Acoustic properties of nanoscale oxide heterostructures probed by UV Raman spectroscopy

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Abstract. We study high quality molecular-beam epitaxy grown BaTiO\(_3\)/SrTiO\(_3\) superlattices using ultraviolet Raman spectroscopy. In the low energy spectral region, acoustic phonon doublets are observed. These are due to the artificial superlattice periodicity and consequent folding of the acoustic phonon dispersion. From the study of samples with different BaTiO\(_3\)/SrTiO\(_3\) layer thicknesses the effective sound velocities within each of the layers are obtained.

1. Introduction and motivation

The study of vibrational and thermal properties at the nanometric scale also referred to as “nano-phononics”, related to the engineering and design of terahertz (THz) acoustic devices, has attracted much attention in the last few years from both the basic research and from the applications point of view. The recent possibility to confine acoustic phonons in cavities\([1, 2]\), to enhance the phonon-photon interaction \([2]\), to generate coherent and monochromatic acoustic modes\([3, 4, 5, 6]\), as well as the development of new techniques to study these processes, opened a promising path towards the conception of phonon devices including sound amplification by stimulated emission of radiation. Acoustic phonon cavities \([1]\) and acoustic Bragg reflectors are interesting since they could serve as the required feedback system for such a “phonon laser”.

The search for additional mechanisms to generate and manipulate phonons, and to control their interaction with light and electronic excitations \([5, 7]\), led to the investigation and search for new materials with additional or different properties. Multifunctional oxides, mostly perovskite oxides, are well known for their versatile properties. Their conducting, magnetic or electric (e.g. piezoelectric or ferroelectric) properties can be tuned by changing composition, strain, external fields, etc. Thanks to the recent striking advances in the high quality epitaxial growth of such multifunctional oxides \([8, 9]\), a door to an interesting nearly unexplored and promising research field has been opened. Heterostructures of such compounds combine the bulk properties together with the new effects that come from the reduction of size to the nanoscale, and the new imposed electrostatic and mechanical boundary conditions due to the epitaxial alternate layering of the

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Figure 1. Scheme of the band structure of SrTiO$_3$ (STO). The energy corresponding to visible light falls well below the absorption edge, whereas for ultraviolet excitation (UV) the energy, being slightly above, leads to a much shorter penetration and resonant excitation of the sample.

Figure 2. Typical room temperature back-scattering Raman spectrum, obtained for a [BTO$_m$/STO$_n$]$_N$ SL for UV light excitation ($\lambda_L=325$ nm). The inset shows a sketch of the sample: n(m) stands for the STO(BTO) layer width in number of unit cells, and $d_{SL}$ for the SL’s period.

materials [8]. Recently heterostructures of oxide materials such as BaTiO$_3$ (BTO) and SrTiO$_3$ (STO) have been shown to have a strain-enhanced ferroelectric polarized phase, with a transition temperature that can be tuned (from ~ 150K to ~ 600K) by varying the thicknesses of the BTO and STO layers [8]. Since piezoelectricity and ferroelectricity are intimately related to crystal deformation, and since these materials are known to have a strong opto-acoustic coupling, such structures are very attractive for the conception of efficient phonon devices operating at THz frequencies and for manipulating charge and light by using sound. Moreover the viability of the design and fabrication of THz acoustic Bragg reflectors and cavities based on BTO and STO has been recently demonstrated, as well as their superior acoustic properties as compared to semiconductor (GaAs/AlAs) based structures [9].

In the present work we study the folded acoustic vibrations of BTO/STO based superlattices (SLs) using high resolution ultraviolet (UV) Raman scattering. Different SLs with varying period and layer thicknesses are studied, and effective sound velocities within each of the layers are derived.

