

Synthesis of Ferroelectric Lead Titanate Nanohoneycomb Arrays via Lead Supplement Process

Bongsoo Kim^a, Seungbum Hong^{a,b,*}, Gun Ahn^a, Kwangsoo No^{a,*}

^aDepartment of Materials Science and Engineering, KAIST, Daejeon 305-701, Korea. Email: seungbum@kaist.ac.kr, ksno@kaist.ac.kr

^bMaterials Science Division, Argonne National Laboratory, Lemont, IL 60439 Email: hong@anl.gov

Here we demonstrate a novel process to convert TiO₂ nanotubes into ferroelectric nano-honeycombs, comprised of vertically-aligned PbTiO₃ nanotubes. Tube-bottom-opening process enabled effective infiltration of lead acetate precursor into the nanotubes. Nano-honeycombs, which were converted via additional lead supplement process, showed uniform conversion and well-defined ferroelectric properties with the effective piezoelectric coefficient of approximately 20 pm/V, which was measured by piezoresponse force microscopy.

Introduction

Lead titanate (PbTiO₃, hereafter PTO) is one of the fascinating and typical perovskite ferroelectric materials due to its high phase transition temperature (T_c) of 493°C, high spontaneous polarization ($> 90 \mu\text{C}/\text{cm}^2$) and large piezoelectric coefficient ($> 150 \text{ pC}/\text{N}$)^{1,2} In the hope of enhancing performance of ferroelectric devices such as sensors, actuators, nonvolatile memories and probe-based data storage devices,³⁻⁹ nano-structured PTO has attracted great attention with their high surface-to-volume ratio.¹⁰⁻¹⁴ Anodized TiO₂ nanotube (NT) arrays are one of the promising base materials to fabricate nanoscale ferroelectric arrays due to its high degree of vertical alignment and simple fabrication process.¹³⁻¹⁶ In order to convert TiO₂ into PTO, lead acetate precursor has been typically used. However, the precursor solution cannot fill the NT channels, in particular, deep inside of the channels, by only capillary force since the bottom-ends of conventional TiO₂ NTs are closed.^{19,20} This phenomenon may results in incomplete conversion. Hydrothermal method has been generally used to convert TiO₂ NTs into PTO, but it still has weakness of structural rupture caused by the high pressure.¹⁵

We previously reported on synthesis of rupture-free PTO nanohoneycomb (NH) arrays using vacuum infiltration of lead acetate precursor and PbO vapour phase reaction.¹⁸ However, vacuum infiltration is inadequate to fill deep inside of the nanotubes when the length reaches about 10 μm because it is hard to extract trapped air at the deep bottom through the open top-ends.

In this work, we focus on synthesis of rupture-free PTO NHs with a length approaching 25 μm . To tackle the problem of incomplete infiltration of lead acetate precursor, we used a bottom opening technique²¹ which provides permeability in the

sense that fluids are able to flow through the whole NTs. By using vacuum infiltration and one additional annealing on the bottom-open NTs, TiO_2 could be fully converted into PTO since lead acetate precursor could fill the whole inside of NTs, which makes any further processes such as PbO vapor phase reaction needless.²² We also confirmed the ferroelectricity of PTO NHs by piezoresponse loop measurement using a continuous dc mode.²³

Experimental Procedure

We degreased commercially available Ti foil (Nilaco, 99.5 % purity, 0.2 mm thickness) in acetone and ethanol, and rinsed it with deionized water. Vertically-aligned TiO_2 NTs were grown on Ti foils with an exposed area of 1 cm^2 by the common two electrode anodization in ethylene glycol containing 0.25 wt% NH_4F and 2 vol% H_2O at 60 V for 1 h with a Pt wire as the counter electrode in ambient condition.

