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Absence of a $PbTiO_3$ phase transition in $PbTiO_3/BaTiO_3$ superlattices

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Abstract

We have performed X-ray diffraction and Raman spectroscopy on three $PbTiO_3/BaTiO_3$ superlattices (PTO/BTO) from room temperature (RT) to 600°C. The superlattices were 4000 Å thick and the modulation wavelengths Λ, with equally thick layers of PTO and BTO, were 136, 187 and 357 Å. The samples were laser deposited onto single crystal MgO substrates buffered with 50 Å of $SrTiO_3$ (STO). We observe no X-ray evidence of a phase transition in the PTO layers of these three superlattice samples up to 600°C. This result was reinforced by X-ray modeling of the samples. We also monitored the E(1TO) or "soft " mode by Raman spectroscopy up to 550°C and found only a linear decrease of mode frequency with temperature for all three superlattices: another sign that no phase transition is taking place in this temperature range. © 2001 Elsevier Science Ltd.

Keywords: Ferroelectric properties; Films; Perovskites; Spectroscopy; X-ray methods

1. Introduction

We have recently used the ferroelectric materials $PbTiO_3$ (PTO) and $BaTiO_3$ (BTO) to fabricate a series of superlattices[1] with modulation wavelengths Λ varying between 48 and 357 Å. These were grown on MgO substrates buffered with 50 Å of $SrTiO_3$ so as to promote *c*-axis growth and to make the multilayers amenable to spectroscopic investigation. In our room temperature study of these superlattices, we found, by modelling the X-ray diffraction results and by Raman spectroscopy, that, surprisingly, the *a*-axis of the PTO layers of the superlattices are oriented perpendicular to the film surface and so the multilayer structural arrangement is *a*-PTO/*c*-BTO. This is in contrast to thin films of PTO grown on buffered MgO in which the orientation is predominantly *c*-axis. One reason for constructing artificially modulated structures using ferroelectrics as constituents, aside from observing structural anomalies, is to investigate the role that size plays in the paraelectric to ferroelectric transition. The role of size is becoming increasingly relevant as ferroelectric materials begin to find their way into integrated microelectronic and micromechanical systems. Specht et al.[2] have previously investigated $KTaO_3/KNbO_3$ superlattices in which they observed a suppression of the Curie temperature as a function of decreasing $KNbO_3$ layer thickness. The phase transition temperature saturated below a certain layer thickness because, they claimed, interlayer coupling was taking place. In this work, we investigate, by X-ray diffraction and Raman spectroscopy, to temperatures well above the PTO bulk value of 493°C, three anomalously structured *a*-PTO/*c*-BTO superlattices of wavelengths 136, 187 and 357 Å. Hence this work, an extension of Ref. 1 to higher temperatures, looks into the possible effects that artificial structuring has on the phase transition and what effect, if any, layer thickness has on the physical behavior of the constituent materials.

2. Experimental procedure

The films were deposited using pulsed laser ablation. The 50 Å STO buffer layer was deposited at a substrate temperature T_s of 800°C in a partial oxygen pressure P_{O2} of 10^{-3} mbar. The PTO and BTO layers were deposited at $T_s = 640$°C and $P_{O2} = 0.1$ mbar. The

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multilayers were fabricated with nominally equal thickness PTO and BTO. RHEED streaks, indicative of smooth surfaces, were observed for all films presented in this study. The Raman spectra were recorded in backscattering geometry using a microprobe device, which focuses the laser beam to a spot of 2 μm. The spectral resolution was set to 3 cm^{-1} and the samples were heated up to 550°C. The X-ray measurements were performed using an in-house designed goniometer permitting high resolution measurements up to 600°C. More details on the deposition and experimental procedures may be found in Refs. 1 and 3 and the references contained therein.

3. Results and discussion

In order to appreciate better the multilayer results we first present X-ray diffraction results on a 2500 Å thick PTO film grown on a STO buffered (100) MgO substrate. Fig. 1 shows the evolution of the lattice parameters as a function of temperature up to 600°C. At low temperatures the PTO is tetragonal and, in addition, *c*- and *a*-domains coexist[4] in films grown on MgO. Buffering the MgO with STO reduces the percentage of a-domains in the PTO film.[3] Even so, because of the presence of both domains, we are able to track the *a*- and *c*-axis evolution as a function of temperature using only θ–2θ diffractometry. As the temperature is increased the percentage of *a*-domains increases at the expense of the *c*-domains[3] and the values of the respective lattice parameters merge towards a single value. The Curie temperature marks the transition from the tetragonal to the cubic phase. From Fig. 1 we can assign a Curie temperature of about 505°C to this PTO film. This is to be compared with the 493°C value[5] for the bulk material. We tentatively assign the increase of T_C to the strains produced by the film-STO-buffered substrate mismatch.

