Research Article

A Comparative Analysis of Asymmetric $(\text{BaTiO}_3)_{(1-x)\Lambda}/(\text{BaZrO}_3)_{x\Lambda}$ Superlattices via X-Ray Diffraction and Raman Spectroscopy

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This work is aimed at studying asymmetric $(\text{BaTiO}_3)_{(1-x)\Lambda}/(\text{BaZrO}_3)_{x\Lambda}$ ((BT)_{(1-x)Λ}/(BZ)_{xΛ}) superlattices, grown by pulsed laser deposition onto (001) MgO substrates. The thicknesses of BT (ferroelectric) and BZ (paraelectric) layers were varied so that x ranged from 0 to 1 at a modulation period Λ of about 80 Å. The films were 400 nm thick. The out-of-plane lattice parameters of constituents were assessed using X-ray diffraction. The lattice dynamic peculiarities of superlattices were probed via Raman spectroscopy; special attention is paid to the analysis of E(1TO) and A₁(2TO) ferroelectric soft modes. A comparative analysis of data acquired via both experimental techniques reveals the enhancement of stress between BT and BZ layers with a decrease in symmetry from the tetragonal to a monoclinic phase due to strains induced by the lattice parameter mismatch between the constituents.

1. Introduction

Over the last 50 years, materials based on ferroelectric perovskites, such as artificial superlattices, have attracted attention of researchers due to their outstanding properties, such as high dielectric constants, high polarization, low dielectric losses, and high Curie temperature, which find application in various optoelectronic and microelectronic devices: nonvolatile random access memory devices, integrated systems, and tunable microwave elements [1–10]. In contradistinction to single-composition ferroelectric thin films, artificial superlattices (SLs) ensure high permittivity and great polarization in the relevant systems [3, 9]. The structures, where one constituent is ferroelectric BaTiO_3 (BT) and another is dielectric SrTiO_3 (ST) or PbTiO_3 (PT) or paraelectric BaZrO_3 (BZ), are among the most extensively studied objects. This is due to the fact that their physical

characteristics are determined by epitaxial strain that is caused by the lattice parameter mismatch between constituents. Another important moment is the possibility to tune strain in heterostructures by varying the composition (stoichiometry) or the thickness of one of constituents composing a superlattice. Strains induced by the lattice parameter mismatch of the adjacent layers alter the ion positions and lattice vibrations, especially in low-frequency ferroelectric soft modes (E(1TO)) that are highly sensitive to ion displacements in thin films. Thus, the soft modes may furnish detailed information on misfit strains and, consequently, on the phase transitions in ferroelectric superlattices, which is essential in terms of the fundamental science and the practical use of these structures.

Earlier, we have studied the PLD grown superlattices onto MgO substrates, where one constituent was BaTiO_3 and another was a solid solution with Ba atoms partly substituted

with Sr, that is, $\text{Ba}_{(1-x)}\text{Sr}_x\text{TiO}_3$ (BT/BST) [11–13]. In those systems, E(1TO) ferroelectric soft modes were monitored via Raman spectroscopy that is a powerful nondestructive tool for this purpose [2, 4, 9, 14, 15]. The E(1TO) frequency was found to depend to a large extent on the Ba/Sr content ratio due to the increase in its frequency by three times, while going from a pure BT film towards a pure ST film [12, 13]. This drastic variation in the low-frequency soft mode component was referred to stresses arising between the epitaxial constituent layers in the superlattice.

The present work is aimed at investigating the influence of layer thickness ratio in superlattices on the soft mode behavior by the example of asymmetric $(\text{BaTiO}_3)_{(1-x)\Lambda}/(\text{BaZrO}_3)_{x\Lambda}$ $((\text{BT})_{(1-x)\Lambda}/(\text{BZ})_{x\Lambda})$ superlattices prepared via pulsed laser deposition onto (001) MgO substrates, where $\text{La}_{0.5}\text{Sr}_{0.5}\text{CoO}_3$ oxides served as buffer layers. The microstructural characteristics (phase composition and lattice parameters) and lattice dynamics of these systems were experimentally probed via X-ray diffraction and Raman spectroscopy. X-ray diffraction is known to be one of the most reliable methods for studying epitaxial strain in superlattices [16–18], because it ensures information on the degree of structural perfection of films and allows one to determine the lattice parameters and to establish the orientation between the film and the substrate. Raman spectroscopy is a nondestructive and powerful method for lattice dynamics characterization in perovskites [2, 4, 9, 14, 15, 19] and allows one to detect even the finest atomic displacement in a system under consideration by tracking transformations in ferroelectric soft modes that are the main indicators of misfit strain in such systems.

