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# Hydrothermal–galvanic couple synthesis of directionally oriented $BaTiO_3$ thin films on TiN-coated substrates[☆]

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ABSTRACT

$BaTiO_3$ films were synthesized on TiN-coated Si substrate below 100 °C by a hydrothermal–galvanic couple technique in barium contained alkaline solutions. X-ray diffraction and electron backscatter diffraction results show that the $BaTiO_3$ thin films were directionally oriented grown on the TiN/Si substrates, i.e., (111) $BaTiO_3$ over (111) TiN. The surface morphologies revealed that $BaTiO_3$ nucleated and grew over the TiN surface with a single layer. From kinetic analyses, the growth rates of $BaTiO_3$ films prepared by the hydrothermal–galvanic couple technique were faster than a hydrothermal method. The galvanic effects were confirmed by investigating the induced currents and energies. The galvanic currents were generated and controlled by both the dissolution of TiN and the formation of $BaTiO_3$. The output electric energies increased rapidly with the reaction time and leveled off at the full coverage of $BaTiO_3$.

## 1. Introduction

Barium titanate ($BaTiO_3$) is one of the most important electroceramic materials due to its superior dielectric and ferroelectric properties [1,2]. $BaTiO_3$ films have been widely used in cutting-edge applications, such as dynamic random access memory, chemical sensors, and multilayer chip capacitors [3–5]. In the literature, various techniques have been reported for the synthesis of $BaTiO_3$ films including pulsed laser deposition [6], ion-beam sputtering technique [7], sol–gel process [8], hydrothermal [9–16], and hydrothermal–electrochemical methods [17–25]. Most of the techniques require temperatures higher than 500 °C to enhance crystallinity of the films except hydrothermal and hydrothermal–electrochemical methods which may bring the temperature down near or below 100 °C [13–19]. Fig. 1 summarizes the lowest reaction temperature of the hydrothermal and hydrothermal–electrochemical synthesis of $BaTiO_3$ films, reported from the literature including our previous work on the hydrothermal–galvanic couple (HT–GC) and hydrothermal (HT) synthesis of $BaTiO_3$ films [26–28]. This technique can reduce the reaction temperature down even below 55 °C.

As reported in our previous work, synthesis of $BaTiO_3$ films by a HT–GC technique may significantly enhance the growth rates of the films. During the galvanic couple setup, no external power supply was required but the growth of $BaTiO_3$ films could be enhanced significantly by the induced current/voltage. Moreover, unlike the conventionally used bulk Ti, Ti/Si, or $TiO_2$ substrates [29–34], TiN/Si substrates were used during the synthesis of $BaTiO_3$. Because of the low resistivity and highly preferred orientation of TiN, $BaTiO_3$ films were found to grow directionally over the TiN/Si substrates [26]. Nevertheless, the growth kinetics of synthesizing the films by the HT–GC technique has not yet been investigated. The galvanic effects during the synthesis of the films have not yet been explored, either.

Thus, this work was aimed to investigate the growth kinetics of $BaTiO_3$ films synthesized by the HT–GC method and then to compare the results with those made by the sole hydrothermal method. The effect of the galvanic couple setup on the growth of the films has also been explored.

## 2. Experiment

TiN films were prepared on n-type (100) silicon substrates by DC reactive sputtering, as reported in our previous work [28]. The deposition time was 3 min and the resulting thickness of TiN was 400 nm. The resistivity of the obtained TiN was in the range of 310–350 $\mu\Omega$ cm.

In the HT–GC synthesis, the reaction solution was a mixture of 0.5 M $Ba(CH_3COO)_2$ (99.5%, J.T. Baker, U.S.A) and 2 M NaOH (99%, Riedel-de Haën, Germany) alkaline solutions. The reaction temperatures were kept below 100 °C and hence, no autoclave was required. As for the

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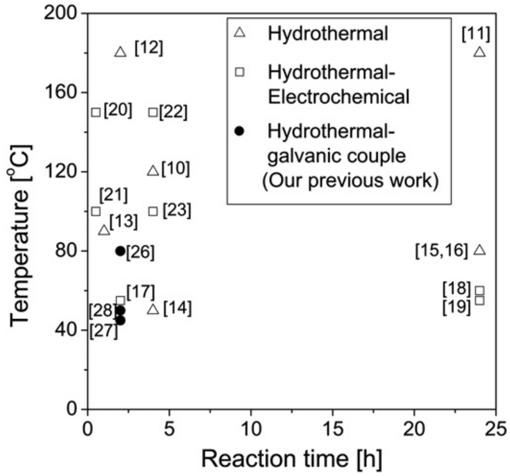

**Fig. 1.** The lowest reaction temperatures of the hydrothermal and hydrothermal–electrochemical synthesis of $BaTiO_3$ films, reported from the literature including our previous work [26–28].

galvanic couple setup, the working electrode was the TiN/Si specimens and the counter electrode was Pt while the two electrodes were directly connected without applying any external power sources.