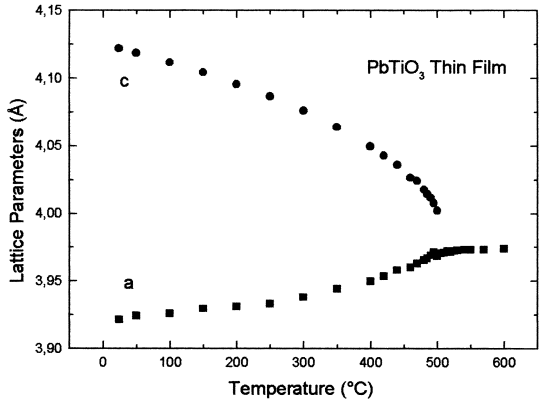

Fig. 1. Low temperature tetragonal phase and high temperature cubic phase, determined by θ-2θ X-ray diffractometry, of a 2500 Å $PbTiO_3$ film deposited on $SrTiO_3$ buffered MgO substrate.

BTO films grown on MgO are single phase. We have determined by an asymmetric rocking curve technique[6] that 2500 Å thick BTO films at room temperature are cubic. However, from X-ray diffraction we observe an anomaly, in the form of a change in slope, in the lattice parameter at about 120°C, which happens to be the Curie temperature of bulk BTO. The results[3] of thin film BTO and of PTO on buffered MgO will be the subject of a future publication.

We now turn to the PTO/BTO multilayers. We present a typical diffraction pattern of a PTO/BTO multilayer in Fig. 2 as an aid to the following discussion on our designation the average lattice parameter a_{ave}. In Fig. 2 we observe a series of satellite peaks in the vicinity of the first and second order diffraction peaks of bulk PTO and BTO. The angular distance between the peaks is inversely related to the multilayer periodicity Λ. Since it is the entire superlattice structure that diffracts, the Bragg diffraction condition for a periodic superlattice is

$$n\lambda_x = 2\Lambda\sin\theta_n \quad (1)$$

where n is the order of the diffraction peak, λ_x is the X-ray wavelength and θ_n is the angular position of the n^{th} order peak. The diffraction order n corresponds to a value much greater than the orders 1 or 2 usually encountered in diffraction from the individual species. For example, the most intense diffraction peak from the $\Lambda = 187$ Å multilayer is located at a 2θ angle of 22.2°. For CuK_α radiation, this corresponds to order $n = 47$. In fact, each superlattice diffraction peak corresponds to a certain distinct order and its 2θ position allows us to determine the periodicity of the superlattice structure. Now, by following the temperature evolution of one satellite peak, we gain access to the temperature dependence of the superlattice wavelength. The wavelength Λ is the weighted average of the interplanar lattice spacing of the constituents, and is given by

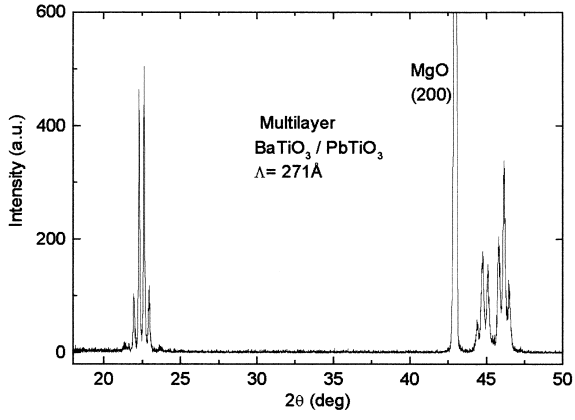

Fig. 2. The room temperature X-ray diffraction pattern of a PTO/BTO superlattice having a modulation wavelength of 271 Å.

$$\Lambda = N_1 d_1 + N_2 d_2 \quad (2)$$

N_1 and N_2 are the number of unit cells respectively of PTO and BTO, d_1 and d_2 are the respective lattice parameters of PTO and BTO.

Thus any anomaly in the temperature variation of the interlayer spacings d_1 and d_2 should be detected in the temperature evolution of Λ. From the angular position of a satellite peak and using Eq. (1), we define $a_{ave} = \Lambda/n$, which is the weighted average of the interplanar lattice spacing of the PTO/BTO superlattice.

