Well-ordered large-area arrays of epitaxial ferroelectric $(Bi,La)_4Ti_3O_{12}$ nanostructures fabricated by gold nanotube-membrane lithography

Sung Kyun Lee,[a] Woo Lee,[b] Marin Alexe, Kornelius Nielsch, Dietrich Hesse, and Ulrich Gösele
Max Planck Institute of Microstructure Physics, Weinberg 2, D-06120 Halle/Saale, Germany

(Received 17 December 2004; accepted 21 February 2005; published online 5 April 2005)

Two-dimensionally well-ordered, large-area arrays of epitaxial, ferroelectric, La-substituted $Bi_4Ti_3O_{12}$ (BLT) nanostructures are prepared using gold nanotube membranes as a liftoff mask. Epitaxial nanostructures with a height of about 65 nm and a lateral size of about 150 nm, with either (001) ("*c*-axis") orientation, or mixed (118)/(100) ("non-*c*-axis") orientation, are obtained on (001)- and (011)-oriented $SrTiO_3$ substrates, respectively. The ferroelectric properties are probed by piezoresponse scanning force microscopy. Non-*c*-axis-oriented BLT nanostructures show an effective piezoresponse coefficient ($2d_{zz}$) of about 38.0 pm/V, whereas *c*-axis-oriented structures show one of only about 4.9 pm/V.
 [DOI: 10.1063/1.1899239]

La-substituted $Bi_4Ti_3O_{12}$ (BLT) thin films have attracted attention because of their possible application to nonvolatile ferroelectric random access memories and to microelectromechanical systems, due mostly to high fatigue endurance along with low deposition temperature.[1–3] $Bi_4Ti_3O_{12}$, as well as BLT, have been rather intensively studied concerning both fundamental properties and their device applications, but little has been done regarding the size effect.[4] The latter remains one of the most important issues in the field of ferroelectrics. Proper studies of size effects in ferroelectrics should enable the discrimination between intrinsic and extrinsic size effects. Such studies require, however, high-quality single-crystal nanoscale structures and eventually perfectly ordered arrays. To date, various attempts to fabricate nanostructured ferroelectric materials by electron beam direct writing,[5] focused ion beam milling,[6] nanoimprint lithography,[7] self-patterning methods,[8] and nanosphere lithography,[9] have been reported. Most of these methods are unfortunately not appropriate to fabricate two-dimensionally (2D) periodic large-area arrays of nanoscale structures.

In this letter we report on fabrication, crystallographic structure, and ferroelectric properties of two-dimensionally periodic, hexagonally ordered, large-area arrays of BLT nanostructures epitaxially grown on $SrRuO_3$-covered (001)- and (011)-oriented $SrTiO_3$ single-crystal substrates, respectively, using gold nanotube membranes of square centimeter sizes as shadow masks.

First, a 10 to 20 nm thick $SrRuO_3$ bottom electrode, also serving as an epitaxial template, was deposited by pulsed-laser deposition (PLD) from a stoichiometric target employing a KrF excimer laser ($\lambda = 248$ nm) operated at an energy fluence of 1.7 J/cm^2 and a repetition rate of 5 Hz. The PLD process was performed in oxygen at a pressure of 0.14 mbar, and the substrates were heated to 700 °C.

Gold nanotube membranes with sizes of 2×2 mm^2 to 10×10 mm^2 were transferred onto the $SrRuO_3/SrTiO_3$ substrates immediately after $SrRuO_3$ deposition. Details on the fabrication of these freestanding large-area gold nanotube membranes are reported elsewhere.[10] Perfectly ordered nanoporous alumina templates[11] were electrochemically covered by gold. By a wet-chemical etch the resulting gold nanotube membrane is detached from the oxide pore structure and subsequently transferred to the desired substrate. The mask-covered $SrRuO_3/SrTiO_3$ substrates were then loaded into the PLD chamber, which was pumped to 2×10^{-7} mbar. The deposition of BLT material through the gold nanotubes was carried out at room temperature in an oxygen pressure of 1×10^{-4} mbar using a laser energy fluence of 2.3 J/cm^2. After BLT deposition, the nanostructures were obtained by simply lifting off the gold membrane. To obtain crystalline BLT structures, and to ensure ferroelectric properties, the as-deposited amorphous structures were crystallized at 700 °C for 30 min. in a pure oxygen-flow ambient using a quartz tube furnace. In this way, large areas (about 10×10 mm^2) of well-ordered BLT nanostructures with hexagonal arrangement can be easily fabricated.

