Production and PFM Characterization of Barium Titanate Nanofibers

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Production and PFM Characterization of Barium Titanate Nanofibers

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Continuous nanofibers of barium titanate (BaTiO₃) with average diameter of 150–300 nm have been produced by means of mutual sol-gel and electrospinning routines with subsequent calcination step. The structural characterization of the obtained nanofibers has been performed by XRD and Raman spectroscopy. Their individual grain and domain structures were studied by piezoresponse force microscopy (PFM). The results show that the fibers consist of stacked tetragonal ferroelectric BaTiO₃ grains with average size of about 50–100 nm and random initial orientations. The piezoelectric response is similar to that obtained for domain model in ferroelectric tetragonal perovskites.

I. Introduction

Ferroelectric low-dimensional nanowires or nanofibers are very interesting for ferroelectric random access memory (FRAM) devices with matrix addressing and/or accessing methods [1–3]. In matrix addressing the fibers are arranged as intersection pattern of addressing rows and columns. The principal of the driving of this devise is “coincident half-select” addressing, when the writing is accomplished by applying of half-signal amplitude 0.5S to the rod and column that only intersect (address) receives the full switching S (if threshold switching ST conforms to 0.5S < ST < S). The other intersects on the addressing row and column receive only half-amplitude signal while all other addresses in the array receive zero. Since the reading is the inverse of writing, the matrix addressed array can be read out by simply reversing the polarity of the signals used for writing (either non-destructive optical reading).

The decrease of the dimensionality of the functional elements is highly desirable for these applications since it will reduce the addressing power (in case of volatile memory – the storage power) and significantly increase the storage density. On the other hand, different physical properties of the complex oxide ferroelectrics are related to their size. In studying the effect of the crystallite size on the structure and related properties, special attention has been given to the perovskite ferroelectric barium titanate. For instance, it was stated that with decreasing crystallite sizes below a few micrometers, the proportion the crystal influenced by the surface layer increases, so that below a critical size the tetragonal
phase is not stabilized and the resulting BaTiO$_3$ samples remain paraelectric [4]. Also, the decrease of the size of isolated crystallites in the submicrometer region may decrease the ferroelectric transition temperature and dielectric constant. Because these properties are dependent on the structure and finite grain size, the control of the synthesis of oxide ferroelectrics in terms of size, shape and morphology is an important task.

Here, a study of the synthesis of barium titanate (BaTiO$_3$) nanofibers is presented, including their structural characterization and study of their ferroelectric properties. The interest on this material is caused by its size-dependent properties and potential for application as a low-dimensional element in ferroelectric nonvolatile random memory devices. In spite of the fact that several approaches and methods for the production of BaTiO$_3$ nanowires and nanofibers have been recently implemented, a comprehensive study of the ferroelectric properties in these nanostructures is very limited. The aim of this work is the investigation the domain structure in continuous nanofibers of BaTiO$_3$, synthesized by the electrospinning technique combined with a sol-gel approach.

The electrospinning technique enables the fabrication of continuous, individual or mat assembled fibers with submicrometer diameters. The method is based on the jet drawing from a polymer solution or melt by a strong electric field. In the framework of ferroelectric memory applications, it is important to note that the electrospinning technique is a very effective tool for controlling fiber deposition and structuring towards producing two- and three-dimensional fiber arrays suitable for FRAM with matrix addressing.

II. Experimental

The nanofibers of barium titanate have been prepared following the routine described in [5]. To prepare the electrospinning precursor solution, 2 g of poly(vinyl pyrrolidone) (PVP, $M_w = 43,000$) was dissolved in 3 ml of ethanol. Then, 1.15 g of titanium isopropanoxide (Ti[OCH(CH$_3$)$_2$])$_4$ was added to 3 ml acetic acid, where 1 g of barium acetate ((CH$_3$COO)$_2$Ba) was previously dissolved. Subsequently, the acidic solution was mixed with the PVP-alcohol solution and the obtained mixture was stirred for several hours prior electrospinning. The obtained fibers were electrospun under 15 kV applied electric tension, with 9 cm of distance between syringe needle and collector and a 1 ml/h of rate. They were dried at 100°C for 1 h, after preparation. The as-prepared samples consisted on BaTiO$_3$ grains dispersed inside a polymeric host. In order to vaporize the polymer host, to connect the grains and form continuous BaTiO$_3$ fibers, the as-synthesized fibers were subsequently annealed at different temperatures (700°C, 800°C and 900°C) for 1 hour.

