



Abrupt PbTiO₃/SrTiO₃ superlattices grown by reactive molecular beam epitaxy

J. C. Jiang, X. Q. Pan, W. Tian, C. D. Theis, and D. G. Schlom

Citation: [Applied Physics Letters](#) **74**, 2851 (1999); doi: 10.1063/1.124035

View online: <http://dx.doi.org/10.1063/1.124035>

View Table of Contents: <http://scitation.aip.org/content/aip/journal/apl/74/19?ver=pdfcov>

Published by the [AIP Publishing](#)

Articles you may be interested in

[Improved crystalline properties of laser molecular beam epitaxy grown SrTiO₃ by rutile TiO₂ layer on hexagonal GaN](#)

J. Appl. Phys. **106**, 104120 (2009); 10.1063/1.3257259

[Structural and dielectric properties of epitaxial SrTiO₃ films grown directly on GaAs substrates by laser molecular beam epitaxy](#)

J. Appl. Phys. **104**, 054103 (2008); 10.1063/1.2974796

[Morphology and microstructure of BaTiO₃/SrTiO₃ superlattices grown on SrTiO₃ by laser molecular-beam epitaxy](#)

Appl. Phys. Lett. **75**, 3464 (1999); 10.1063/1.125297

[Crystallographic and microstructural studies of BaTiO₃ thin films grown on SrTiO₃ by laser molecular beam epitaxy](#)

J. Vac. Sci. Technol. A **15**, 275 (1997); 10.1116/1.580524

[BaTiO₃ thin films grown on SrTiO₃ substrates by a molecular-beam-epitaxy method using oxygen radicals](#)

J. Appl. Phys. **81**, 693 (1997); 10.1063/1.364209

An advertisement for the journal AIP Applied Photonics. The background is a vibrant orange and red gradient with a bright sunburst effect in the lower right. On the left, there is a small image of the journal cover, which features a blue and white abstract design. A yellow starburst graphic with the words 'OPEN ACCESS' in red is overlaid on the bottom right of the journal cover image. To the right of the journal cover, the text 'Launching in 2016!' is written in a large, white, sans-serif font. Below this, the text 'The future of applied photonics research is here' is written in a smaller, white, sans-serif font. In the bottom right corner, the AIP logo is displayed, consisting of the letters 'AIP' in a large, white, sans-serif font, followed by a vertical line and the words 'APL Photonics' in a smaller, white, sans-serif font.

Abrupt $\text{PbTiO}_3/\text{SrTiO}_3$ superlattices grown by reactive molecular beam epitaxy

J. C. Jiang, X. Q. Pan,^{a)} and W. Tian

Department of Materials Science and Engineering, The University of Michigan, Ann Arbor, Michigan 48109-2136

C. D. Theis and D. G. Schlom

Department of Materials Science and Engineering, Penn State University, University Park, Pennsylvania 16802-5005

(Received 18 June 1998; accepted for publication 11 March 1999)

$\text{PbTiO}_3/\text{SrTiO}_3$ superlattices were grown on (001) SrTiO_3 substrates by reactive molecular beam epitaxy (MBE). Sharp superlattice reflections were observed by x-ray diffraction. High-resolution transmission electron microscopy of a $[(\text{PbTiO}_3)_{10}/(\text{SrTiO}_3)_{10}]_{15}$ superlattice revealed that the $\text{PbTiO}_3/\text{SrTiO}_3$ interface structure is atomically sharp. The superlattice interfaces are fully coherent; no misfit dislocations or other crystal defects were observed in the superlattice by transmission electron microscopy. Selected area electron diffraction patterns indicated that the PbTiO_3 layers are oriented with the c axis parallel to the growth direction. The dimensional control and interface abruptness achieved in this model system indicate that MBE is a viable method for constructing oxide multilayers on a scale where enhanced dielectric effects are expected. © 1999 American Institute of Physics. [S0003-6951(99)02919-8]