The firstly grown NT layer was peeled off by ultrasonication, which resulted in patterned surfaces on top of the Ti foils. The patterned Ti foil was secondly anodized at the same potentiostatic condition for 1 h. In order to fabricate the bottom-open TiO_2 NTs, the as-grown TiO_2 NT array on the Ti foil was additionally anodized at 150 V for 10 min at 7°C . During the additional anodization at the low temperature of 7°C , the bottom-ends opening and self-detachment occurred. It is worth noting that we experimentally found that anodization at 7°C provided more uniform and wider pores at the bottom-ends than 5°C used in the reference.²¹

To infiltrate lead acetate solution inside the NTs, the TiO_2 NT array was placed on a slide glass with an area of 1 cm^2 , and the lead acetate infiltration was performed by dropping 50 μl of 10 wt% lead acetate solution onto the NT arrays, followed by drying in a vacuum chamber (Jeio Tech, OV-11) to extract the air inside and fill with lead acetate solution. The lead acetate infiltrated- TiO_2 NT array was annealed at 550°C for 1 h to be converted into PTO NH array. We then soaked the sample in 1 wt% lead acetate solution for 0.5 h to remove the residues originated from lead acetate, and rinsed it with deionized water.

In order to obtain a uniform lead concentration distribution along the whole NT from bottom to top, we turned the NT array upside down after the first conversion process, and performed another lead acetate infiltration and annealing process with the same condition as that for the conversion process.

The morphology was characterized by scanning electron microscopy (SEM). The crystal structures were analyzed using X-ray diffraction (XRD). For ferroelectric characterization, we used a commercially available atomic force microscopy (AFM, XE-100; Park Systems) connected to a lock-in amplifier (SR830; Stanford Research Systems). A controlled modulation voltage of $0.5 \text{ V}_{\text{rms}}$ at 17 kHz was applied to the PTO NH array via the conducting AFM tip. The array was attached to a conductive Cu tape that acted as the bottom electrode. A Pt-coated Si tip (Mikromasch, spring constant $k = 6.0 \text{ N/m}$) was used for measuring local electromechanical properties and imaging surface topography of the NHs.

Piezoresponse hysteresis loop measurements were conducted on the PTO NH array to determine the polarization state and its switchability. To obtain a single hysteresis loop at each position, a continuous dc mode was used.²³ The dc voltage was applied to the bottom electrode (sequence 0 V $\rightarrow$ +10 V $\rightarrow$ 0 V $\rightarrow$ -10 V $\rightarrow$ 0 V) and superimposed onto the small ac modulation voltage applied to the tip. Each voltage step was increased by 400 mV and lasted for 200 ms.

Results and Discussion

Figure 1 shows the vertically-aligned TiO₂ NT arrays. Densely packed NTs with diameter between 60 and 70 nm and length of 25 μ m are shown in Figures 1(a) and (b). A high degree of vertical alignment, measured by the angle between long axis of tubes and surface normal of substrate, of $0.12^\circ \pm 0.78^\circ$ was measured.

Figure 1(c) shows the closed bottom-ends of the NT array synthesized by conventional anodization. We were able to open the closed bottom-ends by additional low temperature anodization as shown in Figure 1(d). The average wall thicknesses of the open-bottom-end is 28.7 ± 4.5 nm, and this value is larger than that of the top-end (22.8 ± 5.7 nm). The wall thickness difference between top and bottom is one of the intrinsic properties of anodized NTs since the top part is exposed to the electrolyte for longer time than the bottom part.²⁴ During the low temperature anodization, we observed the self-detachment of the bottom-open TiO₂ NT membrane from the Ti sheet as shown in Figure 1(e).

Figure 2 is a schematic diagram showing the fabrication of PTO NH arrays. When the NT array is immersed in the lead acetate solution, the inside of the NTs are not completely filled with the solution as some of the air bubbles are still trapped inside. During the vacuum infiltration, the trapped air inside the NTs is extracted and replaced by the lead acetate solution. At this moment, some of the lead acetate solution inside the NTs may flow out through the open-bottom-ends due to the gravity. Unfilled regions thus can be formed at the top, which causes an incomplete conversion of TiO₂ into PTO. In order to obtain a uniform lead concentration distribution along the whole NT from the bottom to top, we turned the NT array upside down after the first conversion process, and performed another lead acetate infiltration and annealing process, which we named lead supplement process.

