Microstructure and piezoelectric properties of sub-80 nm high polycrystalline SrBi$_2$Ta$_2$O$_9$ nanostructures within well-ordered arrays

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Well-ordered arrays of sub-80 nm high SrBi$_2$Ta$_2$O$_9$ nanostructures were fabricated on SrTiO$_3$:Nb (111) single-crystal substrates by latex sphere lithography. The as-prepared nanostructures have a pyramid-like shape with around 220 nm lateral dimension at half their height. After annealing, the pyramid-like shape changes due to the formation of nano-sized SrBi$_2$Ta$_2$O$_9$ grains of high crystal anisotropy in the individual nanostructures. Microstructure and piezoelectric properties of the nanostructures were investigated by cross-sectional transmission electron microscopy and piezoresponse force microscopy, respectively. Scattering in piezoelectric strain constants $d_{33}$ was observed, probably arising from varying orientations, high anisotropy, and interfacial diffusion layer of the polycrystalline SrBi$_2$Ta$_2$O$_9$ nanostructures on SrTiO$_3$. The $d_{33}$ increases continuously with dc bias and reaches 8 pm/V at a bias of 20 V. The size effect on piezoelectric properties of SrBi$_2$Ta$_2$O$_9$ was found to be much less severe than that in BaTiO$_3$. The acquired piezoresponse hysterisis loops proved that 30 nm high SrBi$_2$Ta$_2$O$_9$ nanostructures are still ferroelectric. © 2004 American Institute of Physics. [DOI: 10.1063/1.1804603]

The potential for widespread technological applications such as nonvolatile memories and microelectromechanical systems has stimulated great interest in the integration of ferroelectric thin films and nanostructures into microelectronic devices. The ferroelectric phase transition has theoretically been supposed to disappear below a critical size due to a weakening of the cooperative driving force for ferroelectricity and an increasing role of the depolarization field. However, experimental studies prove that ferroelectricity exists in ultrathin (4 nm) Pb(Zr,Ti)O$_3$ (PZT) epitaxial films. Recently, bismuth-layered perovskite oxide thin films such as SrBi$_2$Ta$_2$O$_9$ (SBT) have found considerable interest due to their high fatigue resistance (at $>10^{12}$ switching cycles) even with Pt electrodes, low leakage current, and low coercive field. Accordingly they have a high potential for device applications in nonvolatile ferroelectric random access memories. SBT has a highly anisotropic orthorhombic crystalline structure at room temperature with $a=0.5531$ nm, $b=0.5534$ nm, and $c=2.4984$ nm. The piezoelectricity in SBT is highly anisotropic even in polycrystalline ceramics, which makes it useful for microelectromechanical system applications. With the demand for ultrahigh-density integration, studies of the scaling behavior of ferroelectric and piezoelectric properties in individual submicron ferroelectric capacitors become increasingly important. While the scaling behavior of submicron PZT capacitors has been the subject of numerous studies, to our knowledge there is only one investigation on SBT submicron capacitors. Moreover, the thickness of the previously investigated structures is generally a few hundred nanometers. For Gbit ferroelectric memories, the individual ferroelectric capacitors must not only have submicron lateral size but also have a thickness less than 100 nm. In this letter, we report successful fabrication and the investigation of microstructure and piezoelectric properties of well-ordered arrays of sub-80 nm high SBT nanostructures with submicron lateral dimensions.

For the integration of submicron ferroelectric nanostructures, generally either ion-beam milling or electron beam lithography was used. Both are time-consuming and expensive. In previous letters, we demonstrated that a technique based on nanosphere lithography can be used as a quick and inexpensive method for the fabrication and exploration of ferroelectric oxide nanostructures integrated on substrates. In the present work, the technique has been used to fabricate well-ordered SBT nanostructure arrays. Pulsed laser deposition was carried out at room temperature to deposit SBT onto SrTiO$_3$:Nb substrates through interstices in a monolayer of monodisperse latex spheres with 1 µm diameter. After deposition the polystyrene latex spheres were lifted off in methylene chloride and the as-deposited nanostructures have a monolayer of monodisperse latex spheres with 1 µm diameter. After deposition the polystyrene latex spheres were lifted off in methylene chloride and the as-deposited nanostructures were then annealed in air at 950 °C for 1 h. In order to obtain non-c-oriented SBT structures, SrTiO$_3$ substrates doped with 0.5 wt % Nb were chosen. Figure 1 presents well-ordered arrays of the obtained nanostructures with a lateral dimension of about 220 nm at half their height. The circular structures visible in Fig. 1(a) usually disappear on annealing. Their nature remains unclear; probably they represent residues of the latex spheres. As shown in Figs. 1(b) and 1(d), the as-deposited nanostructures have a pyramid-like shape before annealing. After annealing, the individual nanostructures lose the regular pyramid-like shapes and break into several grains [Figs. 1(c) and 1(e)] presumably of various crystallographic orientations. The shape change is thought to be due to nucleation and growth of highly anisotropic SBT crystallites during postdeposition annealing. Roughly the average vertical shrinkage was around 30%, while the lateral shrinkage during annealing was less than 10%.