Ferroelectric and dielectric superlattices have been extensively studied in recent years, due to their scientific importance and technological promise.¹⁻⁷ Fabrication of such superlattice structures, particularly when controlled on an atomic-layer level, can explore predictions of giant dielectric constants^{8,9} over a wide temperature range⁹ and be used to fabricate new functional devices, e.g., those involving a designed grading of composition in one direction on an atomic scale.^{10,11} Just as the ability to fabricate semiconductor superlattices with unit cell precision enabled the investigation and exploitation of many new electronic and photonic devices, so too should the ability to assemble ferroelectric and dielectric materials at will be expected to lead to improved fundamental understanding of ferroelectric coupling and improved devices that utilize ferroic effects. Lead titanate, PbTiO_3 , together with its solid solutions, is a candidate compound for making superlattices with promising properties. Calculations suggest that a $\text{Pb}(\text{Zr}, \text{Ti})\text{O}_3/\text{SrTiO}_3$ multilayer with layer thicknesses in the 46–140 Å range will exhibit giant dielectric response over a broad temperature range.⁹

Lead titanate is a perovskite with a cubic structure above its Curie temperature (T_C) of 490 °C.¹² Below T_C , PbTiO_3 is ferroelectric with a tetragonal unit cell, lattice constants $a = 3.904$ Å and $c = 4.152$ Å at room temperature, and a distortion (c/a ratio) of 1.063.¹² It is difficult to grow superlattices containing PbTiO_3 ferroelectric layers due to the volatility of lead. PbTiO_3 and SrTiO_3 mixtures form a solid solution over their entire composition range.¹³ Thus, $\text{PbTiO}_3/\text{SrTiO}_3$ superlattices are metastable; it is energetically favorable for the two materials to dissolve into each other, forming a solid solution. In the present work, superlattices of PbTiO_3 and SrTiO_3 layers have been fabricated by reactive molecular beam epitaxy (MBE) and their interfaces investigated by high-resolution transmission electron micros-

copy (HRTEM). The interfacial abruptness and superlattice coherence exceed those of previously reported superlattices containing PbTiO_3 .

The MBE experimental setup is described elsewhere.¹⁴ In short, molecular beams of the constituent elements are supplied to the film surface from thermal sources. Purified ozone is used as the oxidant, which is supplied to the film via a directed inlet nozzle. The SrTiO_3 is deposited by the sequential deposition of SrO and TiO_2 monolayers as shown in Fig. 1, where each monolayer dose of strontium is controlled by feedback from an atomic absorption spectroscopy monitor and each titanium monolayer is supplied using feedback from reflection high-energy electron diffraction (RHEED) intensity oscillations.¹⁵ The PbTiO_3 layers are deposited using adsorption-controlled growth conditions. An excess of lead (~3 times greater than the titanium incident flux) is supplied to the surface of the film while the titanium is supplied in monolayer doses, as shown in Fig. 1. A detailed description of the adsorption-controlled MBE growth of PbTiO_3 has been reported elsewhere.¹⁶ For the growth of the superlattice described below, the substrate temperature is maintained at 580 °C and the ozone background pressure is maintained at 2×10^{-5} Torr.

The $\text{PbTiO}_3/\text{SrTiO}_3$ superlattice described was grown on a SrTiO_3 (001) substrate that was etched with a buffered-HF solution prior to growth, exposing a TiO_2 -terminated surface.¹⁷ The thickness of the PbTiO_3 and SrTiO_3 layers in the superlattice was controlled to be ten unit cells, i.e., the

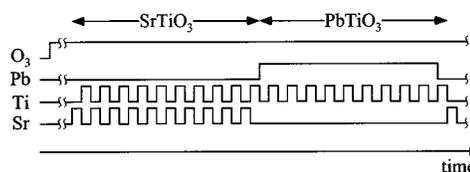


FIG. 1. Timing diagram showing the flux supplied from the molecular beams as a function of time for the growth of the PbTiO_3 and SrTiO_3 layers of the $[(\text{PbTiO}_3)_{10}/(\text{SrTiO}_3)_{10}]_{15}$ superlattice.

