Crystallization of PZT in Porous Alumina Membrane Channels

O. M. ZHIGALINA,¹ E. D. MISHINA,² N. E. SHERSTYUK,²
K. A. VOROTILOV,² V. A. VASILJEV,² A. S. SIGOV,^{2,*}
O. I. LEBEDEV,³ Yu. V. GRIGORIEV,¹ M. P. DE SANTO,⁴
R. BARBERI,⁴ AND Th RASING⁵

¹Institute of Crystallography RAS, Leninskii prospekt, 59, 119333
Moscow, Russia

²Moscow State Institute of Radioengineering, Electronics and Automation
(Technical University), prosp. Vernadskogo, 78, 119454 Moscow, Russia

³EMAT, RUCA, Groenenborgerlaan 171, B2020 Antwerpen, Belgium

⁴CEMIF.CAL, CNR-Licryl Laboratory, Physics Department,
University of Calabria, Rende (Cs), Italy

⁵Institute for Molecules and Materials, University Nijmegen, Toernooiveld 1,
6525ED Nijmegen, The Netherlands

Composite Pb(Zr,Ti)O₃(PZT)/alumina nanostructures are fabricated using 2-dimensional porous alumina as a template. Details of pores filling as well as of crystallization are studied by atomic force microscopy and transmission electron microscopy. The presence of a ferroelectric phase is confirmed by optical second harmonic generation experiments.

Introduction

Templating of a material into a nanoporous membrane is a new technique, which allows fabricating nanostructures with pre-defined size and shape of nanoparticles (tubes, rods, etc.). Template fabrication is quite attractive from a technological point of view since it does not require expensive e-beam lithographic machines and is far less time-consuming. Possible electronic and opto-electronic applications are numerous. Single domain porous alumina with high aspect ratio acts as a two-dimensional photonic crystal with a well-defined photonic band-gap [1]. It was shown that the use of anodically etched Al templates allows a series of nanotransistors with quite good characteristics to be fabricated without a clean room or lithography [2].

However, preparation of arrays of nanotubes and nanorods of functional materials, such as complex oxide ferroelectrics or manganites, still remains a challenge in material science. Ferroelectric oxides are an important class of functional materials since they exhibit

---

Paper originally presented at IMF-11, Iguassu Falls, Brazil, September 5–9, 2005; received for publication January 26, 2006.

*Corresponding author. E-mail: zectoz@mizea.ru

interesting properties such as dielectric polarization, piezo- and pyroelectric effects, high dielectric permittivity. Recently, ferroelectric nanorods with diameters as small as 5 to 60 nm and with lengths of more than 10 μm were obtained by a solution-phase decomposition of bimetallic alkoxide precursors in the presence of coordinating ligands [3]. Ferroelectric lead zirconate titanate and barium titanate nanotubes of 500 nm in diameter and with 100 nm wall thickness were fabricated by wetting of porous silicon templates of polymeric precursors [4]. By means of electrostatic force microscopy, ferroelectric switching was shown in a 12 nm diameter rod [5].

There are two major problems which arise during template fabrication of nanorod (nanotube) arrays. The first one is filling the pores, and the second one is crystallization. While the micron-scale (down to 0.5–1 μm) is just a matter of accurate duplication of thin film processing, with decreasing pore size the problems increase drastically. Although previously we showed the possibility of template fabrication by sol-gel technique of PZT nanoparticles of 10 nm in diameter [5], a reliable procedure of nanotube and nanorod fabrication is still a challenge.

In this paper we report a detailed structural and optical characterization of PZT nanorods fabricated by templating into porous alumina membranes (of 200 nm pore diameter). The PZT nanostructures were characterized by scanning electron microscopy (SEM), transmission electron microscopy (TEM) and atomic force microscopy (AFM), in addition to the nonlinear-optical technique of second harmonic generation (SHG). The latter allows to distinguish between ferroelectric and paraelectric states, since the former (noncentrosymmetric) phase has a SHG signal of dipole origin producing a strong response, while for the latter (centrosymmetric) phase, the dipole process is forbidden, and the intensity of SHG is several orders of magnitude lower.

