

Structural evidence for enhanced polarization in a commensurate short-period BaTiO₃/SrTiO₃ superlattice

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A short-period (BaTiO₃)₆/(SrTiO₃)₅ superlattice was characterized by x-ray diffraction and transmission electron microscopy. The superlattice is epitaxially oriented with the *c* axes of BaTiO₃ and SrTiO₃ normal to the (001) surface of the SrTiO₃ substrate. Despite the large in-plane lattice mismatch between BaTiO₃ and SrTiO₃ (~2.2%), the superlattice interfaces were found to be nearly commensurate. The crystallographic *c/a* ratio of the superlattice was measured and the results agree quantitatively with first-principles calculations and phase-field modeling. The agreement supports the validity of the enhanced spontaneous polarization predicted for short-period BaTiO₃/SrTiO₃ superlattices. © 2006 American Institute of Physics. [DOI: 10.1063/1.2335367]

Superlattices of thin ferroelectric and nonferroelectric perovskite layers have been predicted^{1,2} or reported³⁻⁹ to possess many improved physical properties over homogeneous thin films of the same compositions. Among these are reported enhancements of dielectric constants and remanent polarization in short-period BaTiO₃/SrTiO₃ superlattices.^{3,5} While such reports need to be carefully evaluated considering that the movement of space charge in the superlattices can spuriously produce an apparent significant enhancement of dielectric constant,^{10,11} the improved properties could result from the lattice strain sustained in BaTiO₃ due to its ~2.2% lattice mismatch with SrTiO₃.^{3,5}

Recently, Neaton and Rabe performed first-principles calculations on a series of short-period BaTiO₃/SrTiO₃ superlattices commensurately strained to an underlying SrTiO₃ substrate to investigate their ground-state structures and polarizations.¹² They predicted an overall enhancement of the spontaneous polarization of these ferroelectric superlattices, including the presence of a spontaneous polarization within the SrTiO₃ layers. While an increase of polarization in BaTiO₃ is expected,¹³ the prediction of *unstrained* SrTiO₃ being tetragonal and polar is, at first, surprising. Although strain is known to induce ferroelectricity in SrTiO₃,^{14,15} including SrTiO₃ in superlattices,^{6,7} thick unstrained SrTiO₃ is not ferroelectric at any temperature. Neaton and Rabe, however, predicted that thin unstrained SrTiO₃ layers in proximity to ferroelectric BaTiO₃ polarize due to electrostatic effects. Their calculations shed light on the understanding of ferroelectric superlattices at the atomic scale.

Testing these predictions is challenging, however, due to the difficulty in fabricating such short-period superlattices with sufficient structural perfection. Although short-period BaTiO₃/SrTiO₃ superlattices have been produced by various

methods, convincing evidence of a high degree of structural perfection in terms of interfacial abruptness and coherency has rarely been reported.^{16,17}

Over the last few years, significant progress has been achieved in controlling the synthesis of ferroelectric superlattices at the atomic scale using reactive molecular-beam epitaxy (MBE).^{18,19} In the present letter, we discuss the growth of a short-period superlattice consisting of a six-unit-cell thick BaTiO₃ layer followed by a five-unit-cell thick SrTiO₃ layer, repeated 20 times. We abbreviate this configuration by [(BaTiO₃)₆/(SrTiO₃)₅]₂₀. X-ray diffraction (XRD) and high-resolution transmission electron microscopy (HRTEM) results are presented to demonstrate the structural perfection of this coherent superlattice with abrupt interfaces.

The [(BaTiO₃)₆/(SrTiO₃)₅]₂₀ superlattice thin film was grown by reactive MBE at a substrate temperature of 650 °C and an oxygen background pressure of 2 × 10⁻⁷ Torr.^{19,20} After growth the film was annealed in 1 atm of flowing oxygen at 1000 °C for 13 h to reduce the concentration of oxygen vacancies. HRTEM was performed in a JEOL 4000EX operated at 400 kV. The first-principles calculations are performed with the Vienna *ab initio* simulation package (VASP),^{21,22} and the details can be found elsewhere.¹²