^{a)}Corresponding author. Electronic mail: panx@umich.edu

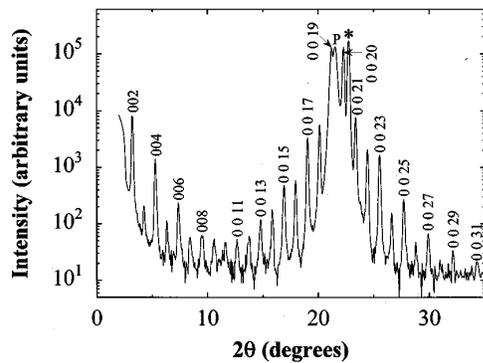


FIG. 2. A θ - 2θ x-ray diffraction scan of the multilayer containing the $[(\text{PbTiO}_3)_{10}/(\text{SrTiO}_3)_{10}]_{15}$ superlattice. The $00l$ reflections of the superlattice are labeled, P denotes the location of the 001 reflection of the thick PbTiO_3 layers, and the 001 reflection of the SrTiO_3 substrate is marked by an asterisk (*).

target thicknesses of the PbTiO_3 and SrTiO_3 layers were 41 and 39 Å, respectively (assuming bulk lattice constants). The target thickness of the entire superlattice was 1200 Å (15 repeats). The structure of the superlattice can be described as $[(\text{PbTiO}_3)_{10}/(\text{SrTiO}_3)_{10}]_{15}$. Before growing this superlattice, a buffer layer consisting of a 1000 Å thick La-doped SrTiO_3 layer followed by a 500 Å thick PbTiO_3 layer was grown on the SrTiO_3 substrate. On top of the $[(\text{PbTiO}_3)_{10}/(\text{SrTiO}_3)_{10}]_{15}$ superlattice, another thin PbTiO_3 layer was grown.

Figure 2 shows a θ - 2θ four-circle x-ray diffraction scan of the heterostructure. Sharp $00l$ superlattice reflections are clearly visible and indicate excellent regularity of the periodic structure. The superlattice constant (83.7 ± 0.2 Å, determined using a Nelson-Riley¹⁸ analysis of the $00l$ reflections) is slightly longer than the attempted period of 80.5 Å. This discrepancy indicates either a slight error in the strontium or titanium doses supplied to the film or a deviation of the lattice constants of these materials from their bulk values when fabricated as ultrathin layers.

For HRTEM analysis, cross-sectional slices were obtained by cutting the $\text{PbTiO}_3/\text{SrTiO}_3$ heterostructures along the $[010]$ direction of SrTiO_3 and then gluing the film surfaces of the slices face to face. Cross-sectional HRTEM specimens were prepared by mechanical grinding, polishing, and dimpling, followed by Ar-ion milling at 5 kV. HRTEM studies were carried out within a JEOL-4000 EX microscope operating at 400 kV, which has a point resolution of 0.17 nm.

A cross-sectional view of the heterostructure is shown in Fig. 3(a). The layers in the image from bottom to top correspond, respectively, to the SrTiO_3 substrate, the 1000 Å thick La-doped SrTiO_3 and 500 Å thick PbTiO_3 buffer layer, the $[(\text{PbTiO}_3)_{10}/(\text{SrTiO}_3)_{10}]_{15}$ superlattice, and the final PbTiO_3 thin layer. A selected area electron diffraction (SAED) pattern taken from the area including the lower PbTiO_3 and La-doped SrTiO_3 buffer layers is shown in Fig. 3(b), which was recorded with the electron beam direction parallel to the $[100]$ zone axis of the SrTiO_3 substrate. It is identified to be a superposition of a $[100]$ zone SAED pattern of cubic SrTiO_3 and a $[100]$ zone SAED pattern of tetragonal PbTiO_3 . The elongated shape of diffraction spots in the diffraction pattern indicates that the a and b axes of tetragonal PbTiO_3 lie in the plane of the interface and that the c axis lies

