

Ferroelectric transition in an epitaxial barium titanate thin film: Raman spectroscopy and x-ray diffraction study

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We have performed x-ray diffraction and Raman spectroscopy measurements in the temperature range of 300–873 K on a single phase epitaxially oriented BaTiO₃ thin film grown by pulsed laser deposition on a single crystal MgO substrate. The θ – 2θ room temperature diffraction measurements and asymmetric rocking curves indicate that the film is very weakly tetragonal with the c -axis parallel to the plane of the film. X-ray diffraction measurements up to high temperature reveal only a change in slope in the perpendicular to the plane lattice parameter around 450 K (in bulk $T_c = 395$ K) indicating that a diffuse-like of phase transition is taking place. Room temperature polarized Raman spectra show that the film is indeed tetragonal with C_{4v} symmetry and with the a -axis perpendicular to the film plane. Monitoring of the overdamped soft mode and the 308 cm⁻¹ mode confirms that the phase transition is taking place over a wide temperature range according to the x-ray results. The increase of the phase transition temperature is attributed to the stress effect induced by the substrate. © 2003 American Institute of Physics. [DOI: 10.1063/1.1596720]

I. INTRODUCTION

Barium titanate (BaTiO₃ or BTO) is one from the most studied perovskite-type ferroelectrics because of its important electrical and optical properties. BTO bulk crystals and ceramics are widely used in multilayer capacitors, infrared detectors, electro-optic elements, memory cells, etc.^{1–4} However, to be integrated in devices such as microactuators, non-volatile dynamic random access memories, electro-optic modulators, and optical waveguides, BTO and BTO-based materials should be manufactured in the thin film form.^{5,6}

Bulk single crystal is known to undergo three structural phase transitions. At $T_1 \approx 193$ K BTO transforms from rhombohedral to an orthorhombic phase, which in turn changes to a tetragonal phase at $T_2 \approx 280$ K and finally to a cubic phase at $T_c \approx 395$ K.⁷ These transitions are of displacive type⁷ but the tetragonal to cubic transition can be better described as intermediate between a displacive and order disorder transition.⁸ According to the order–disorder model, the disorder in the paraelectric phase is associated with the position of the Ti ions. Instead of occupying the body center positions as in an ideal cubic perovskite structure the Ti ions are randomly displaced along the cube diagonals causing disorder.

The vibrational properties of BTO single crystal have been extensively studied as a function of temperature by Raman and infrared measurements.^{9–15} In the paraelectric phase with perfect O_h cubic symmetry, no first order Raman process is expected. The high temperature ($T > T_c$) Raman spectra however show the existence of two broadbands at ~ 260 and 530 cm⁻¹ (Refs. 10, 11, and 16) due to Ti disorder. Luspín *et al.*¹³ showed that the transverse T_{1u} mode exhibits softening in the paraelectric phase which supports the

displacive type mechanism. It was suggested that this mode is overdamped due to Ti disorder and that, on cooling it softens to reach a frequency of 60 cm⁻¹ above T_c .

In the tetragonal ferroelectric phase the T_{1u} soft mode splits onto $A_1 + E$ modes. The E (TO) soft mode is also overdamped. Its frequency is found to be about 38 cm⁻¹ at room temperature while the linewidth is about 108 cm⁻¹.¹¹ The corresponding soft mode A_1 is still stable in the tetragonal phase at ~ 270 cm⁻¹. The tetragonal to cubic transition is also characterized by an abrupt decrease of the Raman intensity of the E mode at ~ 308 cm⁻¹.^{10,16,17}

In the last few years, the development of preparation methods of high quality samples and highly sensitive measurement techniques have led to interesting results concerning the influence of domain structures, defects, and size effects on the ferroelectric properties of BTO.^{16,18–20} By combining polarized light microscopy and piezoreponse force microscopy it was demonstrated that micro-Raman measurements are able to differentiate on a submicrometer scale between the a - and c -domains at room temperature.¹⁸ Numerous studies show a clear relationship between decreasing the crystallite size ($< 1 \mu\text{m}$) and decreasing room-temperature tetragonality.²¹ In addition, Begg *et al.*²⁰ found, from Raman study, an increasing of T_c with decreasing the crystallite size, i.e., with decreasing tetragonality, and showed that this transition occurs over a wider temperature interval for a fine BTO powder ($\sim 0.19 \mu\text{m}$).