Figure 1 shows a scanning electron microscope (SEM) image of a BLT nanostructure array on a $SrRuO_3/SrTiO_3$

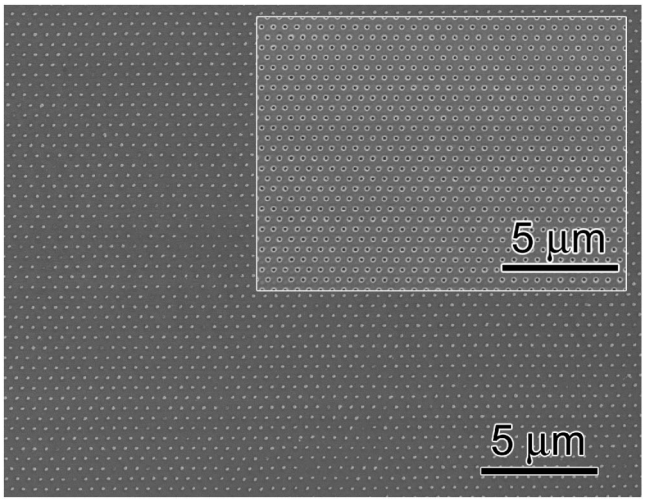

FIG. 1. SEM plan-view image of an as-deposited BLT nanostructure array on a $SrRuO_3$ electrode on a $SrTiO_3$ single-crystal substrate. The inset shows a SEM image of part of a gold nanotube membrane used for patterning.

[a]Electronic mail: sklee@mpi-halle.de
[b]Electronic mail: woolee@mpi-halle.de

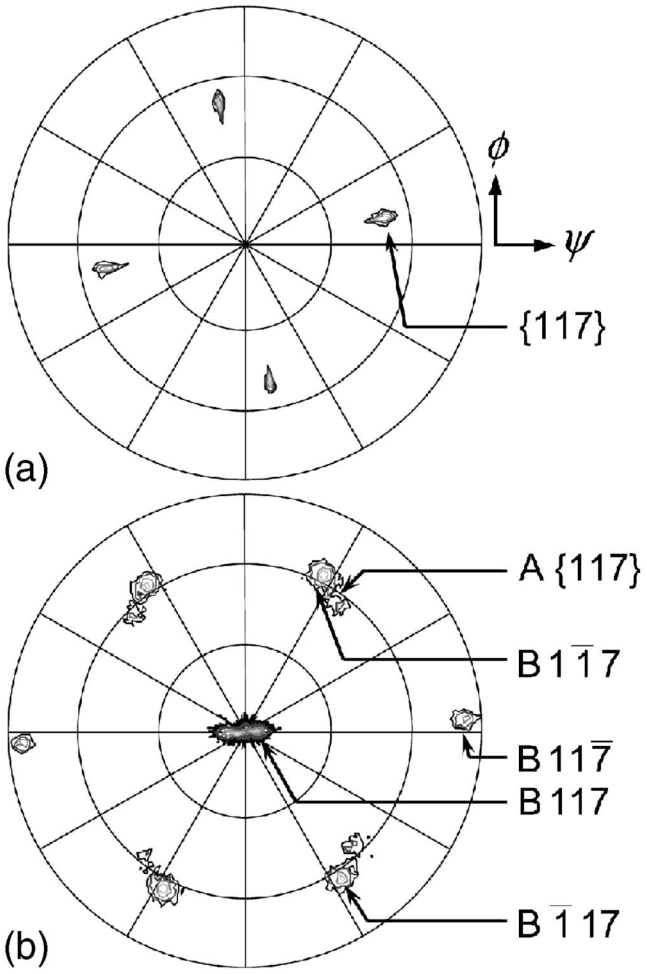

FIG. 2. XRD pole figures of (a) (001)-oriented and (b) (118)/(100)-oriented BLT nanostructure arrays epitaxially grown on $SrRuO_3$-covered (001)- and (011)-oriented $SrTiO_3$ substrates, respectively. The fixed 2θ angle was 30.1° corresponding to the BLT 117 reflection. In (b), peaks originating from the (100)- and (118)-oriented parts of the BLT nanostructures are denoted "A" and "B", respectively.

substrate. Size and pitch of the BLT nanostructures, of 150 and 500 nm, respectively, are identical to those of the gold nanotube membrane. Nevertheless, atomic force microscopy investigations (not shown) revealed that in most of the cases the structures have rather an oval shape with a height of about 100 nm. We believe that the oval shape is either a result of a local deformation of the gold nanotubes or of a small shadow effect that could occur during BLT deposition.