Sample Preparation

For fabrication of PZT/alumina nanostructures commercially available Whatman membranes were used with disordered pores of 200 nm. The thickness of the membrane is 200 μm , which gives an aspect ratio of 10^3 . The surface of a membrane within the inter-pores area is quite rough, with depths of cavities of about 100 nm [6].

During the deposition process several problems have to be solved: (i) increasing of the filling depth up to the total length of the pores, (ii) nanorod formation (rather than nanotubes), (iii) minimization of the film formation on top of the structure, (iv) crystallization in perovskite (rather than pyrochlore) phase.

To avoid formation of the film on top, the membrane was attached to a silicon wafer by a high-temperature glue. Figure 1a shows schematically the deposition arrangement.

PZT precursor solution ($\text{Ti/Zr} = 47/53$) was prepared by dissolution in methoxyethanol of zirconium and titanium isopropoxides and lead acetate trihydrate dehydrated with acetic acid anhydride with a lead excess in solution of 10 mol.% [7].

PZT solution was poured onto the surface of the alumina membrane, after that a spinning procedure was performed for removal of surpluses of the solution. Drying was performed by IR-heating and heat treatment at 400°C, 10 min. After that a next layer was applied by the same manner. Final crystallization was performed at 650°C, 20 min.

Structure

The PZT microstructure was characterized by atomic force microscopy (AFM) with Veeco Instruments AutoProbe CP, transmission electron microscopy (TEM) and high resolution

Figure 1. (a) Schematic of arrangement of a membrane clamped to the silicon substrate and AFM images of the nanostructure cleavage for areas A1 (b) and A2 (c).

electron microscopy (HREM) with Philips EM430 ST electron microscope at accelerating voltage of 200 kV and JEOL4000-EX electron microscope at accelerating voltage of 400 kV. Phase composition was investigated by XRD analysis. Cross-sectional and plane-view samples for TEM and HREM studies were prepared by mechanical polishing, dimpling and ion milling by Ar^+ in Gatan 600.

Figure 1 shows AFM images of the cross-section of the PZT/alumina nanostructures in different areas of the sample. Area (A1) corresponds to the bottom part of the membrane, which was attached to the silicon wafer. Area (A2) corresponds to the top part of the membrane; the precursor was poured on a membrane from this side. Since there was no flow of the precursor through the pores, the filling of the pores is better from the top side. In area A2 almost homogeneous rods of the filler are formed in the pores (Fig. 1c), while in area A1 only grains of the filler can be observed (Fig. 1b). In both areas empty pores also were found probably due to the initial structure of the membrane (blocking from the surface).

Figure 2(a) presents a cross-sectional SEM-image of a membrane. One can see long vertical channels, some of them are branched. Figure 2(b) shows a TEM plane-view image demonstrating holes with PZT crystals on the walls. The diffraction pattern taken from the membrane (insert Fig. 2(b)) shows a bright wide halo that reveals its amorphous state which is confirmed by XRD data. Figure 2(c)–(d) demonstrates a TEM cross-sectional image of the membrane. The diameter of holes is 200 ± 15 nm. As shown in Fig. 2(d), filling of the membrane channels is not continuous, probably as a result of shrinkage during the drying/crystallization processes.

Figure 2. The structure of membrane: (a)—SEM image of membrane cross-section; (b)—TEM plane-view image and diffraction pattern; (c)— (d)—TEM cross sectional images of membrane.

Figure 3 illustrates TEM dark field and bright field images of the cross-sectional sample with corresponding diffraction patterns. Sharp rings and single reflections are observed. Calculation of the diffraction pattern revealed reflections corresponding to atomic distances of 2.88, 2.85, 2.35 Å (perovskite) and rings corresponding to 3.02; 2.64; 1.84 Å (pyrochlore). Perovskite grains have a nonuniform shape with sizes up to 150 nm (Fig. 3(b)). Their distribution is irregular from channel to channel and their quantity increases with increasing distance from the membrane surface. On the other hand, small pyrochlore particles with size in the range of 2–10 nm are also observed both in the body of perovskite grains and separately.

Figure 4 shows a HREM image of pyrochlore particles. As a rule, they have a spherical or similar shape with a minimum particle size of 2 nm. Their distribution inside the channel is irregular: both accumulations closed to each other and single particles infreezed in perovskite crystals are observed.