The distinguishing of the tetragonal phase from the cubic phase in fine BTO nanocrystals by x-ray and electron diffraction is very difficult because of the very small tetragonal distortion.²² In addition, in thin films, the x-ray peaks are generally broadened by strain and disorder. It was established that oxygen pressure during deposition process, modifies the tetragonality of BTO.^{23,24} Thus, films deposited under low oxygen pressures ($P < 5.10^{-2}$ mbar) are tetragonal

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with c -axis orientation whereas those deposited under high oxygen pressure ($P > 2.10^{-1}$ mbar) are tetragonal with a -axis orientation. Intermediate oxygen pressures during deposition promotes the cubic structure. Since in this pressure range the tetragonal distortion should be very close to one, it is very difficult to judge from the x-ray diffraction (XRD) alone whether BTO films are tetragonal or cubic and to differentiate between a -axis and c -axis orientations in the tetragonal case. Raman spectroscopy is a more sensitive method to confirm the existence of the tetragonal phase in BTO, in particular, by observation of the 308 cm^{-1} peak.

In the last few years, physical properties of thin ceramic and epitaxial BTO films have been studied and significant differences with bulk properties were observed.^{25–27} It is desirable for many applications to grow single-crystal thin films in order to exploit the anisotropic ferroelectric properties. In addition, ferroelectric epitaxial thin films are more attractive than ceramic films for studies of stress and size effects. Meanwhile, Raman investigations of epitaxial BTO thin films are still rare in the literature.

In the present work, we report on a coupled x-ray and polarized Raman investigation of an epitaxial BTO thin film deposited under intermediate oxygen pressure of 0.1 mbar by pulsed laser ablation on MgO single-crystal substrate. We compare the results with measurements made on bulk single crystal. We have investigated in detail the ferroelectric phase transition and show that this transition occurs over a wide temperature interval and therefore is diffuse. The character of the transition is therefore different from the discontinuous transition observed in bulk samples. In addition the transition temperature is enhanced in comparison with the bulk transition temperature. We attribute this striking change of transition type to the substrate induced strain and defects. Since the a/c aspect ratio determined by the XRD is very close to unity, we have used Raman measurements to demonstrate that the room temperature phase is tetragonal and is oriented with the a -axis perpendicular to the film substrate. The vanishing of the overdamped soft mode was observed at the transition temperature. We also show by Raman measurements that in the high-temperature paraelectric phase the substrate induced stress disappears when approaching the deposition temperature ($\sim 873\text{ K}$).

II. EXPERIMENTAL CONDITIONS

Epitaxial BTO of thickness 3000 \AA was grown on (001) MgO single-crystalline substrate of size $5 \times 5 \times 1\text{ mm}^3$ by pulsed laser deposition in a ultra high vacuum chamber. The film was deposited at a substrate temperature of 913 K in a partial pressure of oxygen $P = 0.1$ mbar. The crystallinity of thin film was analyzed by various XRD techniques: the θ - 2θ scan, rocking curve, phi scans, and finally by asymmetric rocking curves which is in principle a powerful method to determine the tetragonal strain in films. The x-ray measurements as a function of the temperature were performed using an in-house designed goniometer permitting high resolution measurements up to 873 K . Experiments were carried out using $\text{Cu K}\alpha$ radiation monochromatized by an InP crystal.