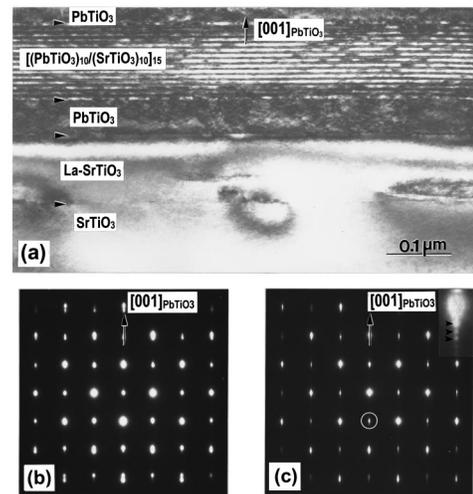


FIG. 3. (a) Bright-field TEM image showing the cross-sectional structure of the $\text{PbTiO}_3/\text{SrTiO}_3$ multilayer. (b) A SAED pattern taken from the area including the La-doped SrTiO_3 and PbTiO_3 layers beneath the superlattice. (c) A SAED pattern from the $[(\text{PbTiO}_3)_{10}/(\text{SrTiO}_3)_{10}]_{15}$ superlattice region; the inset shows an enlargement of the circled reflection.

parallel to the growth direction. This conclusion is also true for the thin PbTiO_3 layer above the $[(\text{PbTiO}_3)_{10}/(\text{SrTiO}_3)_{10}]_{15}$ superlattice according to the HRTEM studies.

In the superlattice region of Fig. 3(a), layers with higher intensities (bright) and lower intensities (dark) correspond to the SrTiO_3 and PbTiO_3 layers, respectively. A constant thickness is seen for each of the individual layers. The corresponding SAED pattern of the $[(\text{PbTiO}_3)_{10}/(\text{SrTiO}_3)_{10}]_{15}$ superlattice structure is shown in Fig. 3(c), which is taken with the electron beam direction parallel to the $[100]$ axis of the SrTiO_3 substrate. Equally spaced satellite reflections corresponding to a periodicity of ~ 80 Å along the growth direction are seen in the inset, which is an enlarged view of the circled spot in Fig. 3(c).

Figure 4(a) is a HRTEM image of the $[(\text{PbTiO}_3)_{10}/(\text{SrTiO}_3)_{10}]_{15}$ superlattice. The individual PbTiO_3 and SrTiO_3 layers show highly perfect single crystalline structures. The c axis PbTiO_3 thin layers in the superlattice region have the parallel to the growth direction. The tetragonality (c/a ratio) of the PbTiO_3 layers is about 1.06, measured from the HRTEM images.

A Fourier-filtered HRTEM image of the interface between PbTiO_3 and SrTiO_3 from the superlattice region is shown in Fig. 4(b). It clearly shows different image characteristics between the PbTiO_3 and SrTiO_3 layers. Figure 4(c) shows a profile of the image intensities along the marked line in Fig. 4(b). The intensity of the bright spots undergoes a sharp change at the interface. From this study it can be deduced that the structural width of the $\text{PbTiO}_3/\text{SrTiO}_3$ interface is about one unit cell.

In PbTiO_3 based heteroepitaxial thin films, tetragonal PbTiO_3 layers may be either a -axis or c -axis oriented, with frequent twinning (i.e., 90° domain boundaries).^{19,20} In the $[(\text{PbTiO}_3)_{10}/(\text{SrTiO}_3)_{10}]_{15}$ superlattice region of the film studied, the PbTiO_3 layers have a tetragonal structure, are c -axis oriented, and are free of twin boundaries. The formation of such a superlattice structure can be understood as follows. At the growth temperature of 580 °C both structures are cubic, with bulk lattice constants of 3.967 Å for PbTiO_3

