Superlattices and Microstructures 87 (2015) 19–24

Contents lists available at ScienceDirect

Superlattices and Microstructures

journal homepage: www.elsevier.com/locate/superlattices

Coexistence of the soft mode and sub-THz central peak in ferroelectric $BaTiO_3$/(Ba,Sr)TiO_3 superlattices

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ARTICLE INFO

Article history:
Received 8 March 2015
Received in revised form 22 June 2015
Accepted 15 July 2015
Available online 15 July 2015

Keywords:
Superlattice
Ferroelectrics
Phase transitions
Raman spectroscopy
Soft mode
Debye relaxator

ABSTRACT

Near- and sub-Terahertz dynamics of soft and Debye-type central modes was studied by the polarized Raman spectroscopy in ferroelectric $BaTiO_3/Ba_{0.3}Sr_{0.7}TiO_3$ (BT/BST) superlattice in the temperature range of 80–400 K where system undergoes the series of phase transitions: paraelectric-tetragonal–monoclinic in BT layers and paraelectric-orthorhombic-monoclinic in BST layers. It was shown that temperature evolution of these modes can be described within the model of coexisted damped harmonic oscillator and Debye relaxator. The occurrence of the pronounced central mode can explain the recently observed relaxor-like dielectric anomaly in such superlattice.

1. Introduction

Elastic strain in artificial superlattices (SLs) composed of alternating ferroelectric layers can be used to create tuneable materials with superior functional properties for device applications [1]. Polarization dynamics that in conventional ferroelectrics spans many frequency decades from microwave to infrared region can also be successfully tailored via strain engineering in artificial SLs. The stress effects change the position of polar ions and lead to significant sensitivity of certain lattice vibrations, including soft modes, to the SL periodicity, lattice mismatches and chemical composition [2,3]. This in particularly is important for the sub-THz (1–30 cm^{-1}) and near-THz (30–100 cm^{-1}) frequency ranges where the soft-mode-related vibrations are active. Therefore, the information related to soft mode behaviour in ferroelectric SLs can be extremely useful for industrial application to fill the existing gap of miniature tuneable THz devices.

Among the most promising and extensively studied multilayer heterostructures, demonstrating the soft mode behaviour are the $BaTiO_3/Ba_{1-x}Sr_xTiO_3$ SLs with compositionally tailored BST layers. For particular compositions these SLs reveal also the relaxor-like dynamics [4].

According to previous Raman and far-infrared studies, the $BaTiO_3$ single crystals exhibit both the displacive and the order–disorder features at ferroelectric transition [5]. It is well known that the ferroelectric soft mode is overdamped in

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http://dx.doi.org/10.1016/j.spmi.2015.07.038
0749-6036/

tetragonal $BaTiO_3$ crystal at room temperature. Its frequency is located in the Terahertz region at $35 \pm 5\ cm^{-1}$ with the half-width of $100 \pm 10\ cm^{-1}$ [6,7]. On heating above the ferroelectric–paraelectric phase transition, this polar mode disappears in the Raman spectra. In addition to the soft mode, the relaxator Debye-like central mode was observed at sub-Terahertz frequencies in $BaTiO_3$ single crystals [8–11], and in $Ba_{1-x}Sr_xTiO_3$ ceramics and in polycrystalline films [12,13]. Similar low-frequency relaxations were also observed in other ferroelectric single crystals [15–18], and classical ferroelectric relaxor $PbMg_{1/3}Nb_{2/3}O_3$ due to polarization fluctuations [19]. Note however that the appearance of the central peak is not a general rule. For instance, the overdamped soft mode was studied by Raman scattering in $BaTiO_3$ and $Ba_{1-x}Sr_xTiO_3$ thin films [20,21] but no central peak was observed.

The coexistence of coupled soft and central modes is clearly related to the dynamics of the polarization-forming displacements of polar ions. It was suggested that the Terahertz frequency soft mode is provided by the in-site vibrations of the ions about the equilibrium positions whereas the sub-Terahertz frequency Debye-type central mode relaxations are due to the intra-site reorientation ionic jumps, described by the eight-site model [22].

In the present work we are interested in coexistence of the soft and central mode vibrations in the artificially grown SLs, composed from $BaTiO_3$ and $Ba_{0.3}Sr_{0.7}TiO_3$ (BT/BST SL) layers deposited on (0 0 1)MgO substrate. To reveal the lattice dynamics we performed micro-Raman study in a broad temperature range of 80–420 K where several phase transitions occurred in alternating layers were observed.