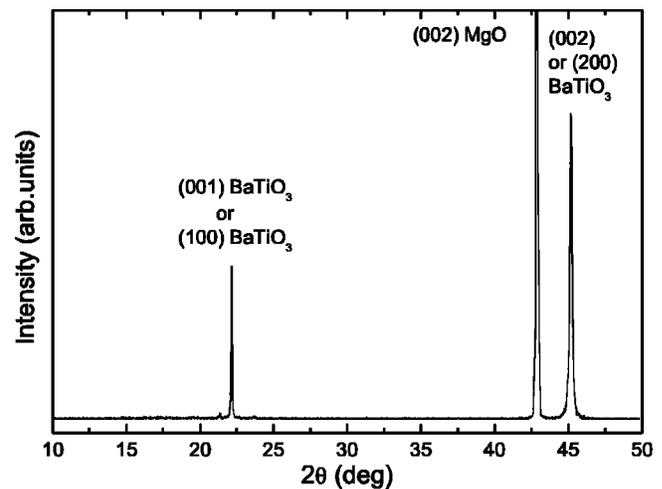


FIG. 1. XRD θ - 2θ diffractogram of the epitaxial BaTiO_3 thin film.

Raman measurements were performed in a backscattering microconfiguration, using the 488.0 nm line from an argon ion laser focused on the sample surface as a spot of $2\text{ }\mu\text{m}$ in diameter. The scattered light was dispersed by a subtractive triple spectrometer (Jobin Yvon Model T64000) and collected with a liquid nitrogen cooled charge coupled device detector for 100 s . The spectrometer provided a wave-number resolution better than 3 cm^{-1} . The spectra were recorded in backscattering geometry. The wave vector of the incident light was perpendicular to the MgO substrate plane while polarization of the incident and scattered light were parallel to MgO cubic axes substrate plan. Two configurations were used: parallel (\parallel) and crossed (\perp) polarizations in which the incident light is polarized, respectively, parallel and perpendicular to the scattered light polarization.

The temperature evolution of the Raman spectra from room-temperature to 873 K was measured using a Linkam hot-stage.

III. RESULTS

A. X-ray diffraction

1. Room temperature

BaTiO_3 is weakly tetragonal even in the bulk (bulk lattice parameter are $a = 3.992\text{ \AA}$ and $c = 4.036\text{ \AA}$ at room temperature which implies $c/a \sim 1.011$). Figure 1 shows a θ - 2θ XRD pattern of a BTO thin film deposited on (001)MgO substrate. This diagram indicates that the film is single phase and well oriented since only one series of peaks is observed. From the Bragg law we determined the film out-of-plane lattice parameter as 4.011 \AA . Since this value is between a - and c -bulk lattice parameters we are unable to determine the growth direction of the film and whether or not it is in the tetragonal state. To determine the tetragonality, we used the asymmetric rocking curve technique²⁸ taken about the $\{303\}$ family of equivalent planes in two perpendicular directions rotated 90° about the surface normal. In this case the (303) and (-303) planes should be successively brought into the diffraction condition. In the cubic phase the angular distance between the peaks for the two diagrams should be 90° . The

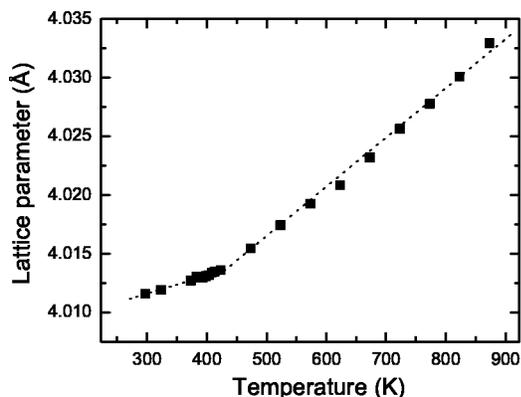


FIG. 2. Temperature dependence of the out of plane lattice parameter of the BaTiO₃ thin film.