Although the BLT nanostructures were amorphous after the liftoff process, and then *ex situ* crystallized, we obtained epitaxial relations between the nanostructures and the substrates. Due to the large size of the BLT nanostructure arrays, x-ray diffractometry was directly applicable. Figure 2 shows x-ray diffraction (XRD) pole figures of BLT nanostructures having *c*-axis and non-*c*-axis orientations on (001)- and (011)-oriented $SrTiO_3$ substrates, respectively. The fixed 2θ angle used to record the pole figures was 30.1° corresponding to the BLT 117 reflection. In the case of the (001)-oriented BLT nanostructure arrays, the pole figure shows four reflection peaks with a fourfold symmetry observed at $\psi \approx 51°$, thus revealing a single-domain situation. The pole figure of the non-*c*-axis-oriented nanostructures is more complex. First of all, it consists of a set of peaks (marked "A") that stem from a (100)-oriented part of the BLT nanostructures, and of another set (marked "B") which stems from a (118)-oriented part. Second, the peaks corresponding to the (118) orientation indicate the presence of two types of azimuthal domains. Set A appears at $\psi \approx 57°$ and consists of the 117, $1\bar{1}7$, $11\bar{7}$, and $1\bar{1}\bar{7}$ reflections from the (100)-oriented part, indicating a single-domain situation. Set B appears at $\psi \approx 4°$, 65°, and 82°, in correspondence to the 117, $\bar{1}17/\bar{1}\bar{1}7$, and $11\bar{7}$ reflections from the (118)-oriented part of BLT. A detailed analysis reveals that the (118)-oriented nanostructures occur with two azimuthal domain variants; that is, in exactly that double-twin situation that is well known from (118)-oriented thin films.[2] Cross-sectional electron diffraction patterns (not shown) point to the additional presence of a minor (117)-oriented BLT part as well. The (117) orientation was already reported to grow when a metalorganic $Bi_{3.25}Ti_{0.75}Ti_4O_{12}$ film of mixed (100)/(118) orientation on $SrRuO_3$(011) is obtained by annealing at 850 °C.[12]

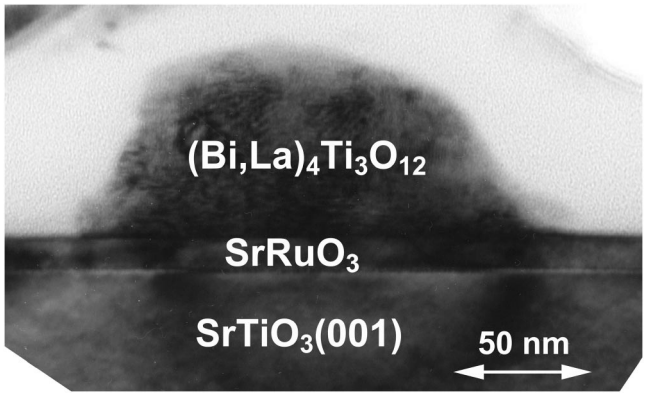

FIG. 3. TEM cross-sectional image of a crystallized BLT nanostructure on $SrRuO_3(001)/SrTiO_3(001)$.

Figure 3 shows a transmission electron microscope (TEM) cross-sectional image of a BLT nanostructure on a 15 nm thick $SrRuO_3(001)$ electrode grown on $SrTiO_3(001)$. The nanostructure is about 65 nm thick and 165 nm wide at its base. Dark-field imaging performed together with electron diffraction (not shown) confirmed the uniform (001) orienta-

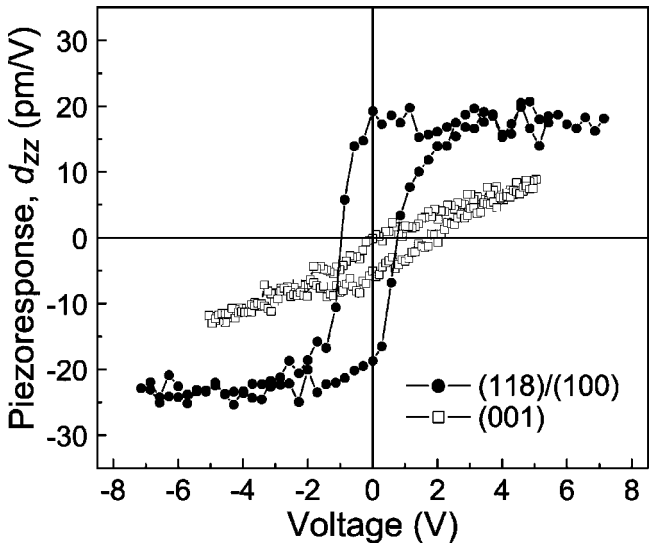

FIG. 4. Piezoelectric hysteresis loops of epitaxial BLT nanostructures with *c*-axis and non-*c*-axis orientation on (001)- and (011)-oriented $SrRuO_3/SrTiO_3$ substrates, respectively.

tion of BLT nanostructures grown on $SrTiO_3(001)$, and the presence of (118)-, (100)-, and occasionally (117)-oriented domains in the BLT nanostructures grown on $SrTiO_3(011)$.