2. Experimental

2.1. Synthesis. Thin-film $(\text{BaTiO}_3)_{(1-x)\Lambda}/(\text{BaZrO}_3)_{x\Lambda}$ $((\text{BT})_{(1-x)\Lambda}/(\text{BZ})_{x\Lambda})$ superlattices (with a total thickness of 400 nm) were synthesized onto (001) MgO substrates via pulsed laser deposition using a KrF excimer laser operating at 248 nm. The 4 nm thick $\text{La}_{0.5}\text{Sr}_{0.5}\text{CoO}_3$ (LSCO, $a_{\text{LSCO}} = 3.805 \text{ \AA}$) buffer layers were applied under an oxygen partial pressure of 0.2 mbar onto the substrates preheated to a temperature of 750°C. The oxygen pressure upon the deposition of BT and BZ constituents was kept at a value of 0.1 mbar. The BT and BZ layers were alternately grown onto MgO substrates with a constant periodicity Λ of about 80 Å, and their thickness ratio was varied so that x was 0, 0.15, 0.3, 0.5, 0.7, 0.85, and 1.

2.2. X-Ray Diffraction Measurements. X-ray diffraction measurements were made at room temperature using a Shimadzu XRD 6000 X-ray diffractometer with $\text{CuK}\alpha_1$ radiation in the θ – 2θ scanning mode. The scan step was $2\theta = 0.01 \text{ deg}$.

2.3. Raman Spectroscopy Measurements. Raman spectra were excited at room temperature by an Ar^+ laser ($\lambda = 514.5 \text{ nm}$) and recorded in the backscattering geometry with an in Via Renishaw Reflex spectrometer equipped with a

coupled-charge device (CCD detector). The laser beam was focused on the film surface in a $\sim 2 \mu\text{m}$ spot using a 100x objective (the Leica microscope). The spectra were acquired in “side-view” ($Y(\text{ZX})\bar{Y}$, $Y(\text{XX})\bar{Y}$, and $Y(\text{ZZ})\bar{Y}$) backscattering geometries (hereinafter referred to as ZX, XX, and ZZ spectra) in obedience to the crystallographic axes of the MgO cubic substrate: $X \parallel [100]$, $Y \parallel [010]$, $Z \parallel [001]$ (for details, see [18]). The obtained spectrograms were then corrected for the Bose–Einstein temperature factor.

3. Results and Discussion

3.1. X-Ray Diffraction Λ . Figure 1(a) displays the XRD spectrograms of $((\text{BT})_{(1-x)\Lambda}/(\text{BZ})_{x\Lambda})$ SLs with x from 0 to 1; here $x = 0$ means a pure BT film and $x = 1$ refers to a BZ film; both are deposited using a similar route to that for SLs (see the Experimental section). According to one series of θ – 2θ peaks observed within the detection limits of the instrument, all samples represent a single-phase well-oriented structure with no extraneous phases. Moreover, as seen in Figure 1(a), the (002) peaks of BZ film and MgO substrate match each other. Using the Bragg law enabled us to evaluate the out-of-plane lattice parameters for parent BT and BZ films. For BT film, the lattice parameter enriches 4.014 Å, being intermediate between the a (3.992 Å) and c (4.036 Å) lattice parameters of the bulk BT crystal. In turn, the c -axis parameter of BZ thin film is 4.236 Å, exceeding the a parameter value of the bulk BZ (4.192 Å). Thus, the BZ thin film is apparently under a compressive tetragonal distortion due to the lattice parameter mismatch between BZ and MgO substrate.

All SLs in this study exhibit satellite peaks being characteristic of modulated heterostructures [17, 20], which evolve with constituent thickness x . Since the angular distance between the peaks is a function of stacking periodicity Λ , the latter was found for each SL to be $\sim 80 \text{ \AA}$ in obedience to the Bragg formula: $\sin\theta_n = n\lambda_x/2\Lambda$, where n is an integer and $\lambda_x = 1.5406 \text{ \AA}$ is the radiation wavelength used in this work.