deviation from 90° indicates the deviation from cubicity. In two perpendicular directions we find the same ratio of 1.003 between the in- and out-of-plane lattice parameters. Within the experimental resolution and fitting errors, it is difficult to conclude about the tetragonality of film. However the knowledge of the in-plane and out-of-plane lattice parameters allows us to determine the unit cell volume for the thin film. We get a value of 64.87 Å³, which is a little larger than the bulk unit cell volume 64.31 Å³. This increase can be attributed to the effect of oxygen vacancies.²⁹

The mosaicity (angular dispersion along the growth direction) was evaluated by the rocking curve measurement. The rocking curve displays a full width at half maximum (FWHM) of 1.2°. This mosaic spread can be attributed to the large lattice mismatch between MgO and BTO (+5.3% with the *a* axis and -4.2% with the *c* axis) which must promote the appearance of dislocations. We have also characterized the epitaxial growth using the phi scans. The angular alignment of the diffraction peaks for {202} MgO and {101} BTO directions implies that the thin film is epitaxially oriented on the substrate.

2. Temperature dependence

We have followed the evolution of the XRD peaks as a function of temperature during heating. The temperature dependency of the out-of-plane lattice parameter of the thin film is shown in Fig. 2. Two regions are observed: a slow expansion for $T < 400$ K and more rapid expansion for $T > 450$ K which correspond to thermal expansion. Since the thermal expansion of the substrate is monotonic as a function of temperature, the change of slope at 400–450 K could correspond to the ferroelectric transition observed in the bulk at $T_c \approx 395$ K. However this “soft” kink-like anomaly is different from the lattice parameter discontinuity occurred in the bulk crystal. There is no change in the FWHM of the diffraction peaks in going from the room temperature to the high temperature region. Generally the FWHM changes when a phase transition occurs. Note finally that the observed expansion lattice parameter for $T < T_c$ excludes a *c*-orientation for thin film since for bulk material the *c* pa-

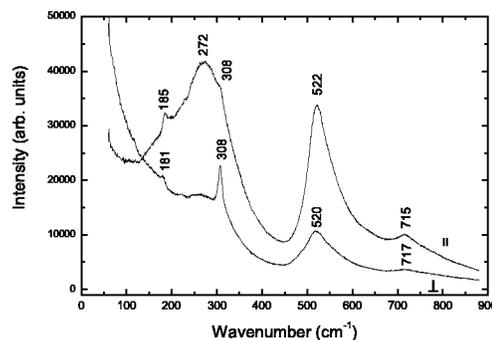


FIG. 3. Room temperature polarized Raman spectra of the BaTiO₃ thin film.

rameter decreases between room temperature and T_c . We can conclude therefore that BTO thin film is either cubic or barely *a*-tetragonal.

B. Raman spectroscopy

Both in the paraelectric and in ferroelectric phase, BTO has one molecule (five atoms) per unit cell that results in 12 optical modes.

A symmetry analysis based on the O_h ($Pm3m$) point group symmetry of the high temperature paraelectric cubic phase shows that only odd infrared modes are active in this phase. Four optical phonon modes belongs to the T_{2u} and three to the T_{1u} threefold degenerate irreducible representations. The T_{2u} mode is silent and the T_{1u} modes are only infrared active. No Raman activity exists in the paraelectric phase with ideal cubic perovskite symmetry.

For C_{4v} ($P4mm$) point group associated of the tetragonal ferroelectric phase, each of the T_{1u} modes splits into a doubly degenerate E mode and nondegenerate A_1 mode, while the T_{2u} silent mode splits into $B_1 + E$ modes. All the A_1 and E modes are both Raman and infrared active and the B_1 mode is only Raman active. The existence of long-range electrostatic forces in the tetragonal ferroelectric phase splits each of the A_1 and E modes into longitudinal (LO) an transverse (TO) components. The Raman^{11,16,18,19,30,31} and infrared¹² spectral modes were reliably identified in BTO bulk crystal in the ferroelectric single and poly domain states. These results will be used in the following section to compare them with our results on the epitaxial film.