It is known that thin film prepared by deposition of PZT solution yields a columnar grain structure [8] as a result of dominating nucleation at the Pt interface over nucleation in the bulk of the film [9, 10]. Perovskite phase in CSD PZT films usually forms as a result of

Figure 3. TEM of PZT alumina membrane: (a)—dark field image of pyrochlore and perovskite particles; (b)—bright field image of perovskite crystals.

transformation via an intermediate metastable phase, e.g. via fluorite/pyrochlore [9, 10]. As shown, the microstructure of PZT nanorods is sufficiently different from the thin film one. There are two phases in the membrane channels: large perovskite crystals (100–150 nm) and small pyrochlore nanocrystals (2–20 nm). Perovskite crystals grow dominantly from the interface. The transformation of the pyrochlore into the perovskite phase is not complete, probably due to a higher energy barrier in the case of crystallization in closed membrane pores in comparison with crystallization on a free surface. A similar structure was observed in PZT channels prepared by micromolding in capillaries [11].

Figure 4. HREM image of Py particles.

Nonlinear Optical Properties

For the SHG measurements the output of a Ti:Sapphire laser at 760 nm with a pulse width of about 100 fs and a repetition rate of 82 MHz was used, with an average power of 100 mW focused onto a spot of about 100 μm . The SHG signal at 380 nm transmitted through the sample was filtered by colour filters and a monochromator and detected by a photomultiplier tube. Polarizations of the fundamental and SHG waves were perpendicular and in the plane of incidence (s- and p-polarization). The angle of incidence was varied by rotating the sample around the vertical in-plane axis. The aperture of the detection system could be varied in the range of 2° – 10° using diaphragms. Since even bare membranes are highly dispersive (white opaque), the same character of interaction with light remains after filling the pores and annealing. In linear reflection the scattering indicatrix is very wide, and no specular peak can be observed. This is the reason to measure the SHG intensity not only in the specular direction, but also to carry out detailed measurements of the SHG scattering indicatrix. These measurements were performed by rotating the whole detection system around the vertical optical axes centred at the sample plane (details of the analysis of SHG scattering indicatrices can be found in [12]).

Application of optical SHG allows to distinguish between the ferroelectric and nonferroelectric phase. Before high-temperature annealing, the PZT aerogel is in the amorphous state, which is centrosymmetric and thus does not produce a high SHG signal. After annealing a mixture of two phases is formed: amorphous (centrosymmetric) pyrochlore and ferroelectric (noncentrosymmetric) perovskites. Only the latter produces a high SHG signal.

Figure 5 shows the SHG intensity as a function of scattering angle for two sides of the sample, A1 and A2. Two polarization combinations were used: p-p and p-s. The p-p geometry in the specular direction provides information of coherent SHG signal, while p-s can be considered as a measure of anisotropy, since the SHG intensity for this polarization equals zero for an isotropic material [13].

To analyse the specular signal the scattered background should be subtracted from the total signal. Then one can see that for both A1 and A2 sides, the specular p-p signal is quite high (Fig. 5(a)) and the specular p-s signal is absent (Fig. 5(b)). For the A2 side, the p-p

Figure 5. SHG scattering indicatrices from two sides of a PZT/alumina nanostructure for the p-p (a) and p-s (b) polarization combinations.

signal (Fig. 5(a), filled circuits) is about 3 times higher than for the A1 side (Fig. 5(a), open circuits). For the specular direction, also the SHG signal for the A1 side of not-annealed sample was measured (Fig. 5(a), star). In the p-p polarization combination it is 4 times lower than for the annealed sample.

The presence and size of the specular SHG signal indicate the presence of the ferroelectric perovskite phase. For a more quantitative analysing, the amount and distribution of perovskite domains should be known. These data are also in agreement with our previous studies of nanostructures with 40–60 nm PZT nanorods [6].

For scattered radiation the difference between the two geometries, p-p and p-s, disappears. Comparison of SHG light scattered from a bare membrane (Fig. 5, triangles) and PZT nanostructures shows that the scattered radiation originates mostly from the membrane itself (Fig. 5(b)).

