Two steps hydrothermal growth and characterisations of BaTiO$_3$ films composed of nanowires

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Abstract. Barium titanate (BaTiO$_3$) films composed of nanowires have gained considerable research interest due to their lead-free composition and strong energy conversion efficiency. BaTiO$_3$ films can be developed with a simple two steps hydrothermal reactions, which are low cost effective. In this research, BaTiO$_3$ films were fabricated on titanium foil through two steps hydrothermal method namely, the growth of TiO$_2$ and followed by BaTiO$_3$ films. The structural evolutions and the dielectric properties of the films were investigated as well. The structural evolutions of titanium dioxide (TiO$_2$) and BaTiO$_3$ nanowires were characterized using X-ray diffraction and scanning electron microscopy. First step of hydrothermal reaction, TiO$_2$ nanowires were prepared in varied temperatures of 160$^\circ$C, 200$^\circ$C and 250$^\circ$C respectively. Second step of hydrothermal reaction was performed to produce a layer of BaTiO$_3$ films.

1. Introduction

Over recent years, ferroelectric materials have been applied to a large scale of sensors [1-3], actuators [4-6] and energy harvesting systems [7-9] due to their strong electromechanical coupling. Ferroelectric nanomaterials such as thin films [10-13], nanowires [14,15], nanorods[16,17], nanotubes [18,19] and nanocubes [20] have been gaining large attention in nanotechnology. Among these nanostructures, one-dimensional (1D) nanowires are having the smallest dimension that can be employed for efficient transport of optical excitations and electron [21-23]. Besides, it is also expected to show high energy conversion efficiency. Additionally, the high sensitivity and random mechanical disturbances make these nanowires potential candidate for harvesting energy from environment and sensing devices at the nanoscale [24]. In order to directly utilize the ferroelectric arrays in energy harvesting and sensors, the vertically aligned nanowires are typically grown on conductive substrates, which directly act as electrodes for the application for measurement of electric fields [25].

Among ferroelectric materials, barium titanate (BaTiO$_3$) has attracted attention because of having strong ferroelectric properties and thus it is environmental friendly. BaTiO$_3$ is considered to be environmental friendly since it is lead-free. There is another type of ferroelectric material that is much better in making sensors than BaTiO$_3$ which is plumbum titanate (PbTiO$_3$) but somehow PbTiO$_3$ is high in toxic which makes it not favorable to be used as it is harmful to environment. Nowadays,
BaTiO$_3$ have been widely studied because of their potential application in sensing and energy harvesting [26-28].

Many methods have been developed to synthesis BaTiO$_3$ films, such as pulse laser deposition (PLD) [29], metalorganic chemical vapor deposition (MOCVD) [30] and magnetron sputtering [31]. However, the aforementioned methods are difficult to scale up, since they require costly equipment and ultrahigh vacuum which limits the batch size and efficiency.

2. Experimental Details

In this research, textured of BaTiO$_3$ films are synthesized through a two-step hydrothermal reaction. As shown in Figure 1, the TiO$_2$ nanowires were first grown on Ti foil by a hydrothermal process. Ti foils were initially cleaned by sonication for 30 minutes in a mixed-solution of deionized water, acetone and 2-propanol with volume ratios of 1:1:1. Then the Ti foils were rinsed with methanol and deionized water. The Ti foils were then placed vertically inside an autoclave, which contained 10 mL of deionized water, 10 mL of hydrochloric acid and 1 mL of titanium isopropoxide. The autoclave was tightly closed and then placed in an oven at $160^\circ$C for 4 hours. The resultant substrate with TiO$_2$ nanowires on its surface was rinsed with deionized water and dried in ambient air. Subsequently, the TiO$_2$ nanowires were converted to sol-gel method also can be applied to synthesis BaTiO$_3$. This method requires low cost and easy to handle. Nevertheless, this method has the bad sides where it requires high annealing temperatures which have high possibility to cause cracking when the thickness of the film is larger than a number of hundred nanometers [32].

A cost effective two-step hydrothermal method is introduced to grow dense BaTiO$_3$ films with controlled stoichiometry. The vertically aligned BaTiO$_3$ nanowires were synthesized by first preparing the vertically aligned TiO$_2$ nanowires as a template during the first step of hydrothermal reaction. The synthesized vertically aligned TiO$_2$ nanowires will then undergo a reaction with Ba$^{2+}$ ions. The reaction will occur in the second step of hydrothermal reaction. The crystallinity, structure and morphology of the BaTiO$_3$ nanowires were characterized by X-ray diffraction (XRD) and scanning electron microscopy (SEM).

BaTiO$_3$ through a second hydrothermal reaction with an aqueous solution of Ba(OH)$_2$.8H$_2$O. After the reaction, the BaTiO$_3$ films were rinsed with deionized water and dried in ambient air. The samples were heated at $600^\circ$C for 30 minutes to remove the hydroxyl ions which results due to the hydrothermal reaction conditions. Different reaction temperatures were applied to the samples during the first step of hydrothermal reaction to see the end result of the BaTiO$_3$ films.

