

## DOMAIN STRUCTURES OF FERROELECTRIC LEAD TITANATE NANOTUBES FABRICATED AT VARIOUS TEMPERATURES

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**Abstract:** We studied the domain structures of ferroelectric PbTiO<sub>3</sub> nanotubes (NTs) fabricated at various temperatures, using piezoresponse force microscopy (PFM). PTO NTs fabricated at above 500 °C underwent mechanical fracture through development of nanocracks due to grain growth, leading to ferroelectric domains with larger size and lower aspect ratio.

**Keywords:** ferroelectrics, nanotubes, domains, PFM

Fabrication and analysis of the domain structures and properties of one-dimensional (1-D) ferroelectric nanomaterials have been widely performed so far [1–4]. However, it is worth noting that most studies on the domain structures and ferroelectric properties of 1-D ferroelectric nanomaterials have centered on nanowires (NWs) and (nanorods) NRs. Few investigations of domain structures of the ferroelectric nanotubes (NTs) have been performed [5]. Furthermore, domain structures of ferroelectric NTs depending on the synthesis temperatures have not been previously reported. For such highly integrated nanosize ferroelectric devices, it is essential that studies on the domain structures and ferroelectric properties of ferroelectric NTs be performed prior to such applications. Therefore, in this paper, we study the domain structures of ferroelectric PTO NTs synthesized at various temperatures.

TiO<sub>2</sub> NTs as starting materials were transformed into the PTO NTs by gas phase reaction with PbO gas at elevated temperatures. Fabrication method of TiO<sub>2</sub> NTs is described in elsewhere [6-8]. Sectional temperatures of the tube furnace were preliminarily measured, and then the TiO<sub>2</sub> NTs were located at each temperature point of 300, 400, 500 and 600 °C, respectively. Domain structures of the PTO NTs were analyzed using piezoresponse force microscope (PFM).

Figure 1 shows the topography, PFM amplitude and phase images of the PTO NTs fabricated at 300, 400, 500 and 600 °C (hereafter, we call them NT<sub>300</sub>, NT<sub>400</sub>, NT<sub>500</sub> and NT<sub>600</sub>, respectively). Ferroelectric PTO phases have been formed above 400 °C where the domain images were clearly obtained as shown in Figures 1(b)–(d). However, NT<sub>300</sub> did not show any obvious domain features [Figure 1(a)]. This implies that the PTO ferroelectric phase can be synthesized at temperature between 300 °C and 400 °C, which is lower than the heat treatment temperature of 500–600 °C that is

normally required to form crystalline PTO in either thin films or other nanostructures [1-4, 9-11].

We obtained X-ray diffraction (XRD) patterns of both TiO<sub>2</sub> NTs and the NT<sub>400</sub> sample for the comparison (see Figure 2). Based on that the phase transition temperature of PTO NTs is near 650 °C [12], it can be speculated that PTO NTs in the whole temperature range have tetragonal phase in this XRD analysis. Anatase [ $2\theta = 36.5^\circ$  for (110) planes] phase of TiO<sub>2</sub> could not be found within the full temperature range in Figure 2(b). Absence of TiO<sub>2</sub> phase suggests that the TiO<sub>2</sub> NTs were perfectly transformed to PTO at 400 °C. Evident decrease of broad peaks in the vicinity of  $2\theta = 28.7^\circ$  comes from the vaporization of excess PbO ( $2\theta = 28.6^\circ$ ).