To calculate out-of-plane lattice parameters c_1 and c_2 of BT and BZ layers, respectively, the relationship $\Lambda = n_1c_1 + n_2c_2$ was used, where n_1 and n_2 are the numbers of unit cells in BT and BZ layers, respectively. For this, the simulations underlying the SL perfect structure have been implemented using Matlab software according to the algorithm described in detail in [17, 20]. The diffraction amplitude was determined in a specular geometry based on the interplanar spacings of the BT and BZ layers along with their individual thicknesses as adjustable parameters. One of the examples of the best simulation of the XRD patterns of SLs is given in Figure 1(b) for $(\text{BT})_{0.3\Lambda}/(\text{BZ})_{0.7\Lambda}$ superlattice. It is important to mention that some theoretical satellites deviate from relevant experimental peaks, which is owing to the influence of imperfect layer/layer interfaces that have not been considered in the simulations [17]. In this respect, Figure 2 displays the out-of-plane parameters calculated for BT and BZ constituents in comparison to the bulk BT and BZ and their single thin film values. As found, the out-of-plane parameter of BT layers decreases from 4.014 Å

FIGURE 1: (a) θ - 2θ XRD profiles of asymmetric $(\text{BaTiO}_3)_{(1-x)\lambda}/(\text{BaZrO}_3)_{x\lambda}$ superlattices at different thicknesses of BT and BZ constituents. (b) XRD profile calculated for $(\text{BaTiO}_3)_{(1-x)\lambda}/(\text{BaZrO}_3)_{x\lambda}$ SL with $x = 0.7$ ($(\text{BT})_{0.3\lambda}/(\text{BZ})_{0.7\lambda}$) (black) in comparison with a measured XRD spectrogram (red). The variance between experiment and theory can be due to imperfect layer/layer interfaces that are neglected in the simulation model.

FIGURE 2: Out-of-plane parameters of BT and BZ layers as a function of BZ thickness.

($x = 0$) to $3.820 \text{ \AA}$ ($x = 0.85$), evidencing that the in-plane tensile stress in the BT layers in the SL is more pronounced than in the BT single film. This implies that in such a system the a -axis of BT layers becomes directed along the normal to the substrate [20].

In turn, the out-of-plane parameter of BZ layers changes slightly and its average value is about $4.23 \text{ \AA}$. However, the parameter value for BZ layers is significantly larger than the a -axis bulk parameter, indicating that BZ layers are under in-plane compressive stress induced by the lattice parameter mismatch between BT and BZ layers. This in-plane compression results in enhanced tetragonal distortion of the BZ layers due to the discrepancy from BT layers.

3.2. Raman Spectroscopy Data. Figure 3 displays the room-temperature ZX, ZZ, and XX polarized Raman spectra of BT/BZ SLs at various constituent thicknesses. The Raman spectra of a pure BT film coincide with those obtained earlier in the same backscattering geometries in works [12, 13], evidencing a broad-wing low-frequency band in ZX spectrum, which is associated with E(1TO) ferroelectric soft mode. By analogy with [12, 13], this band is overdamped, revealing a maximum at about $30\text{--}40 \text{ cm}^{-1}$ and a width of approximately 200 cm^{-1} . However, adding the BZ constituents with increasing their thickness leads to a drastic transformation in the E(1TO) soft mode, as shown by the arrows in Figure 3 for ZX spectrum.

Noticeable changes in the position, intensity, and width of this Raman component, that is, a decrease in its intensity and width along with a dramatic shift towards the higher frequencies, are observed starting with a small thickness of BZ layers ($x = 0.15$), becoming even more pronounced with a further increase in BZ thickness. Thus, being initially overdamped, the E(1TO) component transforms into an underdamped mode.

Unlike the BT crystal, XX and ZZ spectra of the BT film are identical, exhibiting the same interference gap at $\sim 180 \text{ cm}^{-1}$. Meanwhile, introducing BZ layers leads to pronounced differences between these two types of spectra, which are observed in SLs with the periodicity up to $x = 0.85$ ($(\text{BT})_{0.15\lambda}/(\text{BZ})_{0.85\lambda}$). However, arriving at $x = 1$, which corresponds to a pure BZ film, extinguishes the Raman lines in all three spectra, revealing the tetragonal paraelectric phase D_{4h}^1 that allows no polar Raman-active modes [21].

FIGURE 3: Room-temperature Raman spectra of $(\text{BaTiO}_3)_{(1-x)\Lambda}/(\text{BaZrO}_3)_{x\Lambda}$ superlattices, recorded in “side-view” backscattering geometries at various BZ layer thicknesses. The arrows show the transformation of E(1TO) soft mode component at various x values and the dotted line outlines the position of another soft mode (full-symmetrical) component denoted as A1(2TO).