2. Experimental details

Epitaxial BT/BST SL was grown on a cubic (0 0 1)MgO substrate using a pulsed laser deposition technique [4,23] with a variable focusing of a laser beam on the BT and BST targets. The total thickness of superlattice was ~1000 nm. The phase purity of SL, unit cell parameters of the layers, the modulation period Λ, and the average size of the coherent scattering regions were estimated by X-ray diffraction (XRD) using a Rigaku Ultima IV diffractometer (Cu $K\alpha_1$ radiation). The average unit cell parameters of BT and BST layers at room temperature are nearly cubic with c/a ratio close to unit ($c \approx a = 0.3983$ nm). The SL's average modulation period Λ was found to be about 95 Å. According to XRD data, the superlattice was symmetrical with nearly equal thicknesses of BT and BST layers. However, detailed analysis of the XRD patterns revealed slightly different lattice parameters of BT and BST layers. The BT layers with the out-plane, $c_{BT} = 0.4028$ nm and in-plane, $a_{BT} = 0.4020$ nm lattice parameters revealed slight tetragonal distortion ($c/a > 1$), while the BST layers were nearly cubic with $c_{BST} = 0.3930$ nm and $a_{BST} = 0.3933$ nm ($c/a < 1$) [4].

The micro-Raman spectra were excited by the polarized radiation of an argon laser ($\lambda = 514.5$ nm, output power 100 mW) and recorded using a Jobin Yvon T64000 spectrometer equipped with a CCD-detector. The exciting radiation was focused on a sample by an Olympus optical microscope; the focused beam was 2 μm in diameter. For temperature-dependent micro-Raman measurements we used FDCS 196 heating and freezing stage, which gave a temperature stability of ±0.1 K. Polarized Raman spectra have been measured on the samples exactly oriented according to the crystallographic axes of MgO substrate ($X \parallel [1\,0\,0]_{MgO}$, $Y \parallel [0\,1\,0]_{MgO}$, $Z \parallel [0\,0\,1]_{MgO}$). The spectra were obtained in side-view backscattering geometries [24] when the incident beam wave vector was parallel to the substrate and the polarization of the incident and scattered light was parallel or perpendicular to the film. The intensity of spectra was corrected for thermal occupation factor.

3. Results and discussion

The room-temperature polarized Raman spectra of the BT/BST SL for *xx*, *zz* and *xz* scattering geometries are presented in Fig. 1. The parallel polarized *zz* and *xx* spectra contain A_1 transverse (TO) and longitudinal (LO) optical modes, whereas crossed polarized *xz* spectra showed mainly E(TO) and E(LO) modes. In the *xx* spectrum we have observed A_1(1TO) mode at 142 cm^{-1}, broad A_1(2TO) band centered at 280 cm^{-1}, very weak A_1(2LO) peak at 473 cm^{-1}, A_1(3TO) peak at 530 cm^1 and A_1(3LO) peak at 733 cm^{-1}. Raman spectra in the *zz* and *xx* geometries, corresponded to the A_1 symmetry modes, exhibit a clear interference dip at 160 cm^{-1} due to mode coupling. The A_1(2TO) band exhibits strong coupling with the lowest lying A_1(1TO) mode, and the interference dip at 160 cm^{-1} is clearly pronounced in both *xx* and *zz* spectra of SL. Note that similar interference dip in a single-crystalline BT was observed at ~180 cm^{-1} exclusively in *zz* spectrum. This feature seems to be related to the symmetry lowering occurred in BT/BST SL. The *xz* spectrum contains E symmetry modes and leaked A_1(2TO) and A_1(3TO) bands from diagonal geometries. Very weak E modes were observed at about 469 (3LO) cm^{-1} and 492 (4TO) cm^{-1}, and these two peaks are overlapped with a broad leaked A_1(3TO) band at 520 cm^{-1}. We note that the sharp E(3TO, 2LO) peak has practically the same frequency (309 cm^1) as in single crystal BT, whereas the E(2TO, 1LO) peak at 176 cm^{-1} is slightly downshifted.

It is worth noting that the presence of A_1(2TO) and A_1(3TO) lines in the *xz* Raman spectrum of the BT/BST SL excludes the tetragonal symmetry of the BT/BST SL with the *c*-axis being normal to the substrate. The appearance of the A_1 fully symmetrical modes in the crossed-polarized geometries implies symmetry lowering to orthorhombic or monoclinic as was predicted by first-principle and phenomenological calculations for epitaxial perovskites on cubic substrates [25–28].

Polarized Raman spectra of the BT/BST SL are close to those for the single-domain BT crystal. The significant difference appears in the crossed polarized *xz* spectrum of BT/BST SL at low frequency range where the E(1TO) component of soft mode was observed as an underdamped peak with the frequency at about 110 cm^{-1} and with the half-width of 90 cm^{-1}. In