The morphology of the electrospun BaTiO$_3$ fibers was observed under a scanning electron microscope (SEM, Nova NanoSEM 200), after gold coating. The structural studies were performed by X-ray diffraction with a Bruker D8 Discover powder diffractometer using Cu-K$_\alpha$ radiation (40 kV, 50 mA). Raman measurements were performed in a backscattering configuration, using the 488 nm beam from an argon ion laser focused on the fiber mesh plane. The scattered light was dispersed by a subtractive spectrometer and collected with a liquid-nitrogen-cooled charge coupled device (CCD) detector.

The grains and domain structure of the individual BaTiO$_3$ nanofibers were studied by piezoresponse force microscopy (PFM). The PFM technique is based on the detection of the mechanical response of the sample to an applied electric voltage, due to converse piezoelectric effect [6]. A commercial atomic force microscope (NanoScope IIIA, Veeco) with a conductive Si cantilever (Nanosensors) was used, equipped with an external lock-in amplifier (SR830, Stanford Research), a function generator (FG120, Yokogawa) and a
voltage amplifier (7602, Krohn-hite). These were used in order to apply both AC and DC voltages to the fiber surface, for poling and for piezoresponse image acquisition [7] while simultaneously acquiring topographic images. Conductive probes of doped Si (42 N/m, fres∼300 kHz, PPP-NCHR, Nanosensors) were used for the PFM measurements, which performed at ambient temperature. The tip had the shape of a polygon-based pyramid with a height of 10–15 µm and an effective radius of rtip∼10 nm. To provide the conductive bottom electrode, the BaTiO3 fibers were put on a platinum substrate, prior the annealing.

III. Results and Discussion

A. Morphological and Structural Studies

The as-electrospun fibers, containing BaTiO3 grains within the polymeric host, have smooth and uniform topography. Figure 1 presents the SEM images of the BaTiO3 fibers annealed at 700°C for 1 h. The annealed nanofibers are continuous, with lengths up to centimeters and diameters in the range 100–300 nm. Their morphology consist of connected nanoparticles with 58 ± 9 nm grain sizes, stacked together to form the shape of a long fiber. The average grain size, evaluated from the SEM image, is in good agreement with those calculated from the XRD data by using the Scherrer equation [8] (see inset on Fig. 1(b)).

To characterize the progress of the barium titanate phase crystallization, X-ray diffraction spectra of the BaTiO3 nanofibers have been measured on the as-spun and on the fibers annealed at different temperatures. Figure 2 shows the XRD spectra obtained on the as-prepared sample an on the ones annealed at 700°, 800° and 900°C. The as-spun dried composite fiber mat has an amorphous structure while the annealed samples present well-defined diffraction peaks that increase in intensity with annealing temperatures. The average particles size, calculated from X-ray diffraction peak widths are in the range 36–40 nm (Fig. 1(b)).

Due the small size of the particles composing the fibers the diffraction peaks are broad and it is difficult, from the X-ray diffraction results alone, to distinguish which of the BaTiO3 phases (cubic and/or tetragonal) is the dominant one on the samples. In fact, it is known that for grain sizes below 1 µm the tetragonal (ferroelectric) distortion of the barium titanate

![Figure 1. SEM image of BaTiO3 nanofibers. Inset presents the grain size dependence on the annealing temperature calculated from XRD data.](image-url)
crystallites is reduced, due to the presence of a non-ferroelectric grain boundary layer (dead layer) on the grains surface [9–11]. Here, the average particles size, calculated from X-ray diffraction patterns are slightly above the critical size below which the stabilization of the tetragonal phase is hindered ($\leq 30$ nm for BaTiO$_3$ [12]). Also, somewhat larger (200) peak width as compared, for example, with (111) peak, is indicative of the appearance of the (002) peak and, thus, of the presence of a polar distortion of the BaTiO$_3$ unit cell.