According to the Raman tensor for the tetragonal C_{4v} point group, the α_{zz} component involves only A_1 modes. For the α_{xx} and α_{yy} components, the A_1 and B_1 modes are allowed simultaneously, while the E phonons are only allowed for α_{zx} and α_{zy} components. Consequently, the E (TO) soft mode can be observed in distinct scattering geometry and the polarized Raman spectra \parallel and \perp could provide a proof of the existence of *a*- or *c*-domains structure in the epitaxial BTO film.

1. Room temperature spectra

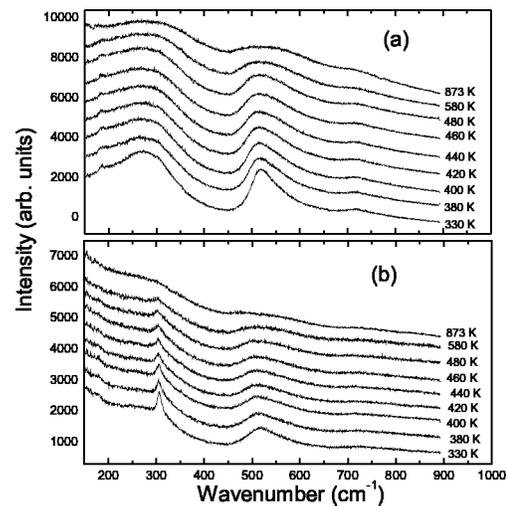
The polarized Raman spectra of the epitaxial BTO thin film recorded at room temperature in the parallel (\parallel) and crossed (\perp) polarization are presented in Fig. 3. The MgO substrate has no Raman lines in the spectral range studied and therefore it does not interfere with the BTO film

TABLE I. Frequencies (in cm^{-1}) of observed Raman lines in the BaTiO_3 single crystal and the thin film in tetragonal phase.

Mode	Single crystal	References	Thin film Present work
$E(\text{TO}), E(\text{LO})$	180	9, 14, 28	181
$A_1(\text{TO})$	175	17	185
	178	9	
	180	14	
	185	28	
$A_1(\text{TO})$	270	28	272
	275	17	
	280	9, 14	
$E(\text{TO}+\text{LO})$	305	28	308
	308	9	
	310	14	
$B_1(\text{TO})$	305	28	308
	308	9, 14	
$E(\text{LO})$	463	28	
$E(\text{TO})$	490	14	520
	498	9	
	518	28	
$A_1(\text{TO})$	515	9, 14	522
	517	17	
	520	28	
$A_1(\text{LO})$	720	14	715
	725	9	
$E(\text{LO})$	715	28	717
	722	9	

spectra.³² Since \parallel and \perp Raman spectra are very different, we conclude that the film has excellent single crystal quality, which reinforce the x-ray data. The Raman peaks of the epitaxial thin film feature the observed spectra of room-temperature BTO single crystals^{11,30,31} and ferroelectric single-domain crystal.^{16,18,19} All frequencies of the detected peaks are listed in Table I, together with the reported bulk data. It is noticeable that all the peaks of BTO single crystal in ferroelectric phase have been clearly observed in the thin film with broadening of the lines. We conclude therefore that the room temperature phase of the thin film is ferroelectric and the microscopic symmetry can be assigned to $P4mm$. The best indicators of the tetragonal BTO phase are the presence of the $E(\text{TO})$ overdamped soft mode and the existence of the very narrow 308 cm^{-1} peak (\perp spectrum of Fig. 3) that could vanish in the paraelectric cubic phase.