Figure 3 shows the scanning electron microscopy (SEM) images of the vertically-aligned NH arrays after the conversion process. The honeycomb synthesized from the bottom-closed TiO₂ NTs showed expansion of walls to an average wall thickness of 35.8 nm (Figure 3(a)), indicative of conversion of TiO₂ NTs into PTO. The bottom surface also showed volume expansion supported by the annihilation of spaces between the NTs as shown in Figure 3(b) compared to TiO₂ NTs before the conversion process (Figure 1(c)).

In the case of NHs converted from the open-bottom NTs, we found that the walls expanded in a non-uniform way to an average thickness of 28.4 nm at the top-ends as shown in Figure 3(d). On the other hand, the bottom-ends showed uniformly thickened walls with an average thickness of 48.6 nm as shown in Figure 3(e). We attribute this non-uniform thickening to the fact that the lead deficient regions were formed during the infiltration process, which is supported by the energy

dispersive spectroscopy (EDS) data that showed lower lead content at the top than the bottom shown in Figure 3(j). We think that this may be due to the gravity and the permeability of the both-ends-open NTs.

The NH array synthesized via the additional lead supplement process shows a uniform wall thickening at both the top and the bottom as shown in Figures 3(g) and (h) with average thicknesses of 36.3 nm and 49.6 nm, respectively. It should be noted that the lead supplement process effectively compensated the lead deficient regions at the top. This uniform conversion is also confirmed by the EDS data shown in Figure 3(k), which nearly corresponds to the stoichiometric ratio of PTO in the whole part of the nano-honeycombs.

Figures 3(c), (f) and (i) indicate that the hollow nano-channels inside the vertically-aligned NH arrays are well-remained in spite of the wall thickening after the conversion into PTO.

Figure 4 illustrates the x-ray diffraction (XRD) patterns of the NH arrays shown in Figure 3. The bottom-closed TiO_2 NTs show partial conversion into PTO supported by the coexistence of PTO peaks of (001), (100), (101), (110), (111), (002), (200), (102), (201), (210), (112), (211) and TiO_2 (anatase) peaks of (101) and (004) planes, respectively, as shown in Figure 4(a). The open-bottom TiO_2 NTs went through significant conversion into PTO as illustrated in Figure 4(b). The TiO_2 peaks, however, still exist with relatively low intensities, which supports our claim of lead deficient regions at the top. Meanwhile, the XRD pattern of the NH array synthesized via lead supplement process in Figure 4(c) shows a thorough conversion into PTO without any TiO_2 peaks in the XRD pattern.

The evidence of formation of ferroelectric PTO NHs is provided by the piezoresponse hysteresis measurement using piezoresponse force microscopy (PFM). Figure 5(a) is the schematic diagram showing the set up of piezoresponse hysteresis measurement on the sample synthesized by the lead supplement process. A conductive Cu tape was placed beneath the sample as the bottom electrode, and the probe tip was placed on the top of the array. The measured piezoresponse hysteresis loop is shown in Figure 5(b). A well-defined piezoresponse hysteresis loop was obtained within the voltage range between -10 V and 10 V. The effective piezoelectric coefficient (d_{eff}) was measured to be approximately 20 pm/V, which is smaller than that reported for PTO thin films synthesized from TiO_2 and characterized by the same method (26 pm/V).²⁰ The voltage change (ΔV , defined by the gap between voltages when piezoresponse changes from 90% to 10% of the value between maximum and minimum saturated piezoresponse) is measured to be 8.58 V. The reason behind smaller value of d_{eff} and relatively large ΔV could be due to the unstable contact between the probe tip and the rough surface comprised of hollow NHs. The average coercive voltage (V_c) was 2.58 V calculated from the positive V_c of 1.52 V and the negative V_c of -3.64 V.

Conclusions

In summary, we converted high aspect ratio TiO_2 nanotube (NT) arrays into a ferroelectric PbTiO_3 (PTO) nano-honeycomb (NH) structure using lead acetate infiltration and annealing. We could infiltrate lead acetate into TiO_2 NT arrays

with open bottom-ends and convert them rapidly into a uniform PTO NH structure via annealing process at 550 °C, which was not the case with the ordinary bottom-closed TiO₂ NT arrays that underwent little to no conversion. The resulting PTO NH structure showed well-defined ferroelectric properties with remanent piezoresponse of 20 pm/V. We envision that high volume-to-surface ratio and regular alignment of PTO honeycomb arrays can be used to enhance the efficiency of ferroelectric devices working under electromechanical and electrochemical stimuli.