To confirm the presence of the tetragonal phase in the annealed barium titanate nanofiber mats and to further characterize their structure, Raman spectroscopy measurements have been performed on the samples. Raman spectroscopy yields phonon parameters reflecting the local crystal symmetry, allowing the detection of the presence of a polar distortion of the grains unit cell. Figure 3 presents the measured Raman spectra obtained on

Figure 2. X-Ray diffraction spectra of the BaTiO$_3$ nanofibers prepared with different annealing temperatures.

Figure 3. Raman spectra measured on the barium titanate nanofibers annealed at 700 $^\circ$C (upper curve) and bulk BaTiO$_3$ sample.
the BaTiO3 nanofibers annealed at 700°C along with a spectrum obtained on a reference powder.

On the spectrum of the reference, Raman peaks are clearly seen at 272 cm$^{-1}$, 307 cm$^{-1}$, 520 cm$^{-1}$ and 716 cm$^{-1}$. They are assigned to the $A_1$(TO1), $B_1$ and $E$(TO+LO), $E$(TO) and $A_1$(TO2), $E$(LO) and $A_1$(LO2) vibrational modes, respectively, and are characteristic of the tetragonal $P4mm$ crystal symmetry of the BaTiO3 ferroelectric phase [13, 14]. On the other hand, the cubic (paraelectric) phase of BaTiO3 has a $Pm3m$ crystal symmetry, which, theoretically, does not have Raman active modes [14, 15]. However, distortions to the perfect cubic cell, induced by disorder on the Ti positions or due to external stresses over the grains, can occur and broad peaks at around 250 cm$^{-1}$ and 520 cm$^{-1}$ have been observed on polycrystalline powders [16].

On the fiber mats four peaks are visible on the spectra, with wavenumber positions that are similar to the corresponding ones on the reference powder. In particular, the peaks at 308 cm$^{-1}$, 520 cm$^{-1}$ and 730 cm$^{-1}$ can be followed on the different samples and their intensity decrease with increasing annealing temperature is due to the corresponding decrease of the BaTiO3 grain size on the fibers as observed on the XRD results. These Raman peaks are characteristic of the BaTiO3 tetragonal (ferroelectric) structure [16] and are indicative of its presence on the prepared barium titanate fibers. On the other hand the Raman peak observed near 630 cm$^{-1}$, on Fig. 3, is indicative of strain and disorder in grain boundary regions, as previously observed on very small nanosized (~30 nm) grains [14].

B. Domain Structure of BaTiO3 Nanofibers

Figure 4(a) presents the three-dimensional image of a single BaTiO3 nanofiber, obtained by the AFM. The fiber topography presents a similar structure as the ones obtained by SEM the stacked grains form a prolonged fiber framework. In contrast to the expected cylindrical shape, the fiber visualized by AFM has attended form with width approximately two times bigger than the fiber height. This is can be due to a slight spreading out of the polymer fiber (before annealing) when it is deposited on the flat surface but not on fiber web (as it is

![Figure 4](image-url)

**Figure 4.** (a) Topography image of an individual BaTiO3 nanofiber; (b) image cross section of the fiber’s edge surface shown on figure (a); (c) power spectrum of diameter distribution, the peak corresponds to 260 nm (Figure available in color online).
Figure 5. (a) AFM topography image of BaTiO$_3$ fiber and two components of piezoresponse contrast: out-of-plane PFM (b), and in-plane PFM (c) images (Figure available in color online).

shown on Fig. 1). Also, the AFM does not present negatively inclined surfaces due to the cantilever and tip design features.

The Figs. 4(b) and (c) characterize the roughness of the BaTiO$_3$ nanofiber surface. The average grain size, estimated from the cross section of the fiber top edge (Fig. 4(b)), is 120 nm. Similar results are obtained from the power spectrum observed from the FFT conversion of the AFM image, shown on Fig. 4(c). It represents the roughness (height of a surface around its mean value) over different spatial frequency ranges. The dominant peak is due to the average fiber thickness while the others are due to the average grain dimensions. The obtained average fiber thickness is 300 nm and the average grain sizes are in the range 50–100 nm.

