

Versatile Hydrothermal Route for the Synthesis of Vertically Aligned Arrays Thin Film BaTiO₃ Nanorod

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Abstract

Recently, BaTiO₃ nanorods thin film has attracted much scientific interest due to its potential application in photovoltaic. In this paper, we synthesize thin film BaTiO₃ in the presence of polyethylene glycol-400 (PEG-400) via rutile TiO₂ nanorods by using modified two-step hydrothermal process. X-ray diffraction and scanning electron microscopy are performed to ascertain the formation of BaTiO₃ nanorods. For 210 °C 2h TiO₂/BaTiO₃ sample, a small peak of cubic BaTiO₃ (JCPDS No. 31-0174) was observed. By increasing reaction time, the intensity of BaTiO₃ peaks dramatically enhanced while the rutile TiO₂ peaks gradually diminished, evidencing the evolving of BaTiO₃ with the consumption of TiO₂. Our study provides a versatile hydrothermal route for the synthesis of vertically aligned arrays thin film BaTiO₃ via rutile TiO₂ nanorods.

1. Introduction

BaTiO₃, 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) BaTiO₃ 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 BaTiO₃ 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 BaTiO₃ via rutile TiO₂ without blocking layer preparation. We find that for 210 °C 2h TiO₂/BaTiO₃ sample, a small peak of cubic BaTiO₃ was observed. We also find that by increasing reaction time, the intensity of BaTiO₃ peaks dramatically enhanced while the rutile TiO₂ peaks gradually diminished, evidencing the evolving of BaTiO₃ with the consumption of TiO₂.

2. Result and Discussion

The preparation of vertically aligned BaTiO₃ nanorod arrays is based on a two-step hydrothermal reaction, i.e., (i) growing oriented rutile TiO₂ nanorods arrays as a precursor and template for the formation of aligned BaTiO₃, and (ii) converting TiO₂ into BaTiO₃ while simultaneously retaining their morphology in the presence of polyethylene glycol (PEG-400).

Firstly, TiO₂ 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 °C 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 TiO₂/BaTiO₃ in the second step hydrothermal reaction include the conversion of TiO₂ nanorods and Ba²⁺ ions into BaTiO₃. Specifically, the TiO₂ 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)₂·8H₂O 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 °C 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 TiO₂ nanorods on FTO glass substrate, where the diffraction peaks correspond to the crystal plane of rutile TiO₂ (JCPDS 21-1276). TiO₂ rutile powder contains crystals with random orientation, and the (110) has the highest intensity which shows similarity for the rod-shaped rutile TiO₂ 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

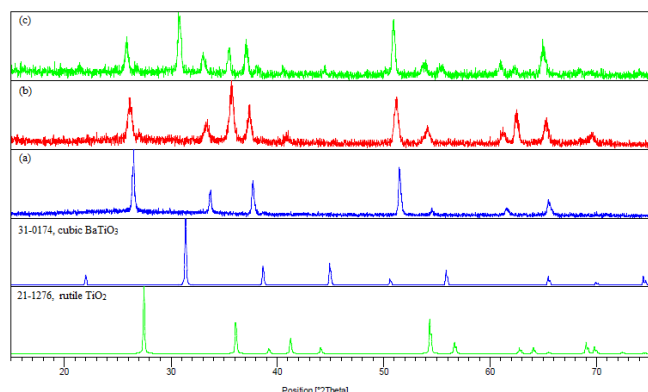


Fig. 1. Comparison of diffraction intensity between (a) FTO glass (Dyesol); (b) TiO_2 grown on FTO; (c) BaTiO_3 at 210 °C for 2 h.

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.

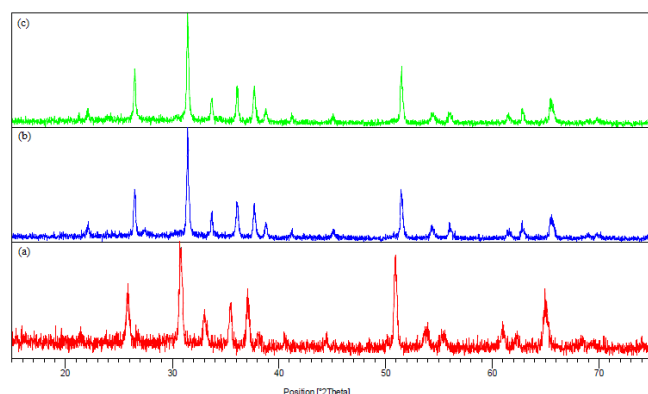


Fig. 2. X-ray diffraction patterns of BaTiO_3 synthesized at 210 °C for (a) 2 h; (b) 4 h; (c) 6 h.

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 $\text{Ti}(\text{OH})_4$ and then reacts with Ba-ions to crystallize BaTiO_3 while maintaining the morphology of the template arrays.³

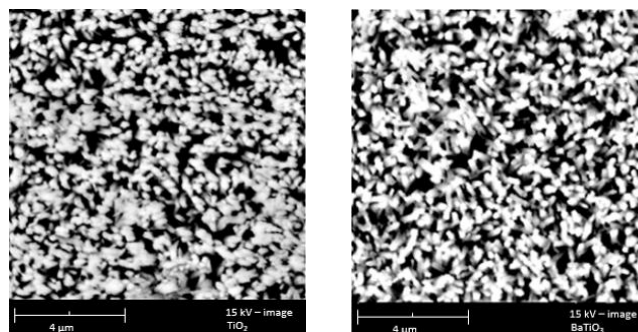


Fig. 3. a plane-view SEM images of (a) rutile TiO_2 ; (b) BaTiO_3 nanorod films.

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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