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Versatile Hydrothermal Route for the Synthesis of Vertically Aligned Arrays Thin Film $BaTiO_3$ Nanorod

Fathah Dian Sari[1], Chotimah[2], and Indriana Kartini[1]

Universitas Gadjah Mada
[1]Departement of Chemistry, [2]Departement of Physics, Faculty of Mathematics and Natural Sciences
Sekip Utara BLS 21 Yogyakarta, Indonesia 55281
E-mail: fathah.dian.sari@mail.ugm.ac.id, indriana@ugm.ac.id

Abstract

Recently, $BaTiO_3$ nanorods thin film has attracted much scientific interest due to its potential application in photovoltaic. In this paper, we synthesize thin film $BaTiO_3$ in the presence of polyethylene glycol-400 (PEG-400) via rutile TiO_2 nanorods by using modified two-step hydrothermal process. X-ray diffraction and scanning electron microscopy are performed to ascertain the formation of $BaTiO_3$ nanorods. For 210 °C 2h $TiO_2/BaTiO_3$ sample, a small peak of cubic $BaTiO_3$ (JCPDS No. 31-0174) was observed. By increasing reaction time, the intensity of $BaTiO_3$ peaks dramatically enhanced while the rutile TiO_2 peaks gradually diminished, evidencing the evolving of $BaTiO_3$ with the consumption of TiO_2. Our study provides a versatile hydrothermal route for the synthesis of vertically aligned arrays thin film $BaTiO_3$ via rutile TiO_2 nanorods.

1. Introduction

$BaTiO_3$, known as one kind of perovskite-type metal oxides, shows a variety of potential application due to its strong ferroelectricity as well as its environmental benefits compared to lead-based ceramics.[1] Recently, one-dimensional (1D) $BaTiO_3$ nanostructures have been extensively studied because of their specific ferroelectric behaviors related to 1D morphologies which can dramatically enhance the ferroelectricity, thus promising for energy harvesting and sensors applications.

Although many methods have been developed to fabricate perovskites nanostructure with various size and morphologies, one of the promising and interesting approaches for synthesizing the 1D nanostructured $BaTiO_3$ is the low-cost and easy hydrothermal method. For the integration of the 1D nanostructures into electronic devices and nanomechanical systems, the design of vertically aligned ferroelectric nanorods which typically grown on the conductive glass is essential to directly act as an electrode for the electric field measurement.

In this paper we report a versatile hydrothermal route for the synthesis of vertically aligned arrays nanorod $BaTiO_3$ via rutile TiO_2 without blocking layer preparation. We find that for 210 °C 2h $TiO_2/BaTiO_3$ sample, a small peak of cubic $BaTiO_3$ was observed. We also find that by increasing reaction time, the intensity of $BaTiO_3$ peaks dramatically enhanced while the rutile TiO_2 peaks gradually diminished, evidencing the evolving of $BaTiO_3$ with the consumption of TiO_2.

2. Result and Discussion

The preparation of vertically aligned $BaTiO_3$ nanorod arrays is based on a two-step hydrothermal reaction, i.e., (i) growing oriented rutile TiO_2 nanorods arrays as a precursor and template for the formation of aligned $BaTiO_3$, and (ii) converting TiO_2 into $BaTiO_3$ while simultaneously retaining their morphology in the presence of polyethylene glycol (PEG-400).

Firstly, TiO_2 nanorods was grown on FTO by a hydrothermal method in a stainless steel autoclave with Teflon liner of 50 mL capacity. The solution was prepared by adding 20 mL 37% hydrochloric acid in the 20 mL of deionized water and sonicated for 5 min. Subsequently, 0.7 mL of titanium (IV) tetraisopropoxide (97%) was added and further sonicated for 5 min. Two pieces of FTO (1 cm ×3 cm) were used as a substrate and positioned tilted inside the Teflon liner with the active layer facing the wall. The hydrothermal reactor was filled with the precursor mixture and heated in the 170 ºC for 2 h 45 min. After cooling down to room temperature, the sample was washed with deionized water and dried in air.[3]

The development of $TiO_2/BaTiO_3$ in the second step hydrothermal reaction include the conversion of TiO_2 nanorods and Ba^{2+} ions into $BaTiO_3$. Specifically, the TiO_2 nanorods were first immersed in a sealed Teflon-lined stainless steel autoclave (50 ml) that filled with a solution of 0.236 g $Ba(OH)_2.8H_2O$ in 5 mL polyethylene glycol 400 (PEG-400), 5 mL ethanol, 1.5 mL 2-propanol, 0.6 g tetrabutylammonium hydroxide solution (TBAH, 40 wt%), and 7 mL deionized water. The hydrothermal reactor was then transferred to an oven and reacted at 210 ºC for 2 h - 6 h. After cooling down to room temperature, the sample was washed with deionized water, ethanol, and dried in air.[4]

The evolution of the crystallographic structure during the hydrothermal treatment was investigated with XRD analysis, and the resulting spectra are collected in Figure 1.