The ferroelectric domain structure of BaTiO$_3$ nanofibers have been observed by using the PFM imaging. Figure 5 presents the AFM topography and two components of the piezoresponse (PFM) contrast—vertical (out-of-plane) and lateral (in-plane) of the barium titanate nanofibers. By combining of these two piezoresponses, it is possible to map out the polarization distribution. On the PFM images shown in Figs. 5(b) and (c), the contrast is associated with the direction of the polarization. For the out-of-plane component of the tip deflection, the bright regions correspond to domains with the polarization vector oriented towards the bottom electrode, referred to as down polarization $p^-$, while the dark regions correspond to domains oriented upward, referred to as up polarization $p^+$. These components depend on the crystallographic orientation of the individual grains of BaTiO$_3$.

In lateral PFM (LPFM) the detection of the piezoelectric shear deformations results from any in-plane polarization component. Amplitude and phase of the torsional vibration of cantilever are linked to polarization (direction and magnitude) through the $d_{15}$ effective piezoelectric coefficient. The contrast on the LPFM image (Fig. 5(c)) indicates the in-plane direction of the polarization. Note that in-plane PFM shows the piezoresponse signal with a higher intensity as compared to the contribution given by the out-of-plane piezoelectric response, similar to that obtained for the domain model in ferroelectric tetragonal perovskites. The evaluated domain size in the BaTiO$_3$ electrospun nanofibers, from PFM imaging, correlates well with the results obtained by SEM and AFM grains composed the fiber structure.

It should be noted that in both VPFM and LPFM images the piezoelectric contrast is more pronounced on the fiber periphery. Figure 6 shows the topography cross section and out-of-plane piezoelectric response distribution obtained by scanning the tip perpendicularly to the fiber direction. Such distribution of the PFM signal is caused by the cylindrical geometry of the fibers and its characterization has been thoroughly analyzed on, e.g.,
The characteristic inhomogeneous distribution of PFM signal with prevail regions possessing small piezoresponse possibly due to the arbitrary orientations of the neighboring grains resulting in cancellation of the total piezoresponse.

The investigation of the ferroelectric switching in the BaTiO$_3$ nanofibers has been attempted. However, saturation of the hysteresis loop was not possible due to the grains damage under the electric field. This fact can be a serious limitation for the application of the electrospun barium titanate nanofibers and further processing improvement is needed to overcome this drawback. One of the possible solution is the increase of the sintering temperature of the as-spun samples, while also increasing the annealing time, in order to promote the increase of BaTiO$_3$ grain size in the fibers. In fact, it is known, that above a critical size the BaTiO$_3$ are formed by a tetragonal core, a surface (non-ferroelectric) shell layer and a transition zone. As the grain size is decreased, the proportion of the tetragonal core is reduced so that below the critical sized it is not stabilized causing the disappearance of the ferroelectric state (what, in fact, can be also a reason for the regions on BaTiO$_3$ nanofibers with the absence of piezoresponse). The increased grain growth would then promote the ferroelectricity of the nanofibers. The work on the precise grain size controlling and nanofiber morphology during the processing is under progress.

IV. Conclusion

Nanofibers of barium titanate have been produced by the electrospinning technique from a sol-gel precursor. The morphology of the obtained fibers was examined by SEM and AFM while their structure was analyzed by XRD and Raman spectroscopy. The fibers presented BaTiO$_3$ crystallites, with sizes in the range the 50–100 nm, stacked together to form a continuous filament structure. The presence of the tetragonal (ferroelectric) BaTiO$_3$ phase was confirmed by Raman spectroscopy. The domain structure of the nanofibers was examined by piezoelectric force microscopy for the first time. The PFM measurements revealed randomly oriented particles possessing high piezoelectric response, consistent with the presence of the tetragonal BaTiO$_3$ (ferroelectric) phase stabilized in the nanofibers.

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