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The preparatory optimal conditions of barium titanate thin film from a hydrothermal method at low temperature

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Abstract The preparation of barium titanate thin films on Ti substrates at low temperature using the hydrothermal process was studied. In addition, the interface relationship between film and substrate was investigated, revealing that the Ba^{2+} ion diffused into the $Ti(OH)_4$ gel formed by Ti in a strong alkaline solution, resulting in a homogeneous film. A 3-level orthogonal array design was utilized to optimize the experimental conditions. The effects of preparatory conditions such as the barium-concentration, NaOH concentration, reaction time and substrate surface treatment were systematically studied. Results indicate that the effects of the NaOH concentration and substrate surface treatment are the significant variables influencing the relative crystal intensity (intensity of (110) $BaTiO_3$ peaks in XRD spectrum/intensity of (001) Ti peak in XRD spectrum) of the films obtained. Polycrystalline, $BaTiO_3$-films were obtained, with improved crystallinity and a dielectric constant of about 915 at 1 MHz.

Introduction

Barium titanate perovskite ceramic is an important electronic material. Its semiconducting properties can be achieved by adding a dopant heterovalent element such as La^{3+} [1], Nb^{5+} [2], Y^{3+} [3], etc. or by sintering in a reducing atmosphere [4]. The semiconducting and dielectric properties of $BaTiO_3$ can be controlled by the grain boundary, and are widely applied for use in photoelectrodes [5], multilayer chip capacitors (MLCC) [6], positive temperature coefficient resistance (PTCR) heaters and sensors [7, 8]. For the rapidly progressing development of very large scale integrated (VLSI) circuits, high purity thin films are required for manufacturing high capacity electronic devices [9].

The hydrothermal method is an attractive process for the synthesis of perovskite-type (ABO_3) thin films [10, 11]. The perovskite thin film can be produced on substrates containing the B-site metal by reaction with A-site elements in an alkaline aqueous solution using an autoclave. This reaction can form a dense perovskite thin-film and has strong adherence to substrates. Furthermore, the perovskite film can be produced by dissolving and deposition processes on any substrate geometry, as long as it is formed by alkali earth ions reacting with a titanium substrate or even a transition metal such as Fe or Zr [12, 13]. In particular, $BaTiO_3$ and $BaZrO_3$ films fabricated using this method are practically free of carbon and OH group contaminants. It is noteworthy that the film is not simply deposited on top of the substrate but actually grows into it. This hydrothermal method is very worthwhile developing due to its advantages of a simple apparatus, lower synthesis temperature, no annealing for crystallization

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after deposition, and the high purity of the films. Yoshimura et al. [14, 15] discovered that a fine $BaTiO_3$ thin film on a Ti substrate can be produced by a hydrothermal bath using a titanium cathode in an alkaline Ba^{2+} solution. Kajiyoshi et al. [16] investigated the microstructure of strontium titanate thin film grown by the hydrothermal method and applied electrochemical apparatus. They obtained a $SrTiO_3$ film using $Sr(NO_3)_2$ or $Sr(OH)_2{\cdot}8H_2O$ as the raw material of strontium and TiO_2 as a source of titanium. Furthermore, a cubic $BaTiO_3$ thin film was prepared by Slamovich et al. [17] by reacting thin layers of titanium organometallic liquid precursors in an aqueous solution at 40–80 °C in a hydrothermal bath.

During the reaction of Ba^{2+} with a Ti-substrate in a strong alkaline solution, $Ti(OH)_4$ gel is formed as the first step [18]. Then, the Ba^{2+} ions diffuse into the surface of the titanium gel to form $BaTiO_3$ film. This diffusion process is controlled by the morphology of the titanium gel [19]. Therefore, both the shape and size of the precursor gel have a strong influence on the properties and composition of the final film. A change in the preparatory variables of the experiment indirectly affects the formation of the $Ti(OH)_4$ gel, changes the mode of the nucleophilic attack of the Ba^{2+} on the titanium-gel, and can even control the grain growth and relative crystal intensity of the produced film.