Crystalline phases of the films were determined by X-ray diffraction (XRD) (MPX3, Mac Science, Japan) operated at 40 kV and 30 mA with a Cu Kα excitation source ($\lambda_{Cu,K\alpha} = 0.1542$ nm). Surface and cross-sectional morphologies of the films were investigated by field-emission scanning electron microscopy (FE-SEM) (JSM-6700 F, JEOL, Japan) operated at 3 kV to minimize the charging effect. Electron backscatter diffraction (EBSD) (JSM-7001 F, JEOL, Japan) was also conducted to examine the grain orientations of the obtained films. The growth kinetics was evaluated by analyzing the coverage of $BaTiO_3$ over the TiN films as a function of the reaction time. The coverage of $BaTiO_3$ was calculated by averaging five selected areas in the SEM micrographs taken from each specimen.

## 3. Results and discussion

### 3.1. Crystallinity

Fig. 2 shows the X-ray diffraction patterns of the as-deposited films and those after the (a) HT–GC and (b) HT syntheses at various temperatures for 2 h. The as-deposited films were rock-salt structured TiN (JCPDS 38-1420) [35] with a highly (111) preferred orientation. As shown in the figure, the crystalline cubic $BaTiO_3$ (JCPDS 31-0174) [35] phase was present after the syntheses at the temperatures above 50 °C and grew directionally over TiN-coated substrates. It is noteworthy that the relative intensities of $BaTiO_3$ obtained in this referenced HT synthesis were slightly different from those reported in our previous work [28]. This is mainly due to the different batch of the specimens, which doesn't affect the conclusions deduced from this work. The directionally oriented growth of $BaTiO_3$ during the HT–GC synthesis, i.e., (111) $BaTiO_3$ over (111) TiN, is also very similar to that for the HT synthesis.

### 3.2. Morphology

In Fig. 3, the as-deposited TiN seeding layer revealed a nano-grained structure and $BaTiO_3$ started to nucleate and grow over the seeding layer for both the (a) HT–GC and (b) HT synthesis. As shown, only a few $BaTiO_3$ particles grew over the TiN surface at 45 °C. The coverage of $BaTiO_3$ increased rapidly with the reaction temperature ranging from 45 °C to 60 °C. At reaction temperatures higher than 60 °C, the $BaTiO_3$ particles almost covered the whole TiN surface. The trend is similar to those synthesized by both the HT–GC and HT methods. At a fixed reaction temperature, the amount of $BaTiO_3$ particles obtained by using the HT–GC was obviously larger than that synthesized by the HT method in the temperature range of 45 °C—60 °C. It clearly indicates that the galvanic couple setup can facilitate the growth of $BaTiO_3$. Here, it also demonstrates that the HT–GC technique can be used to produce $BaTiO_3$ films at lower reaction temperature (<50 °C), compared to the HT and hydrothermal–electrochemical methods, as revealed in Fig. 1.

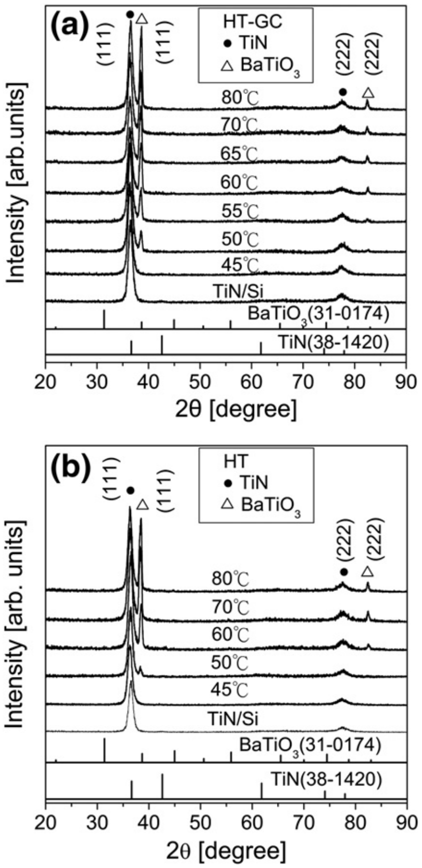

**Fig. 2.** X-ray diffraction patterns of $BaTiO_3$ over TiN/Si synthesized by the (a) HT–GC and (b) HT methods at various temperatures for 2 h.

The cross-sectional view of the $BaTiO_3$ films obtained by the HT–GC method is given in Fig. 4. As-deposited TiN exhibited a characteristic columnar structure. The TiN films were then slightly consumed after the syntheses at various temperatures for 2 h. The $BaTiO_3$ particles were produced, yielding a single layer over the TiN film surface. That's why the coverage instead of thickness was used for analyzing the kinetics. It is noteworthy that the interface between TiN and formed $BaTiO_3$ was rather smooth. Moreover, porosity existed in the $BaTiO_3$ films. The porosity of the $BaTiO_3$ films can be calculated based on the theoretical estimation [36] and experimental observations. Taking the synthesis at 80 °C shown in Fig. 4 as an example, the consumed thickness of TiN was 19 ± 1 nm that should yield 64 ± 1 nm (3.4 times) of a fully dense $BaTiO_3$ film. However, the experimentally observed thickness of $BaTiO_3$ was 71 ± 1 nm. That means the porosity existing in the $BaTiO_3$ film might be about 10%. The discrepancy between the estimation and the observation may also stem from the densities used in the calculation since the bulk and film densities are possibly different and only the former value is available at the moment.

As mentioned earlier in the XRD analysis, directionally-oriented growth of the $BaTiO_3$ films was observed over the TiN seeding layer that exhibited a strong preferred orientation. To further examine the oriented growth, EBSD was also preformed over different grains