La-substituted Bi$_4$Ti$_3$O$_{12}$ (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.\textsuperscript{1–3} Bi$_4$Ti$_3$O$_{12}$, 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.\textsuperscript{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,\textsuperscript{5} focused ion beam milling,\textsuperscript{6} nanoimprint lithography,\textsuperscript{7} self-patterning methods,\textsuperscript{8} and nanosphere lithography,\textsuperscript{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 \degree C.

Gold nanotube membranes with sizes of 2 $\times$ 2 mm$^2$ to 10 $\times$ 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.\textsuperscript{10} Perfectly ordered nanoporous alumina templates\textsuperscript{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 $\times$ 10$^{-7}$ mbar. 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 \degree C for 30 min. in a pure oxygen-flow ambient using a quartz tube furnace. In this way, large areas (about 10 $\times$ 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$_3$ substrate.
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 SrTiO3 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 ψ≈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 ψ≈57° and consists of the 117, 117, 117, and 117 reflections from the (100)-oriented part, indicating a single-domain situation. Set B appears at ψ=4°, 65°, and 82°, in correspondence to the 117, 117, 117, and 117 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. 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 Bi3.25Ti0.75Ti4O12 film of mixed (100)/(118) orientation on SrRuO3(011) is obtained by annealing at 850 °C.

Figure 3 shows a transmission electron microscope (TEM) cross-sectional image of a BLT nanostructure on a 15 nm thick SrRuO3(001) electrode grown on SrTiO3(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-
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. Figure 4 shows typical piezoelectric hysteresis loops recorded from $c$-axis- and non-$c$-axis-oriented BLT nanostructures. The measured remanent effective piezoelectric coefficient $s_{zz}$ 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$_4$Ti$_3$O$_12$ thin films by Harnagea et al., 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$_4$Ti$_3$O$_12$-type materials lies along the $a$ axis.

In summary, well-ordered, 2D, large-area arrays of epitaxial La-doped Bi$_4$Ti$_3$O$_12$ 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.

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)].