Acknowledgement

This research was supported by the Mid-career Researcher Program (2010-0015063) through the National Research Foundation of Korea funded by Ministry of Education, Science and Technology. Work at Argonne National Laboratory (S. H., data analysis and contribution to manuscript writing) was supported by the U.S. Department of Energy, Office of Science, Materials Sciences and Engineering Division.

References

1. C. Ederer and N. A. Spaldin, "Effect of Epitaxial Strain on the Spontaneous Polarization of Thin Film Ferroelectrics," *Phys. Rev. Lett.*, **95**, 257601 (2005).
2. W. Ma and Aize Hao, "Electric field-induced polarization rotation and ultrahigh piezoelectricity in PbTiO₃," *J. Appl. Phys.*, **115**, 104105 (2014).
3. M. C. Gelabert, R. A. Laudise, and R. E. Riman, "Phase stability, solubility and hydrothermal crystal growth of PbTiO₃," *J. Cryst. Growth*, **197**, 195-203 (1999).
4. M. Okuyama, Y. Hamakawa, "Ferroelectric PbTiO₃ thin films and their application," *Int. J. Eng. Sci.*, **29**, 391-400 (1991).
5. A. J. Moulson, J. M. Herbert, *Electroceraics*, 2nd ed., John Wiley & Sons, New York, 2003.
6. J. Kim, J. Hong, M. Park, W. Zhe, D. Kim, Y. J. Jang, D. H. Kim, K. No, "Facile preparation of PbTiO₃ nanodot arrays: Combining nanohybridization with vapor phase reaction sputtering," *Adv. Funct. Mater.*, **21**, 4277 (2011).
7. H. Ko, K. Ryu, H. Park, C. Park, D. Jeon, Y. K. Kim, J. Jung, D.-K. Min, Y. Kim, H. N. Lee, Y. Park, H. Shin, S. Hong, "High-Resolution Field Effect Sensing of Ferroelectric Charges," *Nano Lett.*, **11**, 1428-1433 (2011).
8. H. Park, J. Jung, D.-K. Min, S. Kim, S. Hong, H. Shin, "Scanning resistive probe microscopy: Imaging ferroelectric domains," *Appl. Phys. Lett.*, **84**, 1734-1736 (2004).
9. S. Hong, N. Park, 'Resistive Probe Storage: Read/Write Mechanism. In Scanning Probe Microscopy: Electrical and Electromechanical Phenomena at the Nanoscale'; pp 943-973 in *Springer, New York*, Vol. 2. Edited by S. V. Kalinin, A. Gruverman, 2006.
10. M. Remskar, "Inorganic nanotubes," *Adv. Mater.*, **16**, 1497-1504 (2004).
11. C. N. R. Rao, F. L. Deepak, G. Gundiah, A. Govindaraj, "Inorganic nanowires," *Prog. Solid State Chem.*, **31**, 5-147 (2003).
12. Z. L. Wang, "New developments in transmission electron microscopy for nanotechnology," *Adv. Mater.*, **15**, 1497-1514 (2003).
13. P. D. Yang, C. M. Lieber, "Nanorod-superconductor composites: A pathway to materials with high critical current densities," *Science*, **273**, 1836 (1996).
14. P. M. Ajayan, J. M. Tour, "Materials science: Nanotube composites," *Nature*, **447**, 1066 (2007).