Figure 1 shows the θ -2 θ x-ray diffraction scan of an as-grown [(BaTiO₃)₆/(SrTiO₃)₅]₂₀ superlattice. The full widths at half maximum of the 00 $\bar{2}0$ superlattice reflection are 0.26° and 0.22° in 2 θ and ω , respectively. These values are close to the instrumental resolution of our Picker four-circle x-ray diffractometer. The presence and sharpness of the superlattice reflections indicate its long-range structural coherence. The bilayer periodicity of the superlattice determined by a Nelson-Riley analysis²³ of the 00 ℓ superlattice reflections is 44.5 ± 0.2 Å, compared to the 43.74 Å of a (BaTiO₃)₆/(SrTiO₃)₅ superlattice assuming unstrained *c*-axis BaTiO₃ and SrTiO₃ lattice constants. A ϕ scan of the 1011

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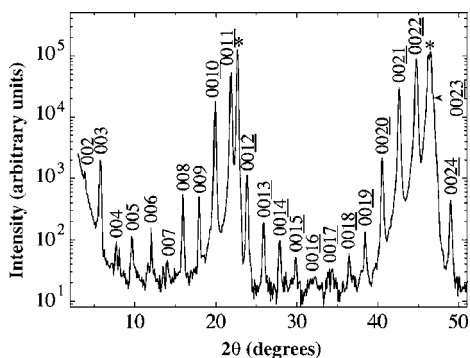


FIG. 1. θ - 2θ x-ray diffraction pattern of a $[(\text{BaTiO}_3)_6/(\text{SrTiO}_3)_5]_{20}$ superlattice grown on (001) SrTiO_3 indicating a superlattice period of 44.5 ± 0.2 Å. Substrate peaks are labeled with “*”.

superlattice reflection of the thin film (plot not shown) reveals that the film is epitaxially grown on the (001) surface of SrTiO_3 and has an in-plane film-substrate orientation relationship of $\text{BaTiO}_3\langle 010 \rangle \parallel \text{SrTiO}_3\langle 010 \rangle$. From both scans the in-plane lattice constant is determined to be $a = 3.91 \pm 0.01$ Å, resulting in a c/a ratio of 11.38 ± 0.06 for the $(\text{BaTiO}_3)_6/(\text{SrTiO}_3)_5$ supercell.

A careful examination throughout the thin area of a plane-view TEM specimen (images not shown) reveals a linear density of misfit dislocations of $2.9 \times 10^3/\text{cm}$, which corresponds to the preservation of approximately 99.5% of the in-plane lattice mismatch strain in the BaTiO_3 layers.

Figure 2 is a cross-sectional HRTEM image of the same $[(\text{BaTiO}_3)_6/(\text{SrTiO}_3)_5]_{20}$ superlattice after anneal. The HRTEM images obtained at specific imaging conditions appropriate to the “chemical lattice imaging” technique²⁴ re-

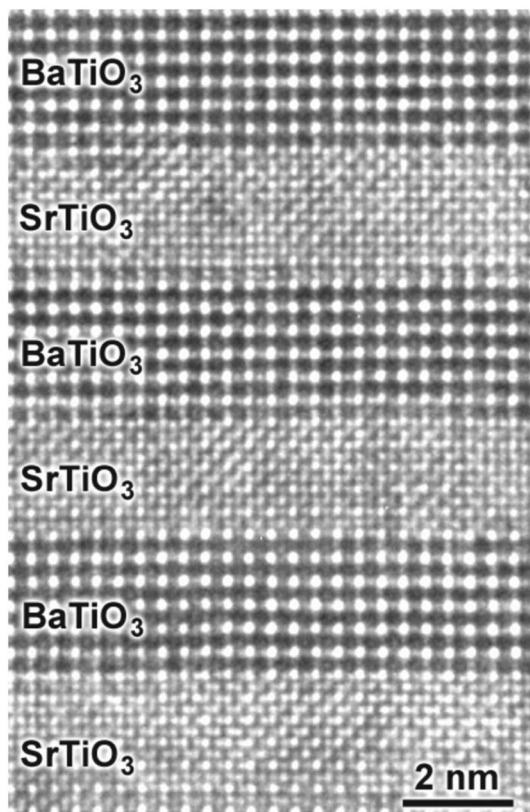


FIG. 2. An HRTEM image of a portion of the same $[(\text{BaTiO}_3)_6/(\text{SrTiO}_3)_5]_{20}$ superlattice as analyzed in Fig. 1 with the incident electron beam along the [100] zone axis of SrTiO_3 .