An interesting observation is the appearance of a doublet below 200 cm^{-1} in ZX Raman spectra of samples with concentrations of $0.3 \leq x \leq 0.7$. This doublet even manifests in ZZ spectra (seeming to leak from ZX spectra), along with a pronounced pair of peaks in a range of $300\text{--}400\text{ cm}^{-1}$, but is absent in XX spectra. The computer simulation of ZX spectra using Lorentzians in OriginLab processing medium (see Figure 4) reveals that the components of the doublet are centered at ~ 136 and $\sim 168\text{ cm}^{-1}$. Similar spectral features within the same wavenumber range were observed by Chemarin et al. [22] in polydomain $\text{BaCe}_x\text{Zr}_{(1-x)}\text{O}_3$ solid solutions, exposed to hydrostatic pressure. They were assigned to E modes originating from Ba–O stretching and O–Ba–O bending force constants [22]. In $\text{BaCe}_x\text{Zr}_{(1-x)}\text{O}_3$ specimens with $x=0.8$ and $x=1$ this doublet was observed even under ambient conditions but disappeared at pressures above 21 GPa. As mentioned in [22], the doublet seems to be due to nanodomains and nanophases, which then tend to vanish with increasing pressure and finally merge into a homogeneous phase. This leads to the complete connection of the frontier atoms between nanophases and, respectively, to the disappearance of a low-frequency doublet. Based on this fact, it appears that our samples with the periodicity asymmetry of $0.3 \leq x \leq 0.85$ may undergo a pressure-like effect. Firth of all, there is the superposition of the signals from BT and BZ constituents due to the strong lattice parameter mismatch between the adjacent layers. According to XRD results (Figure 2), BZ layers are being under in-plane compression at simultaneous tension of BT constituents, and their lattice parameters in SLs slightly exceed the appropriate value in unconstrained BZ. Such a lattice distortion makes triply degenerated modes of cubic BZ split into the Raman-

FIGURE 4: Example of computer simulation of ZX Raman spectrum using Lorentzians for a $(\text{BaTiO}_3)_{0.7\Lambda}/(\text{BaZrO}_3)_{0.3\Lambda}$ SL. E1 and E2 are presumably the doublet components described by Chemarin et al. [22]. E(1TO) and A1(2TO) are the soft modes.

active components, as seen in Figure 3, thus playing the identical role of hydrostatic pressure, described by Chemarin et al. [22], and indicating the structural phase transitions to the lower symmetry. The appearance of the identical doublet was also observed in symmetrical $(\text{BT})_{\Lambda/2}/(\text{BZ})_{\Lambda/2}$ SLs in study [23], whose stacking periodicity varied between $32\text{ \AA}$ and $256\text{ \AA}$. Furthermore, a visual comparison of ZX spectra presented in [23] with our ZX spectra reveals that the spectrum of $(\text{BT})_{\Lambda/2}/(\text{BZ})_{\Lambda/2}$ SL with $\Lambda = 256\text{ \AA}$ is similar to that of the $(\text{BT})_{(1-x)\Lambda}/(\text{BZ})_{x\Lambda}$ SL with $x=0.3$; the spectral profile of the $(\text{BT})_{\Lambda/2}/(\text{BZ})_{\Lambda/2}$ SL with $\Lambda = 62\text{ \AA}$ almost

FIGURE 5: Frequency (ν , cm^{-1}) and width (FWHM, cm^{-1}) of E(1TO) and A1(2TO) ferroelectric soft modes versus BZ layer thickness x .