In the \parallel spectrum (Fig. 3) a narrow peak at 185 cm^{-1} [$A_1(\text{TO})$], the broad peaks at 272 and 522 cm^{-1} [$A_1(\text{TO})$], and the peak at 308 cm^{-1} [$B_1(\text{TO})$] are similar to the $Y(\text{XX})\bar{Y}$ or $X(\text{YY})\bar{X}$ spectra of single crystal.^{11,16,19,30,31} These results show that the c -axis of the epitaxial film is parallel to the substrate and that demonstrate the existence of a -domains structure having the C_{4v} point group. If the domains were to be c -oriented with the C_{4v} symmetry, the parallel spectra would consist only of $A_1(\text{LO})$ and B_1 modes since the phonon wave vector is perpendicular to the MgO substrate. The existence of the a -oriented domains can be confirmed also by the analysis of the crossed (\perp) spectrum which involves only E modes (Fig. 3): the overdamped $E(\text{TO})$ soft mode and the 181 and 308 cm^{-1} E modes. The high-frequency E modes at ~ 463 (LO) and at 490 (TO) cm^{-1} are weak even in the bulk.^{11,16,19,30,31} In the film these

FIG. 4. Temperature dependence of the Raman spectra in Parallel (\parallel) (a) and crossed (\perp) (b) scattering geometry of the BaTiO_3 thin film.

peaks are broad, due to the strains generated by the substrate, and overlap with the broad peak at 520 cm^{-1} . The crossed (\perp) spectrum correspond to the xz or yz spectra of single crystal,^{11,16,19,30,31} which, together with XRD, confirm that only a -domains exist in the film. For a c -oriented domain having the C_{4v} point group the crossed Raman spectra should not show any lines. The weak longitudinal A_1 and E modes observed, respectively, at 715 and 717 cm^{-1} can be attributed to light scattering from domains walls.^{16,19}

2. Temperature evolution of the Raman spectra

The temperature evolution of the Raman spectra of the BTO thin film were measured in the range from 300 to 873 K . The polarized Raman spectra recorded in parallel and in crossed polarization at different temperatures, are plotted in Fig. 4. An examination of these results shows that the temperature dependent behavior of the BTO film is qualitatively similar to that observed in the single crystal. With increasing the temperature the intensity of Raman peaks decreases and their width becomes broader. There are however some important differences between the spectra behavior in the thin film and in the single crystal. Unlike the bulk case, the intensity of \parallel spectra does not show any abrupt decrease at any temperature [Fig. 4(a)] but decreases with increasing temperature. At high temperature the \parallel spectra are similar to what has been observed in the paraelectric phase of single crystal, i.e., the existence of two broad peaks centered at ~ 300 and $\sim 522 \text{ cm}^{-1}$. Important information is obtained by a detailed examination of the temperature dependent behavior of the crossed polarized spectra, since it is in this geometry that the $E(\text{TO})$ overdamped soft mode and the 308 cm^{-1} E mode are observed.

Figure 5 shows the temperature dependence of the low-frequency part of the crossed polarized Raman spectra. The intensities have been corrected for the Bose-Einstein factor. The overdamped $E(\text{TO})$ soft mode has practically the same shape in the film and in the single crystal.^{11,16,30} However, as can be seen from Fig. 5, the overdamped $E(\text{TO})$ soft mode intensity does not vanish abruptly at any temperature but

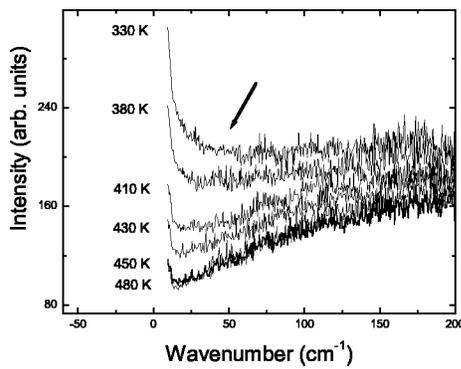


FIG. 5. Temperature evolution of the low-frequency part of the crossed polarized Raman spectra. The intensities have been corrected for the Bose–Einstein factor. The arrow indicates the region of the overdamped soft mode.

decreases gradually on heating contrary to what is observed in the single crystal. Note that the intensity of the overdamped soft mode vanishes at about 450 K and no shape variation is observed for $T > 450$ K in the low-frequency part.