Thus, a_{ave} is what we plot versus temperature in Fig. 3 for the Λ = 136 Å PTO/BTO superlattice. There are two aspects of the curves worthy of note. First, there is the change in slope of a_{ave} in the vicinity of 120°C. Recall that 120°C is the Curie temperature of bulk BTO. Second is the *absence* of any anomaly in a_{ave} at higher temperatures up to 600°C : there is no indication of a phase transition in the vicinity of the PTO bulk value of 493°C. To get an idea of what we should see if there were a phase transition in the PTO layers, we have simulated a $\Lambda = 136$ Å *a*-PTO/*c*-BTO superlattice in which the temperature variations of the lattice parameters were those determined experimentally from the individual 2500 Å PTO, for which we do indeed observe a change in phase near 500°C (see Fig. 1 above) and BTO thin films (not shown) grown on MgO. In constructing this fictional superlattice we have set $N_1 = N_2 = 17$ and we have chosen the order of diffraction $n = 34$, which is the most intense peak for this wavelength. Fig. 4 represents the temperature evolution of a_{ave} for this fictive superlattice. The contrast is striking between Figs. 3 and 4 in the vicinity of 500°C, and strongly indicates that if there were a phase transition taking place in the PTO layers, we would be able to detect it using X-ray diffractometry. We observe similar featureless behavior of a_{ave}(T) for the Λ = 187 and 357 Å superlattices. Thus, we have obtained no evidence from X-ray diffraction for a structural phase transition in the PTO layers in the *a*-PTO/*c*-BTO superlattices. This startling observation does not stand alone. We will now present Raman scattering results on these three superlattices, at temperatures up to 550°C, which further support the lack of phase transition.

Raman spectra have been taken for the three multilayer samples as well as for the 2500 Å PTO sample of Fig. 1. From our previous (room temperature) study[1] we demonstrated from symmetry considerations that only the *a*-oriented PTO layers produce detectable Raman modes from the PTO/BTO superlattices. Here, we monitor the E(1TO) mode — the so-called soft mode which pilots the ferroelectric phase transition in the perovskites[7] — up to 550°C. Previous Raman investigations on single crystal bulk PTO show[8] that the soft mode frequency decreases non-linearly — as $(T–T_c)^{\alpha}$ where $\alpha \leqslant 0.5$ over a large temperature range — as a function of temperature and vanishes at the phase transition. The Raman signal vanishes because of the cubic symmetry of the high temperature paraelectric phase: the material is then Raman inactive. Thick PTO films grown on MgO[9] also follow similar non-linear behavior up to a certain temperature, roughly the Curie temperature, before saturating at a certain frequency. This saturation of the signal is due to substrate-film lattice strains which prevent the films from attaining full cubic symmetry: the film remains Raman active.

In Fig. 5 we present the soft mode frequency as a function of T for both the 2500 Å PTO thin film and for the 136 and 187 Å PTO/BTO multilayer samples. The scatter in the data is related to the small amount of material available to produce a Raman signal in the thin film and multilayer materials. Even so, the trends in the data as a function of temperature are apparent. The linear decrease with temperature of both multilayer soft mode frequencies clearly differs from the dependence of the PTO thin film sample whose behavior is similar to that

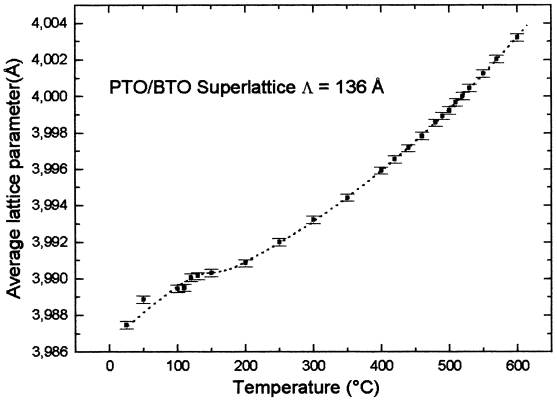

Fig. 3. The average lattice parameter a_{ave} (see text) versus temperature for a $\Lambda = 136$ Å *a*-PTO/*c*-BTO superlattice fabricated by laser ablation. The dotted lines are a guide to the eye.

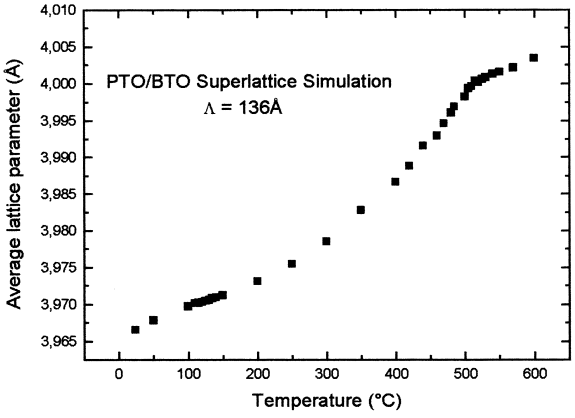

Fig. 4. The average lattice parameter a_{ave} (see text) versus temperature for a simulated $\Lambda = 136$ Å *a*-PTO/*c*-BTO superlattice using the a (T) values of the PTO film of Fig. 1 and the $c(T)$ values of a 2500 Å BTO thin film from Ref. 3.