2. Sample description and experimental details

The analyzed BTO/STO SLs were grown by reactive-MBE on (001) oriented SrTiO$_3$ substrates. The SLs are denoted by [BTO$_m$/STO$_n$]$_N$, where $n$ and $m$ refer to the thickness in unit cells (UC) of the respective BaTiO$_3$ and SrTiO$_3$ layers, and $N$ is the number of the repeated SLs periods. A sketch of the samples is shown in the inset of Fig. 2. High-resolution transition electron microscopy and X-ray diffraction (XRD) reveal the outstanding quality of the samples [8, 9]. And from XRD the period ($d_{SL}$) of each SL was derived. For further details on sample growth and structural characterization refer to Refs.[8, 9] and references therein. The samples were studied by ultraviolet (UV) Raman spectroscopy. As schematically shown for STO in Fig. 1, these oxides have very large electronic band-gaps $E_g$(STO) $\approx$ 3.4 eV (365 nm) and $E_g$(BTO) $\approx$ 3.35 eV (381 nm), and are therefore completely transparent to visible light. In addition, the SL full thickness is typically < 150 nm. Since the Raman efficiency for visible excitation of such thin samples is very small, their contribution is overwhelmed by that due
to the substrate. For UV excitation, the photon energy is above the band gap, leading to a stronger absorption and consequently to a much shorter penetration depth (of the order of the sample width). In addition, for these excitation conditions electronic resonant contributions to the Raman process are also present thus amplifying the Raman efficiency. This makes UV Raman spectroscopy a very suited technique to characterize these samples [8]. All experiments shown in this work were performed at room temperature in back-scattering geometry using the $\lambda_L=325$ nm UV line of a He-Cd laser. For the detection we used a triple UV-optimized spectrometer in subtractive configuration to provide high resolution ($\sim 3$ cm$^{-1}$) and an efficient stray light reduction. We were able to measure spectral features down to $\sim 10$ cm$^{-1}$.

3. Results and discussion

Figure 2 shows an example of a typical room temperature UV Raman spectrum of a [BTO$_4$/STO$_4$]$_{25}$ SL. In the optical phonon region, first order Raman peaks can be identified (see Ref.[8] for details). In the low energy region the first zone center folded acoustic (FA) phonon doublet is observed. These peaks are an additional corroboration of the excellent periodicity and quality of these samples, and will be the central issue of this work. Figure 3 (right panel), shows the detail of the highlighted region of Fig. 2. This doublet appears due to the new artificial periodicity imposed by the multilayered structure [10]. The consequent folding of the acoustic phonon dispersion and the opening of forbidden “mini-gaps”, is shown in Fig. 3 (left panel). The vertical dotted line indicates the phonon wave vector ($q=2k_L$) that is accessible to Raman experiments for the used scattering configuration and excitation wave length ($\lambda_L$). Here the wave vector of the light in the sample is $k_L = \frac{2\pi}{\lambda_L} n_{eff}$, and the effective refraction index $n_{eff}$ was measured using spectroscopic ellipsometry. The position for both peaks of the doublet are shown with circles: empty and full for the low or higher energy peak, respectively. The calculated center between them is indicated by a cross.

For a sample set of SLs with fixed STO layer width ($n=4$) the measured energy of the doublet is plotted as function of the BTO thickness ($m$) in Fig. 4. The dotted line shows the calculated energy of the doublet center, using a Rytov model [10]. The effective sound velocities within each of the layers, that best fit the complete set of measured data are $v_{BTO} \sim 4870$ m/s and $v_{STO} \sim 7970$ m/s. Although the SLs were as thin as 3 UC per period, we found that these
Figure 4. Position of the FA phonon doublet for a set of SL’s with fixed STO layer width (n=4) and varying BTO width (m), derived from UV Raman spectra. The position for the low(high) energy peak corresponds to the full(empty) circles, and the doublet centers are indicated by a crosses. The dotted line corresponds to the calculation of the doublet center using a Rytov model and the effective sound velocities ($v_{BTO}$ and $v_{STO}$), which best fit the experimental center.

values are in agreement with the bulk sound velocities for acoustic longitudinal phonons given in the literature [11]. The value for $v_{BTO}$ is found to be slightly smaller, in consistency with the BTO’s unit cells expansion in the c-axis (001) direction due to the in-plane compressive strain [8].

4. Conclusions
We investigated high quality oxide BaTiO$_3$/SrTiO$_3$ based epitaxial multilayers using ultraviolet Raman spectroscopy. The folded acoustic phonon doublets were observed, which appear due to the new artificial periodicity. Analyzing the central position of the doublet for different samples, effective sound velocities in each layer have been derived.

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