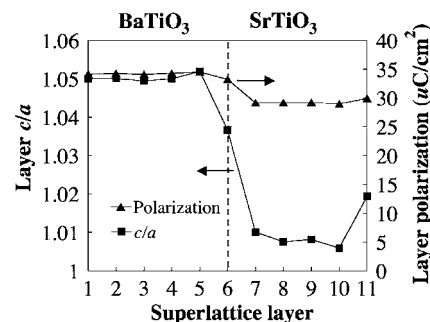


FIG. 3. Local crystallographic c/a ratio and polarization within BaTiO_3 and SrTiO_3 perovskite unit cells in one period of the superlattice structure based on atomic positions obtained from the first-principles calculation. The vertical dashed line indicates the interface between BaTiO_3 and SrTiO_3 .

veal that no significant interdiffusion of Ba^{2+} and Sr^{2+} takes place during annealing.²⁵

The crystallographic c/a ratio of the BaTiO_3 and SrTiO_3 layers was measured by a quantitative analysis of the HRTEM images using Gatan’s DIGITALMICROGRAPH software. In the HRTEM images, the positions of the intensity maxima at each barium and strontium atom column (bright spots in Fig. 2) were taken to measure the lattice constant. The measured c/a ratios are $\sim 1.05 \pm 0.02$ and 1.00 ± 0.01 for BaTiO_3 and SrTiO_3 , respectively. Note that the c/a ratio of bulk BaTiO_3 is 1.013. A substantial increase of the tetragonality of BaTiO_3 is evident. In contrast, the c/a ratio of the SrTiO_3 layers remains very close to unity.

Recent experimental results on thin PbTiO_3 thin films²⁶ and $\text{PbTiO}_3/\text{SrTiO}_3$ superlattices²⁷ suggests that a change in tetragonality is related to a change in polarization. To understand the effect of increased tetragonality upon the polarization of our superlattice, first-principles calculations were performed. The atomic positions were calculated by constraining the in-plane lattice parameter of a periodically repeated $(\text{BaTiO}_3)_6/(\text{SrTiO}_3)_5$ supercell to the lattice parameter of SrTiO_3 determined by first-principles calculations within the local density approximation ($a = 3.863$ Å) and relaxing the internal structural parameters with the space group $P4mm$, allowing a nonzero polarization vector parallel to c . This procedure predicts c/a of 11.34 for the supercell, in good agreement with the measured value from XRD 11.38 ± 0.06 .

For each perovskite unit cell layer in one period of the superlattice, we plot in Fig. 3 the calculated local c/a ratio and polarization, the latter estimated using first-principles bulk effective charges. The effects of both strain and electrostatics are clearly evident. As expected from electrostatic arguments,¹² the polarization appears to be nearly constant throughout the superlattice layers except near the interface, where a somewhat exaggerated discontinuity arises from approximating the interface polarization with bulk effective charges. For the BaTiO_3 layers, the average local c/a ratio is computed to be ~ 1.0503 , and the polarization is $34.27 \mu\text{C}/\text{cm}^2$. Both are significantly larger than for unstrained tetragonal BaTiO_3 , for which we find a calculated c/a ratio of 1.013, in precise agreement with experiment, and a calculated spontaneous polarization¹² of $24.97 \mu\text{C}/\text{cm}^2$, very close to the measured value²⁸ of $26 \mu\text{C}/\text{cm}^2$. The calculations also indicate that the SrTiO_3 layers are tetragonal with an average c/a ratio of 1.008. While significant, the deviation from $c/a = 1$ of SrTiO_3 is too small to be resolved by HRTEM. Summing the contribution

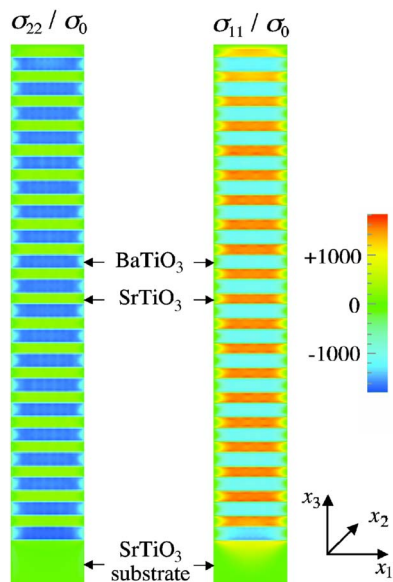


FIG. 4. (Color online) Simulated stresses σ_{22} and σ_{11} in the TEM specimen of the $[(\text{BaTiO}_3)_6/(\text{SrTiO}_3)_5]_{20}$ superlattice calculated using phase-field modeling. The normalization factor is $\sigma_0=2.6$ MPa. Compressive and tensile stresses are indicated by “-” and “+”, respectively.