![Figure 1. Schematic illustration to grow textured of BaTiO$_3$ films](image-url)
3. Characterization

The crystalline structure of the synthesized TiO\textsubscript{2} and BaTiO\textsubscript{3} nanowires were analyzed by XRD using Rigaku Miniflex II Diffractometer with CuK\textalpha radiation ($\lambda=1.5406$), by scanning from angle of 20\(^\circ\) to 80\(^\circ\). The morphology and size of the grown TiO\textsubscript{2} and BaTiO\textsubscript{3} nanowires were characterized by SEM (JEOL) operated at 15 kV.

4. Results and Discussion

First step hydrothermal reaction: Formation of TiO\textsubscript{2} nanowires.

Figure 2. XRD patterns of (a) Ti foil and TiO\textsubscript{2} films at different reaction temperatures, (b) 160 \(^\circ\)C, (c) 200 \(^\circ\)C and (d) 250 \(^\circ\)C.

Figure 2 shows the XRD pattern of first hydrothermal reaction of TiO\textsubscript{2} films prepared at different reaction temperatures namely 160 \(^\circ\)C, 200 \(^\circ\)C and 250 \(^\circ\)C. Figure 2 (a) shows the XRD pattern of a bare TiO\textsubscript{2} film which is the substrate. When the sample was heated at 160 \(^\circ\)C, the low peak intensity (as shown in Figure 2 (b)) is suggested that the TiO\textsubscript{2} nanowires were not fully formed and still in intermediate phase. The fingerprint of TiO\textsubscript{2} rutile pattern was clearly observed at 200 \(^\circ\)C. With the increase of the first hydrothermal reaction temperature at 200 \(^\circ\)C, the intermediate phase (Figure 2 (b)) turned into rutile structure (Figure 2 (c)). With the further increase of heated temperature up to 250 \(^\circ\)C, the change of peak intensity of (111) at 2\(\theta\) of 41.26 \(^\circ\), indicating the increased on crystalinity of TiO\textsubscript{2}. Other rutile peaks are observed at 2\(\theta\) of 27.37 \(^\circ\), 36.10 \(^\circ\) and 56.36 \(^\circ\) with \textit{hkl} orientations of (110), (101) and (211). However, the presence of minor Ti\textsubscript{0.72}O\textsubscript{2} anatase (PDF No. 86-1157) was observed at 25.43 \(^\circ\) with marginal peak intensity of (101). Based on the XRD patterns for Figure 2 (c) and (d), the form of major rutile phase and minor anatase phase were observed. Second step hydrothermal reaction: Formation of a layer of BaTiO\textsubscript{3} nanowires.
Figure 3. XRD patterns of (a) Ti foil and BaTiO₃ films at different reaction temperatures, (b) 160 °C, (c) 200 °C and (d) 250 °C.

Figure 3 shows the XRD pattern of BaTiO₃ films prepared from TiO₂ nanowires grown on TiO₂ film, which obtained via the first hydrothermal reaction at different reaction temperatures. The XRD pattern of the prepared BaTiO₃ samples as in Figure 3 could be readily indexed to tetragonal BaTiO₃ (PDF No. 75-2121) with a lattice parameter a = b = 3.9886 Å, c = 4.00060 Å. When the sample is heated with 160 °C, the peaks formed were scattered as shown in Figure 3 (b). The scattered peak indicates that BaTiO₃ films haven’t form although the peaks started to show the little presence of BaTiO₃ phase. But the crystallinity of BaTiO₃ synthesised at 160 °C was low.

The fingerprint of BaTiO₃ rutile clearly observed at 200 °C. With the increase of the heated temperature, the intermediate phase (Figure 3 (b)) turned to rutile structure (Figure 3 (c)). With the further increase of heated temperature up to 250 °C, some of the peak intensity were enhanced such as at (001), (101), (111), and (202). Whereas others disappeared which are for peak intensity of (101) and (211). At 250 °C, the change of peak intensity of (101) BaTiO₃ at 2θ of 31.62 ° was clearly observed, which affirmed the formation of high crystalline BaTiO₃. Instead of the peak showed BaTiO₃ and Ti foil, presence of BaO was also determined.

Morphology of TiO₂ films (First step hydrothermal reaction at 200 °C).

Figure 4. (a) TiO₂ surface morphology (b) TiO₂ cross sectional area (c) Thickness of TiO₂
For SEM analysis of TiO$_2$ films, only one sample was measured which the sample is for optimum temperature. The synthesis of the desired BaTiO$_3$ films begins with the growth of densely packed TiO$_2$ nanowires on the surface of Ti foil as shown in Figure 4 through the first hydrothermal reaction step. When observed in cross sectional as in Figure 4 (b), the top of the TiO$_2$ films has more free space and less dense than the base of TiO$_2$ nanowires. This indicated that there were sufficient space for the infusion of Ba$^{2+}$ ions from the precursor used in the second hydrothermal reaction to react with TiO$_2$ nanowires. The grain and length of TiO$_2$ nanowires can be controlled and modified by differ reaction heating time in the first hydrothermal reaction as shown in Figure 4 (a). The first step hydrothermal reaction causes the vertically alligned TiO$_2$ nanowires grow on the Ti foil surface at 200 °C.