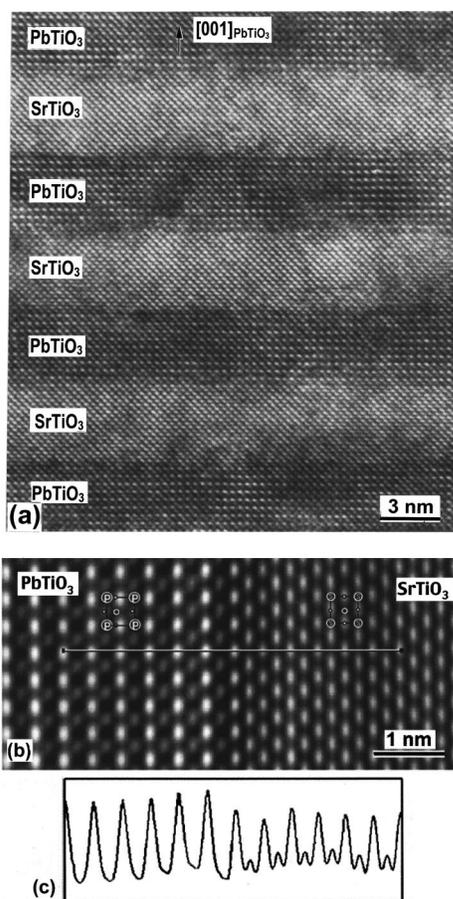


FIG. 4. (a) A HRTEM image of the $[(\text{PbTiO}_3)_{10}/(\text{SrTiO}_3)_{10}]_{15}$ superlattice structure taken with the electron beam parallel to the $[100]$ axis of SrTiO_3 . (b) Fourier-filtered HRTEM image of the $[(\text{PbTiO}_3)_{10}/(\text{SrTiO}_3)_{10}]_{15}$ superlattice. (c) A profile of the image intensity from the area marked in (b).

and 3.929 \AA for SrTiO_3 .²¹ The lattice strain between the SrTiO_3 and PbTiO_3 thin layers is calculated to be 1% using the formula $(a_{\text{PbTiO}_3} - a_{\text{SrTiO}_3})/a_{\text{SrTiO}_3}$. For thin layers such strain can be accommodated through elastic distortion, rather than being relaxed through the formation of dislocations. This compressive lattice strain in the cubic PbTiO_3 layers is maintained until the specimen is cooled to T_C (490°C for bulk PbTiO_3).¹² When the cubic PbTiO_3 transforms to tetragonal PbTiO_3 at T_C , compressive strain within the PbTiO_3 layer leads to a matching of the a -axis of the tetragonal PbTiO_3 with the a -axis of SrTiO_3 in order to minimize strain energy. At room temperature, the magnitude of the lattice strain between the a axis of SrTiO_3 ($a = 3.905 \text{ \AA}$)²¹ and PbTiO_3 is less than 0.1%, whereas that between the a axis of SrTiO_3 and c axis of PbTiO_3 is 6.3%, leading to an energetic preference of the observed orientation. We note that this analysis is based on bulk lattice constants and realize that there may be deviations in the properties of ultrathin PbTiO_3 layers (e.g., T_C , equilibrium lattice constants, ferroelectric properties, etc.).

In contrast to $\text{PbTiO}_3/\text{SrTiO}_3$ superlattices prepared using a sol-gel method in which smeared interfaces and significant interdiffusion were seen,²² our MBE-grown superlattice is more than an order of magnitude thinner and shows very sharp interfaces. This is clearly shown in the bright-field TEM micrograph in Fig. 3(a) and in the HRTEM image in Fig. 4(a). Furthermore, the structural width of the interface is

deduced to be about one unit cell from the measurement of lattice spacings of both SrTiO_3 and PbTiO_3 in the HRTEM image of the interface shown in Fig. 4(b). It should be pointed out that the chemical width of the interface, which is a measure of atomic diffusion across the superlattice interface, cannot be precisely determined by HRTEM, but may be done using spatially resolved analytical electron microscopy.

In conclusion, high quality PbTiO_3 layers and a $\text{PbTiO}_3/\text{SrTiO}_3$ superlattice were grown on (001) SrTiO_3 by reactive MBE. The thin PbTiO_3 layers are single crystalline with the $[001]$ direction parallel to the growth direction. The interfaces between PbTiO_3 and SrTiO_3 in this metastable superlattice are extremely sharp. Such interfacial abruptness and layer thickness control are comparable with what has been achieved in the growth of metastable compound semiconductor superlattices^{23,24} and is desired for studying predictions of enhanced dielectric performance in nanoscale dielectric and ferroelectric superlattices.^{8,9}

We gratefully acknowledge the financial support of the College of Engineering at the University of Michigan and the Department of Energy through Grant No. DE-FG02-97ER45638. C.D.T. gratefully acknowledges the support of the IMAPS Educational Foundation.