Piezoelectric hysteresis loops of the crystallized BLT nanostructures were recorded using scanning force microscopy in the piezoresponse mode. Details on this method are available elsewhere.[13] Figure 4 shows typical piezoelectric hysteresis loops recorded from *c*-axis- and non-*c*-axis-oriented BLT nanostructures. The measured remanent effective piezoelectric coefficient (d_{zz}) of the *c*-axis-oriented BLT nanostructure is about 2.5 pm/V, whereas a considerably higher value of about 19.0 pm/V is obtained from the non-*c*-axis-oriented BLT nanostructures. In addition, a slight imprint towards negative d_{zz} direction is revealed in both cases. These results are in agreement with those obtained on $Bi_4Ti_3O_{12}$ thin films by Harnagea *et al.*,[13] who had obtained higher piezoresponse values for non-*c*-axis-oriented films than for *c*-axis-oriented films. The crystallographic origin of this relation is the fact that the predominant component of the spontaneous polarization in $Bi_4Ti_3O_{12}$-type materials lies along the *a* axis.[14]

In summary, well-ordered, 2D, large-area arrays of epitaxial La-doped $Bi_4Ti_3O_{12}$ nanostructures with (001) and (118)/(100) orientations have been obtained on $SrRuO_3$-covered $SrTiO_3$ substrates of two different orientations. The arrays were achieved using a liftoff method based on gold nanotube membranes as shadow masks. In spite of their small lateral size and thickness, the nanostructures of the arrays were clearly revealed to have ferroelectric properties, the values of which depend on their crystallographic orientation.

[1] B. H. Park, B. S. Kang, S. D. Bu, T. W. Noh, J. Lee, and W. Jo, Nature (London) **401**, 682 (1999).
[2] H. N. Lee and D. Hesse, Appl. Phys. Lett. **80**, 1040 (2002).
[3] H. Maiwa, N. Iizawa, D. Togawa, T. Hayashi, W. Sakamoto, M. Yamada, and S. Hirano, Appl. Phys. Lett. **82**, 1760 (2003).
[4] Y. L. Du, M. S. Zhang, Q. Chen, Z. R. Yuan, Z. Yin, and Q. A. Zhang, Solid State Commun. **124**, 113 (2002).
[5] M. Hiratani, C. Okazaki, H. Hasegawa, N. Sugii, Y. Tarutani, and K. Takagi, Jpn. J. Appl. Phys., Part 1 **36**, 5219 (1997).
[6] C. S. Ganpule, A. Stanishevsky, S. Aggarwal, J. Melngailis, E. Williams, R. Ramesh, V. Joshi, and C. A. P. de Araujo, Appl. Phys. Lett. **75**, 3874 (1999).
[7] C. Harnagea, M. Alexe, J. Schilling, J. Choi, R. B. Wehrspohn, D. Hesse, and U. Gösele, Appl. Phys. Lett. **83**, 1827 (2003).
[8] A. Roelofs, T. Schneller, K. Szot, and R. Waser, Appl. Phys. Lett. **81**, 5231 (2002).
[9] W. Ma, C. Harnagea, D. Hesse, and U. Gösele, Appl. Phys. Lett. **83**, 3770 (2003).
[10] W. Lee *et al.*, 2004 MRS Fall Meeting, Symposium on Innovations for Sub-100 nm Lithography-Materials and Processes, Boston, MA. C5.5 [Chem. Mater. (submitted)].
[11] J. Choi, K. Nielsch, M. Reiche, R. B. Wehrspohn, and U. Gösele, J. Vac. Sci. Technol. B **21**, 763 (2003).
[12] T. Sakai, T. Watanabe, H. Funakubo, K. Saito, and M. Osada, Jpn. J. Appl. Phys., Part 1 **42**, 166 (2003).
[13] C. Harnagea, A. Pignolet, M. Alexe, D. Hesse, and U. Gösele, Appl. Phys. A: Mater. Sci. Process. **70**, 261 (2000).
[14] S. E. Cummins and L. E. Cross, J. Appl. Phys. **39**, 2268 (1968).