To investigate the polycrystalline nature and the phase composition of the nanostructures, cross-section investigations by transmission electron microscopy (TEM) and selected area electron diffraction (SAED) were performed on nanostructure arrays with average height of about 80 nm.

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FIG. 1. (a) Topographic image (top view, 5 μm × 5 μm area) of a well-ordered array of SrBi₂Ta₂O₉ nanostructures (annealed) prepared on conductive SrTiO₃:Nb (111) single-crystal substrates; (b) surface plot of 1.8 × 1.8 μm area in the unannealed sample; (c) surface plot of 1.8 × 1.8 μm area in the annealed sample; (d) and (e) typical surface profiles along the diagonal of the hexagonally ordered patterns for the unannealed pyramid-shaped nanostructures shown in (b) and the annealed nanostructures shown in (c), respectively.

Figure 2(a) shows an overview of two such nanostructures, whereas Figs. 2(b) and 2(c) show a bright-field and (022)SBT-dark field image, respectively, of a third one. The polycrystalline nature of the nanostructures is well visible, the grain size amounting to about 30 to 50 nm. Figure 3(a) shows a SAED pattern of the right part of the nanostructure of Figs. 2(b) and 2(c) after tilting the sample by a few degrees to obtain a regular diffraction pattern. Using SrTiO₃ diffraction patterns (not shown) as internal standards, the d values (interplanar spacings) of, and the angles between, the diffraction spots of the predominant regular pattern of Fig. 3(a) were carefully evaluated, resulting in the [522] zone axis pattern of SBT [Fig. 3(b)]. This pattern is formed by a rhomboid-type spot pattern scanned by the 022 and 205 spots of SBT. The measured d values for the (022), (205), (223), and (227) spots deviated by less than 0.4% from the theoretical ones. The interplanar angles ∠(227); (022) = 44.83°, ∠(022); (223) = 51.50°, and ∠(223); (205) = 44.51° were found to be correct within less than 0.1°. In Fig. 2(b) the nanostructure extends about 15 nm into the substrate, pointing to an interfacial diffusion-reaction process which most probably is due to the rather high annealing temperature of 950 °C. In accordance with this observation, SAED and dark-field investigations (not shown) revealed the presence of one or more non-identified phases different from SBT close to the interface. Note that also the SBT grain in Fig. 2(c) does not reach the interface by a distance of about 15 nm.

Piezoelectric properties of the obtained SBT nanostructures were investigated by measuring the electric field induced converse piezoelectric effect using a piezoresponse force microscope (PFM), and the experimental setup and the procedures were similar to those reported before. A TiN-coated conductive silicon cantilever (typical force constant k = 40 N/m) was used, with a typical tip radius less than 35 nm. Piezoresponse hysteresis loops were acquired by positioning the PFM tip at the center of a nanostructure and measuring the local piezoresponse signal as a function of dc bias voltages (−20 to +20 V) superimposed on a small ac voltage (frequency 16.52 kHz; amplitude 1 V). The generated local mechanical displacement was detected using the PFM tip and analyzed by a lock-in amplifier, deriving d₃₃ according to the procedure given by Harnagea and Pignolet. The conversion factor between the photodiode signal of the PFM and the mechanical displacement of the PFM tip was obtained by careful calibration using an X-cut quartz (d₁₁ = 2.3 pm/V).