Conclusions

Both microscopy and SHG experiments show that the crystallization of PZT precursor in 200 nm alumina membrane channels leads to the formation of two phases: perovskite and pyrochlore/fluorite. The channels are filled up discontinuously as a result of shrinkage during drying and crystallization. The morphology and size of pyrochlore/fluorite and perovskite phases are different: perovskite crystals grow up to 150 nm and present an arbitrary shape. Pyrochlore/fluorite particles grow in the range of 2–10 nm and have mainly a spherical shape. In the case of blocked pores at the backside of the membrane (by tight attaching to silicon in our experiments) PZT precursor does not fill a pore completely. However, with transparent porous matrix optical properties can be measured and explored preferably from the back side, for which they are not distorted by thin film always formed on top of the structure during preparation.

The work is supported by RFBR (Grants 04-02-16804, 03-02-16945, 05-02-08052) and INTAS (grant 01-0075). The authors are grateful to doctor Diakonova N. B. for help with the XRD measurements.

References

1. J. Choi, Y. Luo, R. B. Wehrspohn, R. Hillebrand, J. Schilling, and U. Gösele, Perfect two-dimensional porous alumina photonic crystals with duplex oxide layers. *J. Appl. Phys.* **94**, 4757–4762 (2003).
2. T. Wade and J.-E. Wegrowe, Template synthesis of nanomaterials. *Eur. Phys. J. Appl. Phys.* **29**, 3–22 (2005).
3. J. J. Urban, W. S. Yun, Q. Gu, and H. Park, Synthesis of single-crystalline perovskite nanorods composed of barium titanate and strontium titanate. *J. Am. Chem. Soc.* **124**, 1186–1187 (2002).
4. Y. Luo, I. Szafraniak, V. Nagarajan, R. B. Wehrspohn, M. Steinhart, J. H. Wendorff, N. D. Zakharov, R. Ramesh, and M. Alexe, Ferroelectric lead zirconate titanate and barium titanate nanotubes. *Integrated Ferroelectrics*. **59**, 1513–1520 (2003).
5. W. S. Yun, J. J. Urban, Q. Gu, and H. Park, Ferroelectric Properties of Individual Barium Titanate Nanowires Investigated by Scanned Probe Microscopy. *Nanoletters*. **2**, 447–450 (2002).
6. E. D. Mishina, A. S. Sigov, Yu. I. Golovko, V. M. Mukhorotov, T. Tamura, S. Nakabayashi, and H. Masuda, Ferroelectric nanostructures sputtered on alumina membranes. *Physica E: Low-dimensional Systems and Nanostructures*. **25**, 35–41 (2004).
7. K. A. Vorotilov, M. I. Yanovskaya, E. P. Turevskaya, and A. S. Sigov, Sol-gel derived ferroelectric thin films: Avenues for control of microstructural and electric properties. *J. Sol-Gel Science and Technology*. **16**, 109–118 (1999).

8. P. V. Burmistrova, A. S. Sigov, A. L. Vasiliev, K. A. Vorotilov, and O. M. Zhigalina, Effect of lead content on the microstructure and electrical properties of sol-gel PZT thin films. *Ferroelectrics*. **271**, 51–56 (2002).
9. R. W. Schwartz, Chemical solution deposition of perovskite thin films. *Chem. Mat.* **9**, 2325–2340 (1997).
10. R. W. Schwartz, J. A. Voigt, B. A. Tuttle, D. A. Payne, T. L. Reichert, and R. S. DaSalla, Comments on the effects of solution precursor characteristics and thermal processing conditions on the crystallization behaviour of sol-gel derived lead zirconate titanate thin films. *J. Mat. Research*. **12**, 444–456 (1997).
11. J. S. Vartuli, M. Ozenbas, C.-M. Chun, M. Trau, and I. A. Aksay, Micropatterned lead zirconium titanate thin films. *J. Mat. Research*. **18**, 1259–1265 (2003).
12. E. D. Mishina, T. V. Misuryaev, A. A. Nikulin, V. R. Novak, Th. Rasing, and O. A. Aktsipetrov, Hyper-Rayleigh scattering from Langmuir films of C₆₀ and its derivatives. *J. Opt. Soc. Am. B*. **16**, 1692–1696 (1999).
13. O. A. Aktsipetrov, I. M. Baranova, and Yu. A. Il'inskii, Surface contribution to the generation of reflected SH for centrosymmetric semiconductors. *Sov. Phys. JETP* **64**, 167–173 (1986).