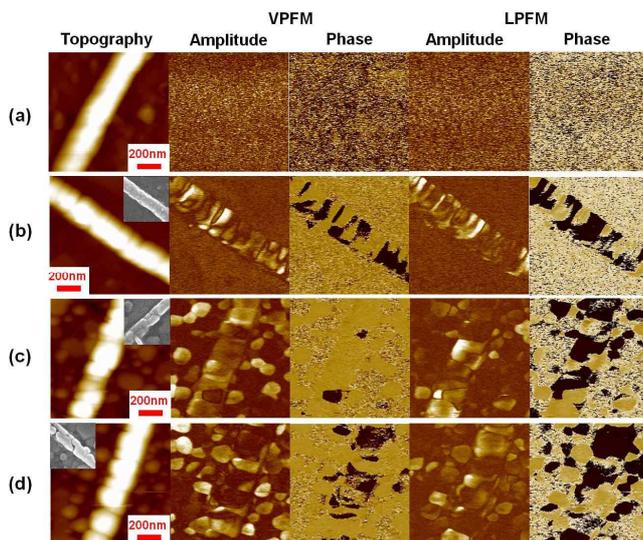
It is worth noting, though, that T<sub>500</sub> and T<sub>600</sub> underwent partial fracture into particles which show ferroelectric domain structure as shown in Figures 1(c) and (d). We deduce that the reason behind the partial fractures in NT<sub>500</sub> and NT<sub>600</sub> is the stress-induced cracking, which depends on the grain size of each NT. In case of NT<sub>400</sub>, as the NTs are cooled down after annealing, the elastic strain energy from the thermal expansion coefficient difference of each grain is accumulated across the grains. However, this strain energy is not so ample that internal stresses by the strain energy cannot cause the cracking, because of small grain size of NT<sub>400</sub> as shown in Table 1. On the other hand, NT<sub>500</sub> and NT<sub>600</sub> showed larger grains by the sufficient grain growth at higher annealing temperatures. When the NTs are cooled down, the internal stresses are developed due to the accumulation of large amount of elastic strain energy across the grains, and cause the cracking [13]. As the cracks begin to form, the stored elastic strain energy converts to the fracture surface energy, which leads to the partial fracture of NTs. When the grain size is significantly larger than critical grain size, the cracks are formed.

For the purpose of better understanding on how ferroelectric domain configurations of PTO NTs change after the partial fracture, we performed another experiment. First, we fabricated PTO NTs at 400 °C and PFM analysis was conducted. Then, we annealed the same NTs at 600 °C to induce the partial fracture, and quenched them in air. Finally, we conducted PFM imaging of the same parts of the NTs again. We analyzed five NTs by the above-mentioned process. Average size and aspect ratio (AR) of grains and domains of five NTs are summarized in Table 2. By assuming that both vertical and lateral components of

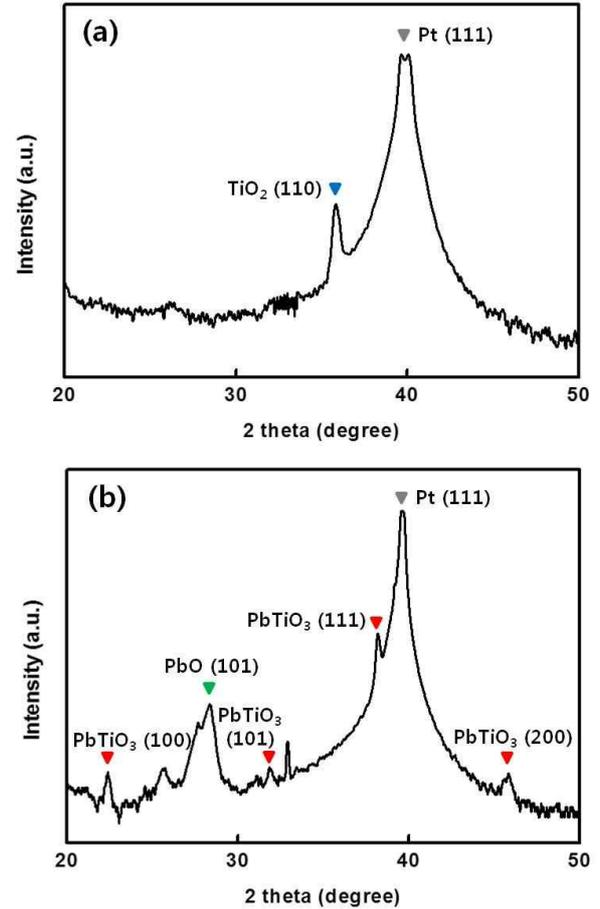
domains can be treated independently and assume the average of those two components is close to the real domain size, we can obtain the average domain size. We found that the average size and AR of grains and domains in NTs are very similar either before or after the heat treatment, which suggests a strong coupling between the ferroelectric domain wall and grain boundary, which is not always the case for ferroelectric thin films [14]. Average domain size increased from 114.8 nm to 166.47 nm and AR decreased from 2.1:1 to 1.44:1 after the partial fracture as shown in Table 2. The trend of increase in domain size and decrease in domain AR are well represented in Figure 3. Before the partial fracture (for 400 °C) where sufficient internal stresses are not developed in the NT, domains of the NT have small average size with high AR, due to the confinement of domains into the small grains with high AR. On the other hand, after the partial fracture (for 600 °C) where the large internal stresses are built up, domains become larger with lower AR. As mentioned above the grain size significantly increases with decrease of AR. After cooling, the domains created in such grains could show larger size with lower AR.