Morphology of BaTiO$_3$ films (Second step hydrothermal reaction at 160 °C)

![Figure 5](image)

**Figure 5.** (a) BaTiO$_3$ surface morphology (b) Width of BaTiO$_3$ (c) BaTiO$_3$ cross sectional area (d) Thickness of BaTiO$_3$

Figure 4 (a) showed the resultant layer of vertically alligned TiO$_2$ nanowires was obtained after the first step of hydrothermal reaction. We believed that 200 °C is the optimum temperature for the growth of TiO$_2$ nanowires on the Ti foil surface. It is because, the TiO$_2$ films prepared a 200 °C showed the structure of nanowires as compared to other temperatures which are 160 °C and 250 °C. From the Figure 4 (a), it is obviously observed that the surface morphology of the TiO$_2$ nanowires is flaky and forming grains. The thickness of the TiO$_2$ nanowires in the range of 2.27 μm to 2.40 μm was measured as depicted in Figure 4 (c). Observation of the surface morphology of BaTiO$_3$ sample heated at 160 °C showed the elongation of the vertically alligned BaTiO$_3$ nanowires. Figure 5 (a) also showed the surface morphology of BaTiO$_3$ nanowires that synthesised by hydrothermal reaction with 4 hours soaking time at heating temperature of 160 °C. In the second hydrothermal reaction, the growth of BaTiO$_3$ structure formed nanorod rather than nanowire as shown in Figure 5 (c) and (d). The transformation of nanorod to nanowire occurs due to low temperature which might causes partial reaction. The cross sectional area and the results proved that the heights of BaTiO$_3$ nanowires were not uniform. The height of the BaTiO$_3$ nanowires were in the range of 47.240 μm to 50.810 μm. The mean of the height is 48.970 μm. The width of the BaTiO$_3$ nanowires was measured with a mean value of 0.179 μm in the range of 0.164 μm to 0.209 μm.

Morphology of BaTiO$_3$ films (Second step hydrothermal reaction at 200 °C).

![Figure 6](image)

**Figure 6.** (a) BaTiO$_3$ surface morphology (b) Width of BaTiO$_3$ (c) BaTiO$_3$ cross sectional area (d) Thickness of BaTiO$_3$
Observation of the surface morphology of BaTiO$_3$ that heated at 200 °C showed that the height of the vertically aligned BaTiO$_3$ nanowires are slightly to be uniformed. With the increase of heating temperature up to 200 °C in the second hydrothermal reaction, the growth of BaTiO$_3$ structure is fully forming nanowires with spacing rather than forming dense BaTiO$_3$ nanowires. The width of the BaTiO$_3$ nanowires was measured with the mean value of 0.264 μm in the range of 0.230 μm to 0.30 μm as shown in Figure 6 (b). The cross sectional area as in Figure 6 (c) proved that the height of the vertically aligned BaTiO$_3$ nanowires were not uniform and in the range of 9.580 μm to 10.560 μm. The mean value is 9.9630 μm.

Morphology of BaTiO$_3$ films (Second step hydrothermal reaction at 250 °C).

![Morphology of BaTiO$_3$ films](image)

**Figure 7.** (a) BaTiO$_3$ surface morphology (b) Width of BaTiO$_3$ (c) BaTiO$_3$ cross sectional area (d) Thickness of BaTiO$_3$

Observation of the surface morphology of BaTiO$_3$ sample that heated at 250 °C showed that the height of the vertically aligned BaTiO$_3$ nanowires to be more uniform compared to 160 °C and 200 °C. The width of the BaTiO$_3$ nanowires was measured with the mean value of 0.229 μm in the range of 0.209 μm to 0.266 μm. The cross sectional area as in Figure 7 (c) indicated that the height of the vertically aligned BaTiO$_3$ nanowires were obviously not uniform and they are very dense. The height of the BaTiO$_3$ nanowires were in the range of 19.170 μm to 22.740 μm with the mean value of 21.357 μm.

5. Conclusion

Single phase BaTiO$_3$ films were successfully fabricated by using a two-step hydrothermal reaction. The Ti foil is very suitable to grow the BaTiO$_3$ films on it through the use of vertically aligned TiO$_2$ nanowires as the template. The crystalinity of the samples were seen throughout the XRD characterization and it was found out that the scattered peak at heating reaction of 160 °C in the first and second hydrothermal reaction happened because of the partial reaction occurred at that temperature. For the SEM analysis, the image of nanowires were seen to form at the heating temperature of 200 °C. This has made the temperature as the optimum temperature to grow the desired nanowires. Besides, this hydrothermal method offers a low cost method to produce thin films for microelectronics.
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