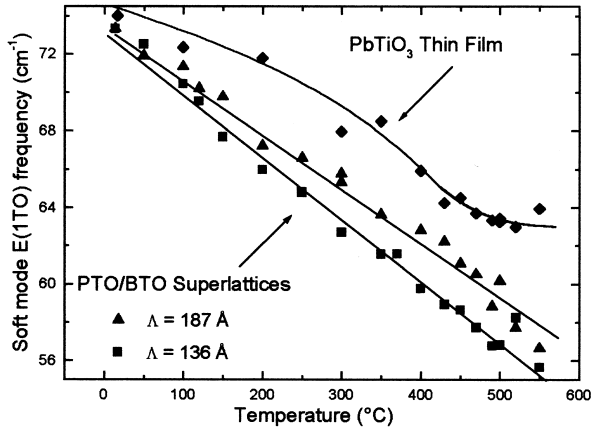

Fig. 5. The E(1TO) soft mode frequency versus temperature for the PTO film of Fig. 1 and the $\Lambda = 136$ and 187 Å *a*-PTO/*c*-BTO superlattices. The lines are a guide to the eye. In addition to being softer than the thin film mode, the superlattice soft modes decrease linearly with temperature up to 550°C, unlike thin film or bulk PTO samples.

for the PTO thick film discussed in the preceding paragraph. For this 2500 Å PTO film we can assign a T_c of about 500°C, which is where saturation of the soft mode frequency sets in. However, for the multilayer samples, it would be problematic to assign a T_c since the linear decrease of the soft mode frequency shown in Fig. 5 makes it highly improbable that a phase transition is taking place. It seems rather that the linear softening of this mode is simply a reflection of the lattice dynamics of the multilayers as they are heated. We observe similar linear decrease of the frequency for the third superlattice sample ($\Lambda = 357$ Å) investigated in this study.

In conclusion, we have performed X-ray diffraction measurements up to 600°C and Raman light scattering measurements up to 550°C on three different *a*-$PbTiO_3$/*c*-$BaTiO_3$ superlattices grown on single crystal MgO substrates buffered with $SrTiO_3$. We observe no indication of a structural phase transition in the $PbTiO_3$ superlattice layers. This is in contrast with our X-ray and Raman measurements which clearly indicate that such a transition taking place in a 2500 Å thin film of $PbTiO_3$ grown on STO buffered MgO.

Acknowledgements

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References

1. Le Marrec, F., Farhi, R., El Marssi, M., Dellis, J.-L., Karkut, M. G. and Ariosa, D., Ferroelectric $PbTiO_3/BaTiO_3$ superlattices: growth anomalies and confined modes. *Phys. Rev. B*, 2000, **61**, R6447–R6450.
2. Specht, E. D., Christian, H. -M., Norton, D. P. and Boatner, L. A., X-Ray diffraction measurement of the effect of layer thickness on the ferroelectric transition in epitaxial $KTaO_3$/$KNbO_3$ multilayers. *Phys. Rev. Lett.*, 1998, **80**, 4317–4320.
3. Le Marrec, F., *Croissance, etude structurale et spectroscopie Raman de films minces et super-réseaux d'oxydes ferroélectriques basés sur $PbTiO_3$ et $BaTiO_3$*. PhD thesis, University of Picardy Jules Verne, Amiens, France, 2000.
4. Foster, C. M., Li, Z., Buckett, M., Miller, D., Baldo, P. M., Rehn, L. E., Bai, G. R., Guo, D., You, H. and Merkle, K. L., Substrate effects on the structure of epitaxial $PbTiO_3$ thin films prepared on MgO, $LaAlO_3$ and $SrTiO_3$ by metalorganic chemical-vapor depostion. *J. Appl. Phys.*, 1995, **78**, 2607–2622.
5. Jaffe, B., Cook, W. R. and Jaffe, H., *Piezoelectric Ceramics*. Academic Press, New York, 1971.
6. Kang, Y. M., Kang, Ku. J. and Baik, S., Crystallographic characterization of tetragonal (Pb,La)TiO_3 epitaxial thin films grown by pulsed laser deposition. *J. Appl. Phys.*, 1995, **78**, 2601–2606.
7. Cochran, W., Crystal stability and the theory of ferroelectricity. *Adv. Phys.*, 1960, **9**, 387–423.
8. Burns, G. and Scott, B., Lattice modes in ferroelectric perovskites: $PbTiO_3$. *Phys. Rev. B*, 1973, **7**, 3088–3101.
9. Yuzyuk, Y. I., Farhi, R., Lorman, V. L., Rabkin, L. M., Sapoznikov, L. A., Sviridov, E. V. and Zakharchenko, I. N., A comparative Raman study of ferroelectric $PbTiO_3$ single crystal and thin film prepared on MgO substrate. *J. Appl. Phys.*, 1998, **84**, 452–457.