Figure 1 (b) shows the X-ray diffraction (XRD) patterns of vertically grown TiO_2 nanorods on FTO glass substrate, where the diffraction peaks correspond to the crystal plane of rutile TiO_2 (JCPDS 21-1276). TiO_2 rutile powder contains crystals with random orientation, and the (110) has the highest intensity which shows similarity for the rod-shaped rutile TiO_2 nanoparticles. In the present case, the (110) peak intensity is noticeably weak, whereas the (101) has the highest intensity. The highly intense (101) peak along with the enhanced (002) peak in the nanorods film suggests that the rutile crystal grows with (101) plane parallel to the FTO

substrate and the nanorods are oriented along the (002) direction.[2]

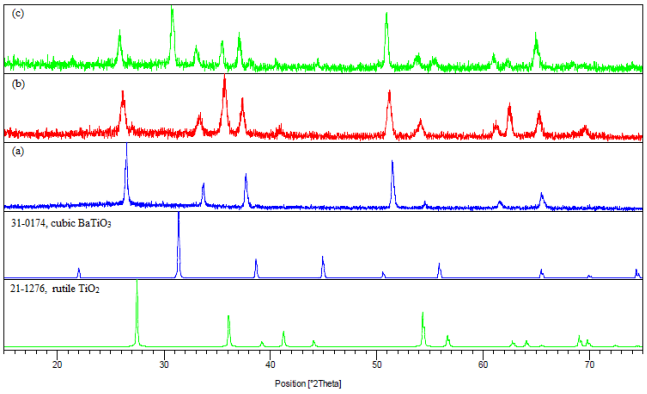

Fig. 1. Comparison of diffraction intensity between (a) FTO glass (Dyesol); (b) TiO_2 grown on FTO; (c) $BaTiO_3$ at 210 °C for 2 h.

Figure 1 also confirms the conversion of TiO_2 nanorod arrays into $BaTiO_3$. After the second hydrothermal reaction, it is shown that rutile TiO_2 nanorod arrays on FTO glass have been converted to $BaTiO_3$. For 210 °C 2 h $BaTiO_3$ sample, the diffraction peaks in figure 1 (c) correspond to the crystal plane of $BaTiO_3$ (JCPDS 31-0174). The strong peak of $BaTiO_3$ along with a very small peak belonging to the residual TiO_2 phase in the nanorod arrays. With the rising of reaction time, the intensity of TiO_2 peaks gradually diminished, evidencing the evolving of $BaTiO_3$ with the consumption of TiO_2 as shown in figure 3. The strong and sharp peaks suggest that $BaTiO_3$ nanorods are highly crystalline. The successful transformation of $BaTiO_3$ nanorods is also confirmed due to the presence of Ba, O, and Ti in EDX pattern without any other metal element, which indicates the high purity of the product.

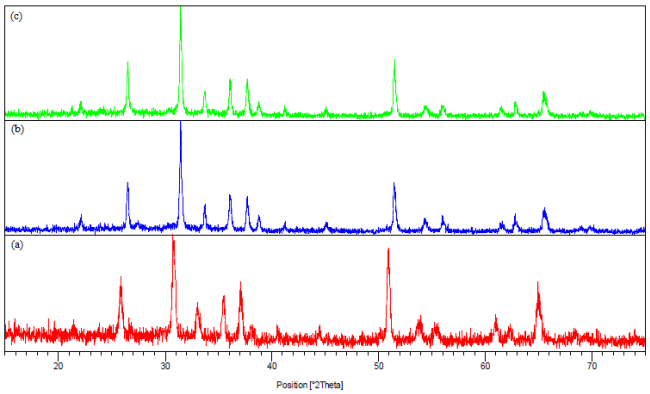

Fig. 2. X-ray diffraction patterns of $BaTiO_3$ synthesized at 210 °C for (a) 2 h; (b) 4 h; (c) 6 h.

The reaction through a second hydrothermal involves a dissolution, nucleation, and recrystallization mechanism in an alkaline solution, in which the OH^- plays a key role in the process.[2] The alkaline environment is kept at the pH value around 12.5 to prevent etching of the FTO-coated glass substrate and allows the titanium dissolution by the hydrolysis of Ti-O-Ti bonds to form $Ti(OH)_4$ and then reacts with Ba-ions to crystallize $BaTiO_3$ while maintaining the morphology of the template arrays.[3]

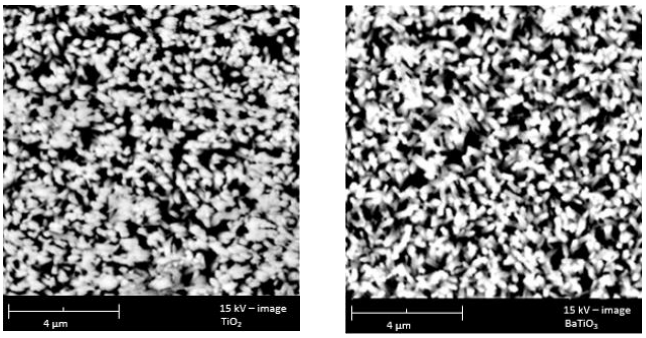

Fig. 3. a plane-view SEM images of (a) rutile TiO_2; (b) $BaTiO_3$ nanorod films.

The growth of $BaTiO_3$ crystals in the vertical (110) direction is not preferable due to the non-polarity, thus induces higher surface energy. To overcome this difficulty, we introduce PEG-400. Because the PEG-400 has polarity in the (110) surface plane, it is expected to assist the orientation of the $BaTiO_3$ crystal in the (110) plane. This is in fact confirmed by our SEM analysis as shown in Figure 3, where the 1D nanorods thin film $BaTiO_3$ crystal is clearly observed with mechanically strong on FTO substrate.

3. Conclusions

We have shown a versatile hydrothermal technique to prepare vertically aligned arrays of $BaTiO_3$ on the FTO substrate. It is also shown that PEG-400 has significant role to direct the crystal growth of nanorods $BaTiO_3$. Complete conversion of TiO_2 into $BaTiO_3$ is still under investigation.

Acknowledgments

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