The temperature variation of the 308 cm^{-1} line is displayed on expanded frequency and intensity scale in Fig. 6(a). The Raman intensity was corrected for the Bose–Einstein factor and the Lorentzian fit was used to determine the integrated intensity and the full width at half maximum at each temperature. The line is well fitted using a Lorentzian function. The results as a function of temperature are plotted in Fig. 6(b). The integrated Raman intensity is seen to decrease with increasing temperature, while its linewidth in-

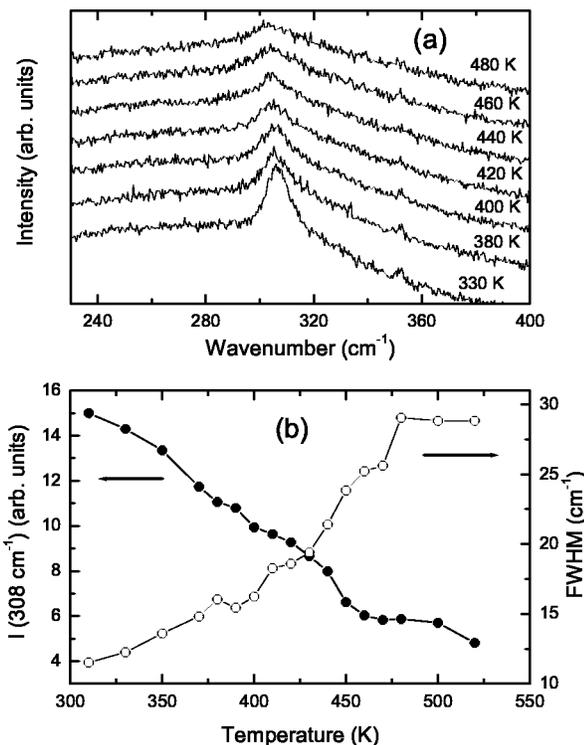


FIG. 6. (a) Temperature dependence of an expanded frequency of crossed polarized Raman spectra from 330 to 480 K. (b) Temperature evolution of the integrate Raman intensity and the full width at half maximum (FWHM) of the 308 cm^{-1} line.

creases. These results are in good agreement with the Raman measurements reported on bulk single crystal between the room temperature and the transition temperature ($T_C \approx 395$ K). However, contrary to what is observed in the bulk, Fig. 6 does not show any abrupt decrease of Raman intensity at any temperature. The Raman intensity of the 308 cm^{-1} peak decreases more gradually near 425 K and reaches its minimum at about 450 K which correspond to the temperature of the vanishing of the overdamped soft mode. The peak is still present above 450 K and its linewidth increases gradually and remains practically constant at $T > 480$ K. At high temperature the intensity of the 308 cm^{-1} peak gradually disappears on approaching the temperature of 873 K which corresponds to the deposition temperature of the film. In the bulk of ceramic and single crystal, the 308 cm^{-1} peak still exist in the paraelectric phase but it disappears very rapidly just above transition temperature.^{16,20}

IV. DISCUSSION

X-ray and reflection high-energy electron diffraction measurements show that BTO thin film is highly oriented single phase. Due to the small tetragonal distortion in the film ($c/a \sim 1$), the XRD analysis which determine an average symmetry, is unable to confirm the existence of a tetragonal ferroelectric phase. Raman spectroscopy can show a local and dynamic symmetry in small region demonstrates that the room temperature phase is assigned to a C_{4v} tetragonal symmetry. In addition, polarized Raman spectra confirm the excellent single crystal quality of the film and show that the tetragonal domains are a -oriented. For the same deposition conditions (pressure), a c -orientation was obtained in the case of SrTiO_3 (STO) substrate.³³ Note that the lattice mismatch between STO and BTO is equal to -2.2% with the a -axis and -3.3% with the c -axis. Since the thermal expansion of the BTO film is larger than thermal expansion of MgO and STO substrates ($\alpha_f > \alpha_{\text{MgO}} > \alpha_{\text{STO}}$), the a -domains orientation in BTO on MgO substrate is mainly attributed to the effect to the epitaxial in-plane tensile-constraints generated by the large mismatch of lattice constants in film and substrate.