from each layer, we estimate the overall polarization to be $31.2 \mu\text{C}/\text{cm}^2$ from the calculation, larger than that of bulk BaTiO_3 . (A rigorous Berry phase calculation of the superlattice polarization gives $29.375 \mu\text{C}/\text{cm}^2$, in excellent agreement with our estimate based on bulk effective charges.)

We note that the stress in the TEM specimen of the superlattice differs from that in the original superlattice due to the thin foil nature of the TEM specimen. To estimate this effect on c/a , the stress distribution and the lattice constants of the superlattice in the TEM sample were calculated by phase-field modeling. In the modeling, BaTiO_3 and SrTiO_3 were assumed to possess their bulk elastic and thermodynamic properties. According to HRTEM image simulations, the thickness of the region imaged in Fig. 2 is in the range of 10–15 nm in the electron beam direction (denoted by x_1). The axis perpendicular to the surface of the substrate is denoted as x_3 and the in-plane axis orthogonal to x_1 is denoted as x_2 . A thin foil with thickness (in the x_1 direction) of 13.6 nm and superlattice film height and substrate height of 88 and 100 nm, respectively, in the x_3 direction was modeled. Periodic boundary conditions were used in the x_2 direction, implying an infinite length along this direction.

The calculated stress distribution is shown in Fig. 4. One can see that the BaTiO_3 layers endure an unrelaxed compressive stress σ_{22} due to the underlying SrTiO_3 substrate and the SrTiO_3 alternative layers and absence of free surface in the x_2 direction, while σ_{22} is close to zero in the SrTiO_3 layers. The stress component σ_{11} , in contrast, is subject to partial relief. Although compressive in the BaTiO_3 layers and tensile in the SrTiO_3 layers, σ_{11} is of the same magnitude in the BaTiO_3 layers and the proximate SrTiO_3 layers. A nearly 30% stress relief of σ_{11} in the BaTiO_3 layers is calculated at the center part of the superlattice thin film. According to the model, the average over the entire TEM foil of the lattice constants of the BaTiO_3 and SrTiO_3 layers in the superlattice are $a_1=3.976 \text{ \AA}$, $a_2=3.905 \text{ \AA}$, and $c=4.038 \text{ \AA}$ for the BaTiO_3 layers and $a_1=3.958 \text{ \AA}$, $a_2=3.905 \text{ \AA}$, and

$c=3.879 \text{ \AA}$ for the SrTiO_3 layers, respectively. Note that a_1 is no longer equal to a_2 in the TEM specimen. As the HRTEM image is a projection of the crystal lattices along the x_1 axis, the lattice parameters measured from HRTEM images are c and a_2 . The c/a_2 ratio of the BaTiO_3 layers obtained from modeling is 1.034, which is slightly smaller than the value measured from the HRTEM images (1.05 ± 0.02).

The lattice constants of the superlattice for the as-grown film (before it was thinned for TEM) were also calculated by phase field modeling. The resulting $c=44.30 \text{ \AA}$, $a=3.905 \text{ \AA}$, and $c/a=11.34$ are in excellent agreement with the first-principles calculations ($c/a=11.34$) and XRD measurement ($c=44.5 \pm 0.2 \text{ \AA}$, $a=3.91 \pm 0.01 \text{ \AA}$, and $c/a=11.38 \pm 0.06$).

These results suggest an enhanced polarization in commensurate short-period $\text{BaTiO}_3/\text{SrTiO}_3$ superlattices.

