\Delta p'=2d_{31}T'. \tag{6}$$

Here T' is the in-plane stress. From piezoelectric constant of $PbTiO_3$ single crystal (Table II), we can find out that the stress along the (001) has an opposite effect on the spontaneous polarization compared with the stresses along (100) and (010). The polarization of $PbTiO_3$ decreases when the hydrostatic pressure increases,[22,23] and as a result, the soft modes have downward shifts, but when only considering the in-plane compressive stress, the polarization will increase and thus make soft modes shift upward.

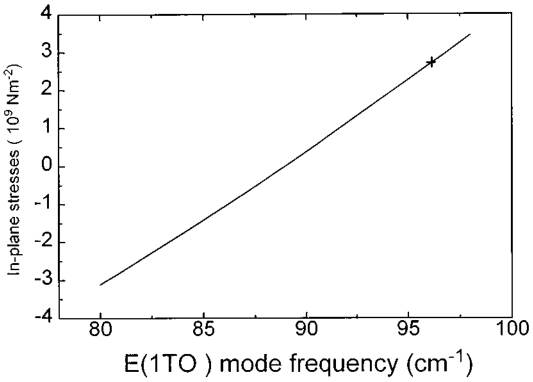

FIG. 5. Calculated E(1TO) soft-mode dependence of in-plane strain. The cross corresponds to the experimental observation.

By substituting Eq. (6) for Eq. (5), ω can be expressed as

$$\omega^2=\omega_0^2\{1-2d_{31}T'/[(2d_{31}+d_{33})P_c]\}. \tag{7}$$

Now we arrive at the equation

$$T'=(1-\omega^2/\omega_0^2)(2d_{31}+d_{33})P_c/2d_{31}. \tag{8}$$

In our case, the E(1TO) mode was found to have a 7-cm^{-1} shift, and using the constants listed in Table II,[24] the in-plane stress in the film was calculated to be 2.6 GPa. According to the elastic equation of tetragonal $PbTiO_3$,

$$S_i=\Sigma s_{ij}T_j \quad (j=1,2,3), \tag{9}$$

where s_{ij} are elastic compliances. The corresponding strain was 1.3%. In Fig. 5 we plot the frequency of the E(1TO) soft modes as a function of the in-plane compressive strain. The strain in our $PbTiO_3$ thin film is shown by a cross.

We noticed that in our Raman measurements, the other soft mode, the A_1(1TO) mode, also had a possible upward shift. But the reported data of this mode in single crystals are quite different,[6,18] and a recent study reported by Foster *et al.* proved the A_1(1TO) mode had anharmonicity.[25] So it is hard to determine the exact value of this mode shift.

We only consider the effect of the two-dimensional compressive stress on the c domains of the $PbTiO_3$, and this in-plane stress should have a reverse effect on the a domains, but a downward shift of the corresponding mode has not been observed. We attribute this to the small percentage of a domains in our sample.

In conclusion, the Raman spectrum of epitaxial $PbTiO_3$ thin films on (110) $NdGaO_3$ substrates displayed a phonon-mode-hardening behavior which was different from studies on ultrafine particles and polycrystalline thin films. When considering the soft-mode behavior under external pressure and the piezoelectric effect of the ferroelectrics, we attribute the mode shift to the in-plane compressive stresses in the c domains of the epitaxial $PbTiO_3$ film. From the $E(1TO)$ mode shift, we estimated the remnant stresses in the film.

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