Due to the small tetragonal distortion in the ferroelectric phase, the evolution of a -lattice parameter as a function of the temperature is different from the bulk evolution since it does not show any discontinuity and there is no change in the FWHM of the diffraction peaks. However, a change in slope in the range of 400–450 K is observed. This behavior is similar to that observed in ferroelectric relaxors which was attributed to a diffuse phase transition. Raman spectroscopy for BTO thin film shows, however, the existence of a true ferroelectric phase at room temperature with a weakly tetragonal symmetry. The diffuse phase transition is confirmed by the gradual decrease of the intensities of the overdamped soft mode and the tetragonal Raman peak at 308 cm^{-1} . The overdamped soft mode disappear and the intensity of the 308 cm^{-1} has a minimum at the same temperature of 450 K when the lattice parameter temperature dependence change the slope. Consequently, the ferroelectric–paraelectric phase transition occurs in a relatively broad region around 450 K

and can be considered as diffuse. This phase transition occurring in a wide temperature region is usually observed in the ferroelectric thin films,^{26,34–36} and can be attributed to a distribution of the critical temperatures because of the presence of the nonuniform stresses and point defects. The corresponding dielectric susceptibility exhibits broad peak and it is difficult to indicate the transition point. In the BTO thin film however, the Raman spectroscopy is able to identify the paraelectric phase which corresponds to disappearing of the overdamped soft mode and of the minimum of the intensity of the 308 cm⁻¹ mode. Consequently, the temperature phase transition in the film corresponds to 450 K that is higher than the T_c in bulk. This result is in agreement with phenomenological theory that predicts an increase in T_c due to the tensile stress generated by the substrate.^{37,38}

The activation of the tetragonal Raman peak (308 cm⁻¹) above T_c is due to strain effect generated mainly by the misfit of the thermal expansion of the BTO film (17×10^{-6} K⁻¹) and MgO substrate (14.8×10^{-6} K⁻¹). On approaching the deposition temperature the tensile thermoelastic strain is practically relaxed and the intensity of the 308 cm⁻¹ E mode gradually disappears. The static distortion leads to the activation of normally forbidden Raman lines and has been discussed by Uwe *et al.*³⁹ These authors have shown that a nonzero Raman intensity can be explained as result of the coupling of normal modes with the static distortion. The Raman intensity of these modes is thus proportional to the Fourier transform of the static distortion and a large part of the Brillouin zone contributes to the scattering. Consequently, the broadening of the Raman lines observed in the film with respect to the bulk single crystal reflects the effect of the strain field. On approaching the deposition temperature the thermoelastic stresses vanish and the Fourier transform of the static distortion becomes equal to zero. Similar to the bulk case, only the two broad bands due to Ti disorder are observed near the deposition temperature.

V. CONCLUSIONS

X-ray diffraction and Raman spectroscopy were used to examine the ferroelectric phase transition and the domains orientation in the epitaxial BTO thin film deposited, in an intermediate oxygen partial pressure of 0.1 mbar, on MgO substrate. We found that the film is highly oriented and room temperature Raman results confirm the existence of a tetragonal ferroelectric phase with the domains being *a*-oriented. The *a*-domain orientation is mainly attributed to the effect of the tensile strains generated by the large mismatch of the in-plane lattice constants between film and substrate. Due to the nonuniform stresses and point defects present in the film, the para- to ferroelectric phase transition occurs in a relatively broad region around 450 K. This transition is accompanied by the slight temperature variation of the out lattice parameter, the gradual disappearance of the overdamped *E*(TO) soft mode and the variation of the integrated intensity of the 308 cm⁻¹ tetragonal mode around 450 K. It is shown that due to the strain effect the tetragonal peak still exist above T_c and disappears on approaching the deposition temperature.

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