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- ¹S. Li, J. A. Eastman, J. M. Vetrone, R. E. Newnham, and L. E. Cross, *Philos. Mag. B* **76**, 47 (1997).
- ²N. Sai, B. Meyer, and D. Vanderbilt, *Phys. Rev. Lett.* **84**, 5636 (2000).
- ³T. Shimuta, O. Nakagawara, T. Makino, S. Arai, H. Tabata, and T. Kawai, *J. Appl. Phys.* **91**, 2290 (2002).
- ⁴M. H. Corbett, R. M. Bowman, J. M. Gregg, and D. T. Foord, *Appl. Phys. Lett.* **79**, 815 (2001).
- ⁵L. Kim, D. Jung, J. Kim, Y. S. Kim, and J. Lee, *Appl. Phys. Lett.* **82**, 2118 (2003).
- ⁶H.-M. Christen, L. A. Knauss, and K. S. Harshvardhan, *Mater. Sci. Eng., B* **56**, 200 (1998).
- ⁷H. M. Christen, E. D. Specht, S. S. Silliman, and K. S. Harshvardhan, *Phys. Rev. B* **68**, 020101 (2003).
- ⁸M. R. Warusawithana, E. V. Colla, J. N. Eckstein, and M. B. Weissman, *Phys. Rev. Lett.* **90**, 036802 (2003).
- ⁹H. N. Lee, H. M. Christen, M. F. Chisholm, C. M. Rouleau, and D. H. Lowndes, *Nature (London)* **433**, 395 (2005).
- ¹⁰D. O’Neill, R. M. Bowman, and J. M. Gregg, *Appl. Phys. Lett.* **77**, 1520 (2000).
- ¹¹G. Catalan, D. O’Neill, R. M. Bowman, and J. M. Gregg, *Appl. Phys. Lett.* **77**, 3078 (2000).
- ¹²J. B. Neaton and K. M. Rabe, *Appl. Phys. Lett.* **82**, 1586 (2003).
- ¹³A. F. Devonshire, *Philos. Mag., Suppl.* **3**, 85 (1954).
- ¹⁴H. Uwe and T. Sakudo, *Phys. Rev. B* **13**, 271 (1976).
- ¹⁵J. H. Haeni, P. Irvin, W. Chang, R. Uecker, P. Reiche, Y. L. Li, S. Choudhury, W. Tian, M. E. Hawley, B. Craigo, A. K. Tagantsev, X. Q. Pan, S. K. Streiffer, L. Q. Chen, S. W. Kirchoefer, J. Levy, and D. G. Schlom, *Nature (London)* **430**, 758 (2004).
- ¹⁶T. M. Shaw, A. Gupta, M. Y. Chern, P. E. Baston, R. B. Laibowitz, and B. A. Scott, *J. Mater. Res.* **9**, 2566 (1994).
- ¹⁷Z. Y. Wang, T. Yasuda, S. Hatatani, and S. Oda, *Jpn. J. Appl. Phys., Part 1* **38**, 6817 (1999).
- ¹⁸J. C. Jiang, X. Q. Pan, W. Tian, C. D. Theis, and D. G. Schlom, *Appl. Phys. Lett.* **74**, 2851 (1999).
- ¹⁹D. G. Schlom, J. H. Haeni, J. Lettieri, C. D. Theis, W. Tian, J. C. Jiang, and X. Q. Pan, *Mater. Sci. Eng., B* **87**, 282 (2001).
- ²⁰J. H. Haeni, C. D. Theis, and D. G. Schlom, *J. Electroceram.* **4**, 385 (2000).
- ²¹G. Kresse and J. Furthmuller, *Phys. Rev. B* **54**, 11169 (1996).
- ²²G. Kresse and D. Joubert, *Phys. Rev. B* **59**, 1758 (1999).
- ²³J. B. Nelson and D. P. Riley, *Proc. Phys. Soc. London* **57**, 160 (1945).
- ²⁴A. Ourmazd, F. H. Baumann, M. Bode, and Y. Kim, *Ultramicroscopy* **34**, 237 (1990).
- ²⁵W. Tian, Ph.D. thesis, University of Michigan, 2002.
- ²⁶C. Lichtensteiger, J.-M. Triscone, J. Junquera, and P. Ghosez, *Phys. Rev. Lett.* **94**, 047603 (2005).
- ²⁷M. Dawber, C. Lichtensteiger, M. Cantoni, M. Veithen, P. Ghosez, K. Johnston, K. M. Rabe, and J.-M. Triscone, *Phys. Rev. Lett.* **95**, 177601 (2005).
- ²⁸G. Shirane, H. Danner, and P. Pepinsky, *Phys. Rev.* **105**, 856 (1957).