Figure 4 presents typical piezoresponse hysteresis loops obtained from the annealed SBT nanostructures with height of about 30 nm. In view of the polycrystalline nature of the nanostructures, it is noted that the d₃₃ measured here is actually an effective piezoelectric coefficient. As shown in Fig. 4, loop a is slimmer than loop b; the positive and negative remnant d₃₃ values are 1.7 and −4.8 pm/V, respectively.
for loop $a$, and 1.0 and $-2.7 \, \text{pm/V}$, respectively, for loop $b$. Considering the polycrystalline nature of the as-prepared nanostructures and high anisotropy of SBT, the reasons for the variation of the loops in Fig. 4 are probably (i) a varying number of grains (of varying size and orientations) contributing to the piezoresponse; and (ii) different thickness or nature of the interface-near reaction-diffusion layer (foreign phase).

It is well known that the electric field distribution under the tip is generally nonuniform in PFM, depending on the aspect ratio between the diameter of the contact area and the sample thickness. A careful consideration of the real field distribution would require rather extensive calculations, cf. Ref. 20. Hence we are reporting here an effective piezoelectric coefficient including both structural and field inhomogeneities. Bismuth certainly being the most reactive component in SBT, an interface-near layer formed by interfacial reaction between SBT and the SrTiO$_3$ substrate will most probably consist of a bismuth-strontium titanate. Even if this layer should be nonferroelectric, it is certainly a high-$k$ dielectric so that its influence onto the electric field within the SBT nanostructure will be rather limited.

In bulk SBT ceramics, a typical $d_{33}$ value was reported to be $23 \, \text{pm/V}$, determined by electric field induced strain measurements.\textsuperscript{19} In the present study, the measured values for the SBT nanostructures are generally $2-4 \, \text{pm/V}$ at zero bias and the maximum $d_{33}$ reaches $8 \, \text{pm/V}$ at a bias voltage of $20 \, \text{V}$. In $180 \, \text{nm}$ high mesoscopic SBT structures obtained by ion beam milling from continuous films, the maximum $d_{33}$ values were measured locally by SFM to be $17 \, \text{pm/V}$,\textsuperscript{12} compared to the value of $8 \, \text{pm/V}$ obtained in our $30 \, \text{nm}$ high SBT nanostructures with only $220 \, \text{nm}$ lateral dimensions and to the bulk ceramic value of $23 \, \text{pm/V}$. The present work clearly shows that the size effect on piezoelectricity of SBT is much less severe than that in BaTiO$_3$. For BaTiO$_3$, $d_{33}$ in bulk ceramics is around $100 \, \text{pm/V}$,\textsuperscript{2} but the value is only about $2 \, \text{pm/V}$ in nanostructures $40 \, \text{nm}$ high and $220 \, \text{nm}$ in lateral dimension (not shown).

As shown in the piezoresponse hysteresis loops obtained from BaTiO$_3$ nanopyramids\textsuperscript{14,15} of similar dimensions, typically the piezoresponse exhibits a decrease after it reaches a maximum value with the increase of dc bias voltage. Comparing loop shapes for SBT nanostructures with those for BaTiO$_3$ nanostructures, we notice that unlike in BaTiO$_3$ the piezoelectric response in SBT nanostructures increases continuously with dc bias. A similar difference was observed by Ganpule et al.\textsuperscript{12} between SBT and PZT nanostructures. In SBT thin films, a similar phenomenon was observed by Kholkin et al. by interferometric studies,\textsuperscript{8} which was attributed to the absence of the contribution from non-180° domain walls. However, experimental results by Ganpule et al. seem to indicate that the decrease of $d_{33}$ values in PZT is not directly related to the non-180° domain switching. Further studies are still needed to clarify this issue.

In summary, well-ordered arrays of sub-80 nm high SrBi$_2$Ta$_2$O$_9$ nanostructures were successfully prepared on SrTiO$_3$:Nb (111) single-crystal substrates. Their microstructure was investigated by cross-sectional TEM and SAED, and piezoelectricity in these nanostructures was investigated by PFM. It was shown that $30 \, \text{nm}$ high SBT nanostructures are still ferroelectric and the $d_{33}$ values reach up to $8 \, \text{pm/V}$ under $20 \, \text{V}$ dc bias.

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\begin{itemize}
\item F. Jona and G. Shirane, \textit{Ferroelectric Crystals} (Dover, New York, 1993).
\item The position of the PFM tip (on the center of a nanostructure) was found by determining the topographically highest point of the nanostructure in the AFM topography mode. The system stability of the AFM scanner against thermal drift had been shown to be equivalent to less than $30 \, \text{nm}$ lateral drift within the time required for the recording of a hysteresis curve.
\item See Ref. 18, pp. 66–77.
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