15. B. Im, H. Jun, K. H. Lee, S. H. Lee, I. K. Yang, Y. H. Jeong, J. S. Lee, "Fabrication of a Vertically Aligned Ferroelectric Perovskite Nanowire Array on conducting Substrate," *Chem. Mater.*, **22**, 4806 (2010).
16. Y. Yang, X. Wang, C. Zhong, C. Sun, G. Yao, L. Li, "Synthesis and Growth Mechanism of lead Titanate Nanotube Arrays by Hydrothermal Method," *J. Am. Ceram. Soc.*, **91**, 3388 (2008).
17. Y. Yang, X. Wang, C. Zhong, C. Sun, L. Li, "Ferroelectric PbTiO₃ nanotube arrays synthesized by hydrothermal method," *Appl. Phys. Lett.*, **92**, 122907 (2008).
18. B. Kim, S. Hong, H. Choi, W. H. Ryu, H. Paik, Y. Y. Choi, H. S. Kwon and K. No, "Fabrication and Characterization of Nanoscale Ferroelectric Honeycombs," *J. Am. Ceram. Soc.*, **96**[5], 1355 (2013).
19. C. J. Lin, W. Y. Yu, Y. T. Lu, S. H. Chien, "Fabrication of open-ended high aspect-ratio anodic TiO₂ nanotube films for photocatalytic and photoelectrocatalytic applications," *Chem. Commun.*, **45**, 6031 (2008).
20. P. L. Hung, M. H. Wen, K. H. Hung, J. S. Bow, H. W. Wang, J. C. C. Han, Y. F. Lu, J. C. Chung, Y. C. Liu, Y. Z. Zeng and K. R. Ratinac, "3D Electrodes for Dye-Sensitized Solar Cells: Synthesis of ITO Nanowire Arrays Inside the TiO₂ Nanotubes," *J. Chin. Chem. Soc.*, **57**[5B], 1157 (2010).
21. H. M. Ouyang, G. T. Fei, Y. Zhang, H. Su, Z. Jin, H. Xu and L. D. Zhang, "Large scale free-standing open-ended TiO₂ nanotube arrays: stress-induced self-detachment and *in situ* pore opening," *J. Mater. Chem. C*, **1**, 7498 (2013).
22. J. Kim, S. Hong, S. Bühlmann, Y. Kim, M. Park, Y. K. Kim, K. No, "Effect of deposition temperature of TiO₂ on the piezoelectric property of PbTiO₃ film grown by PbO gas phase reaction sputtering," *J. Appl. Phys.*, **107**, 104112 (2010).
23. S. Hong, H. Shin, J. U. Jeon, Y. E. Pak, E. L. Colla, N. Setter, E. Kim, K. No, "Principle of ferroelectric domain imaging using atomic force microscope," *J. Appl. Phys.*, **89**, 1377-1386 (2001).
24. J. Chen, J. Lin and X. Chen, "Self-Assembled TiO₂ Nanotube Arrays with U-Shaped Profile by Controlling Anodization Temperature," *J. Nanomater.*, **2010**, 753253 (2010).

Figure Captions

Fig. 1. SEM images of TiO₂ NT arrays: (a) top view, (b) cross-sectional view and (c) bottom view of conventional anodized TiO₂ NTs; (d) bottom view of TiO₂ NTs with open-bottom-ends fabricated by the additional low temperature anodization; (e) self-detachment of the bottom-open TiO₂ NT membrane.

Fig. 2. A schematic diagram showing the fabrication process of PTO NH array.

Fig. 3. SEM images of the vertically-aligned NH arrays: (a), (b) and (c) are top, bottom and cross sectional views of NHs synthesized from bottom-closed TiO₂ NTs by the conversion process, respectively; (e), (f) and (g) are top, bottom and cross sectional views of the NHs synthesized from bottom-open TiO₂ NTs by the conversion process, respectively; (h), (i) and (j) are top, bottom and cross sectional views of NHs synthesized from bottom-open TiO₂ NTs by the additional lead supplement process, respectively; EDS cross-sectional analysis of nanohonycomb array synthesized (j) via the conversion process and (k) lead supplementary process.

Fig. 4. XRD patterns of the vertically-aligned NH arrays: (a) NHs synthesized from bottom-closed TiO₂ NTs by the conversion process; (b) NHs synthesized from bottom-open TiO₂ NTs by the conversion process; (c) NHs synthesized from bottom-open TiO₂ NTs by the additional lead supplement process.

Fig. 5. (a) A schematic diagram showing the piezoelectric characterization of the NH array synthesized via lead supplement process; (b) a piezoresponse hysteresis loop measured from the PTO NH array.