matches that of the $(\text{BT})_{(1-x)\Lambda}/(\text{BZ})_{x\Lambda}$ SL with $x=0.5$, and the signal of the $(\text{BT})_{\Lambda/2}/(\text{BZ})_{\Lambda/2}$ SL with $\Lambda=32\text{ \AA}$ is quasi-identical to that of the $(\text{BT})_{(1-x)\Lambda}/(\text{BZ})_{x\Lambda}$ SL with $x=0.7$. So, the stacking periodicity also plays a significant role in the emergence of the above doublet, and, as seen from our analysis, even maintaining the total periodicity at a constant value (in our case about $80\text{ \AA}$) at varying the layer thickness of constituents allows one to achieve the pressure-induced effect in asymmetric superlattices by analogy with works [22, 23]. The absence of this doublet in SLs with $x=0.15$ and $x=0.85$ is apparently due to a quasi-homogeneous phase in specimens. In the first case, there is the dominance of the thicker BT layers within the SL structure and introducing the thinner BZ layers causes a drastic upshift in the E(1TO) soft mode component due to the strain induced by the lattice parameter mismatch. In the second one, the presence of the much thinner BT layers alternating with the thicker BZ layers reduces the symmetry of the BZ film and alters its Raman spectrum, exciting the E(1TO) soft mode. On the other hand, the disappearance of a doublet below 200 cm^{-1} in the asymmetric SL with $x=0.85$ seems to be a sign of the phase transition owing to the above described pressure-like effect of constituents which undergo noticeable misfit strain due to a pronounced lattice parameter mismatch between them, as seen from XRD data (see Figure 2) for a relevant SL.

As for soft modes, the computer simulation of ZX spectra in obedience to the procedure [12] reveals that the E(1TO) frequency of $(\text{BaTiO}_3)_{0.15\Lambda}/(\text{BaZrO}_3)_{0.85\Lambda}$ superlattice increases by almost seven times in comparison with a pure BT film, achieving 218 cm^{-1} . A too high low-frequency soft-mode position (above 200 cm^{-1}) was frequently found in BT crystals in the ordered low-temperature rhombohedral phase [24–26]. Meanwhile, the symmetry of epitaxial film does not allow the emergence of the rhombohedral phase in them; thus one can assume the monoclinic r -phase that is the closest to the rhombohedral one [23]. The E(1TO) parameters (full width at a half-maximum (FWHM) and frequency

(ν) are plotted in Figure 5 as the functions of BZ layer thickness. As seen in Figure 5, the most drastic transformation of the E(1TO) component occurs upon the transition from a pure BT film to a SL with $x=0.30$. As seen, the thicker BZ layers are, the smaller the variances in E(1TO) frequency and width are. Another soft mode component denoted as A1(2TO) in Figure 3, which is a full-symmetry component thoroughly described in works [24–26], is found to remain unchanged with increasing the BZ layer thickness (Figure 5). It is apparently may be interpreted by the fact that strains caused by the lattice parameter mismatch between BT and BZ constituents exert strong influence on the positions of Ti^{4+} ions in the plane of the substrate, reducing considerably their disorder. Meanwhile, the asymmetric thicknesses of constituents seem to amplify strains between the layers, leading to reorientation of polarization vectors in constituents so that the polarization vector in BT layers, being initially along the c -axis, lies in the plane of the substrate, whereas the polarization in BZ layers is oriented along the normal to the substrate plane, which coincides with the above-described XRD results.

4. Conclusions

A series of ferroelectric/paraelectric $(\text{BaTiO}_3)_{(1-x)\Lambda}/(\text{BaZrO}_3)_{x\Lambda}$ ($(\text{BT})_{(1-x)\Lambda}/(\text{BZ})_{x\Lambda}$) artificial superlattices with varying constituent thicknesses and a constant stacking periodicity was thoroughly probed using room-temperature XRD and Raman spectroscopy techniques. In obedience to the X-ray patterns (both experimental and simulated), the BT layers in the SLs undergo the in-plane tensile stress, at which the a -axis becomes directed along the normal to the substrate. In turn, the BZ layers overcome the in-plane compressive stress because of misfit strains induced by the lattice parameter mismatch between BT and BZ layers. This observation agrees with polarized Raman spectroscopy data. Moreover, according to the Raman spectroscopy, the strain

in BT constituents seems to induce the monoclinic phase in them, decreasing to a large extent the disorder of Ti^{4+} ions, which suggests the appearance of a polar phase in BZ layers, as follows from the drastically upshifted (by seven times) low-frequency E(1TO) soft mode and the unchanged A1(2TO) soft-mode component.

Therefore, in comparison with epitaxial structures with varying stoichiometry in one of the constituent layers [11–13], the design of superlattices with asymmetric constituent thickness at a constant modulation period allows one to achieve a much more drastic transformation of E(1TO) soft modes (by seven times in this study) over against the parent BT film. In this respect, the fabrication of superlattices with a predefined composition enables one to achieve the structures with tunable properties, which ensures their proper application.

Data Availability

The data used to support the findings of this study are available from the corresponding author upon request.

Conflicts of Interest

The authors declare that there are no conflicts of interest associated with this work.

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