In summary, we studied the ferroelectric domain configuration of ferroelectric PTO NTs fabricated at various temperatures, using PFM. We found that PTO ferroelectric phase was synthesized at 400 °C, which is lower than typical heat treatment temperature. In addition, we observed that the PTO NTs fabricated above 500 °C were partially broken into particles due to the cracking by development of internal stresses. This provides a processing vector for ferroelectric PTO NTs with a temperature window above 400 °C. Finally, we correlated the ferroelectric domain size and shape of the nanotubes with grain size and shape before and after the partial mechanical fracture.

## FIGURES AND TABLES



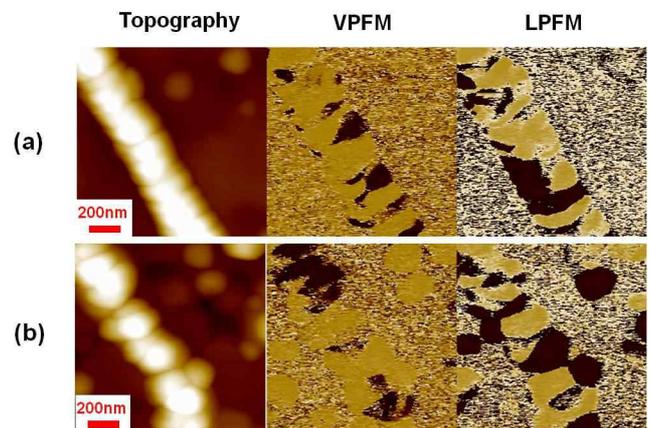
**Figure 1.** Topography, VPFM amplitude and phase, and LPFM amplitude and phase images of the NTs fabricated at various temperatures of (a) 300, (b) 400, (c) 500 and (d) 600 °C, respectively. Insets in topography images show SEM images.



**Figure 2.** X-ray diffraction patterns of (a) TiO<sub>2</sub> NTs and (b) PTO NTs fabricated at 400 °C.

**Tables 1.** Average grain size of PTO NTs fabricated at various temperatures in Figures 1(b)-(d). Average size is defined as  $2(A/\pi)^{1/2}$ , where  $A$  is the average area (in nm<sup>2</sup>) of the grains.

Fabrication temperature (°C)	400	500	600
Grain size (nm)	106.52	167.57	166.57



**Figure 3.** Topography, VPFM phase and LPFM phase images of PTO NT, (a) before and (b) after the partial

mechanical fracture. Both (a) and (b) are same part of the NTs.

**Tables 2.** Average size and aspect ratio (AR) of ferroelectric domains and grains of five PTO NTs before and after the partial fracture. AR is the ratio of the length of long axis to that of short axis of the domains or grains.

	Before fracture	After fracture
	Average	Average
Domain (nm)	114.8	166.47
Grain (nm)	111.7	140.02
Domain AR	2.1:1	1.44:1
Grain AR	2.3:1	1.174:1

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