- ¹K. Iijima, T. Terashima, Y. Bando, K. Kamigaki, and H. Terauchi, *J. Appl. Phys.* **72**, 2840 (1992).
- ²T. M. Shaw, A. Gupta, M. Y. Chern, P. E. Batson, R. B. Laibowitz, and B. A. Scott, *J. Mater. Res.* **9**, 2566 (1994).
- ³I. Kanno, S. Hayashi, R. Takayama, and T. Hirao, *Appl. Phys. Lett.* **68**, 328 (1996).
- ⁴H.-M. Christen, L. A. Boatner, J. D. Budai, M. F. Chisholm, L. A. Géa, P. J. Marrero, and D. P. Norton, *Appl. Phys. Lett.* **68**, 1488 (1996).
- ⁵E. D. Specht, H.-M. Christen, D. P. Norton, and L. A. Boatner, *Phys. Rev. Lett.* **80**, 4317 (1998).
- ⁶H.-M. Christen, E. D. Specht, D. P. Norton, M. F. Chisholm, and L. A. Boatner, *Appl. Phys. Lett.* **72**, 2535 (1998).
- ⁷H.-M. Christen, L. A. Knauss, and K. S. Harshvardhan, *Mater. Sci. Eng., B* **56**, 200 (1998).
- ⁸N. A. Pertsev, G. Arlt, and A. G. Zembilgotov, *Phys. Rev. Lett.* **76**, 1364 (1996).
- ⁹S. Li, J. A. Eastman, J. M. Vetrone, R. E. Newnham, and L. E. Cross, *Philos. Mag. B* **76**, 47 (1997).
- ¹⁰J. V. Mantese, N. W. Schubring, A. L. Micheli, and A. B. Catalan, *Appl. Phys. Lett.* **67**, 721 (1995).
- ¹¹J. V. Mantese, N. W. Schubring, A. L. Micheli, A. B. Catalan, M. S. Mohammed, R. Naik, and G. W. Auner, *Appl. Phys. Lett.* **71**, 2047 (1997).
- ¹²Landolt-Bornstein: *Numerical Data and Functional Relationships in Science and Technology*, New Series, Group III, Vol. 16a, edited by K.-H. Hellwege and A. M. Hellwege (Springer, Berlin, 1981), pp. 77–81.
- ¹³T. Ikeda, *J. Phys. Soc. Jpn.* **14**, 1286 (1959).
- ¹⁴C. D. Theis and D. G. Schlom, *J. Cryst. Growth* **174**, 473 (1997).
- ¹⁵J. H. Haeni, C. D. Theis, and D. G. Schlom, *Mater. Sci. Eng., B* (submitted).
- ¹⁶C. D. Theis, J. Yeh, D. G. Schlom, M. E. Hawley, and G. W. Brown, *Thin Solid Films* **325**, 107 (1998).
- ¹⁷M. Kawasaki, K. Takahashi, T. Maeda, R. Tsuchiya, M. Shinohara, O. Ishiyama, T. Yonezawa, M. Yoshimoto, and H. Koinuma, *Science* **266**, 1540 (1994).
- ¹⁸J. B. Nelson and D. P. Riley, *Proc. Phys. Soc. London* **57**, 160 (1945).
- ¹⁹Y. Gao, G. Bai, K. L. Merkle, Y. Shi, H. L. M. Chang, Z. Shen, and D. J. Lam, *J. Mater. Res.* **8**, 145 (1993).
- ²⁰S. G. Ghonge, E. Goo, and R. Ramesh, *Appl. Phys. Lett.* **62**, 1742 (1993).
- ²¹D. Taylor, *Trans. J. Br. Ceram. Soc.* **84**, 181 (1985).
- ²²Y. Ohya, T. Ito, and Y. Takahashi, *Jpn. J. Appl. Phys., Part 1* **33**, 5272 (1994).
- ²³A. K. Gutakovskii, L. I. Fedina, and A. L. Aseev, *Phys. Status Solidi A* **150**, 127 (1995).
- ²⁴S. Thoma and H. Cerva, *Ultramicroscopy* **53**, 37 (1994).