Orthogonal arrays are often used in the design of experiments because of their orthogonality [20] and because the significant factors and interactions can be tested by analysis of variance. It is also a reliable method of simplifying the process of identifying the most influential preparation variables, and the optimal preparatory conditions are singled out [21]. However, there have been few studies investigating the optimization of experimental conditions in the preparation of $BaTiO_3$ films by a hydrothermal process.

In this study, we use the hydrothermal method to prepare a barium titanate thin film on a Ti substrate. The mechanism of the film formation was investigated to understand the interaction between the crystallinity, the formation process and the microstructure of the obtained $BaTiO_3$ films. A 3-level orthogonal array [22, 23] was employed in planning experiments to study the effects of the preparation variables. The relative crystal intensity (intensity of (110) $BaTiO_3$ peaks in XRD spectrum/intensity of (001) Ti peak in XRD spectrum) was chosen as a parameter to evaluate the character of the produced films. Optimal preparatory conditions could be singled out and a film with a high dielectric constant was prepared under those conditions.

Experimental procedure

Synthesis of barium titanate thin film

Barium titanate films were prepared on titanium substrates by a hydrothermal method using an aqueous solution of $Ba(OH)_2$ in a temperature range of 130–200 °C. The solution was prepared with degassed water boiled for at least 5 min in order to remove dissolved CO_2 that could produce insoluble barium carbonate. The solution was placed in a teflon beaker inside an autoclave. The films were fabricated by putting a 1 mm thick titanium substrate in the solution under hydrothermal conditions. The titanium substrate was put in the beaker horizontally to prevent the concentration gradient from the vertical position.

Fractional factorial design

As to the design of the experiments, a 3-level orthogonal array table $L_{27}(3^{13})$ was implemented by choosing four primary process variables that could affect the characteristics of the films, namely: concentration of Ba^{2+}, concentration of NaOH, reaction time and surface treatment (polished by diamond paste) of the Ti substrate (see Table 1).

If each of these variables were assigned three values, a low, a middle, and a high one, and a factorial experimental design was employed using each of these values, the number of permutations would be 3^4, meaning that 81 experiments would be required to identify the optimal setting of the experimental variables. However, the fractional factorial design approach we used reduced the number of necessary experiments to 27, while maximizing the amount of information

Table 1 Factors and levels for the fractional factorial design

Factors		Levels		
		High (3)	Middle (2)	Low (1)
A	Ba^{2+}-concentration (M)	2	1.25	0.5
B	NaOH concentration (M)	4 M	2 M	Without
A × *B* Consider the interaction of *A* and *B*				
D	Reaction time (h)	8	5	2
E	Surface treatment (by diamond paste)	1 μm	2 μm	Without

derived from this reduced set of experiments. However, every run of $BaTiO_3$ thin film was prepared twice according to the factors assigned to the columns of the orthogonal array $L_{27}(3^{13})$, and the relative crystal intensity (intensity of (110) $BaTiO_3$ peaks in XRD spectrum/intensity of (001) Ti peak in XRD spectrum) was also shown in Table 2.

Testing methods

Scanning electron microscopy (SEM) (Jeol-5610) was used to analyze the microstructures of the films. The phases of the films were examined using an X-ray diffraction analyzer (XRD) (Rigaku, Rint-2000) in the mode of 2θ-θ scan at a rate of 4°/min with Cu $K_\alpha(\lambda = 1.5406\ \text{Å})$. The dielectric constants of the films were measured with an HP impedance analyzer 4284 A.

Results and discussion

Formation of $BaTiO_3$ film on Ti substrate

A polished and degreased Ti-substrate was put into a 2 M NaOH solution in an autoclave at 150 °C for 3 h. The Ti-oxide film produced on the substrate surface was then characterized by XRD, as shown in Fig. 1. It is clear that the film contained some distinct phases, which can be identified as anatase, rutile and a small amount of the Magnéli phase (Ti_2O_3 and Ti_4O_7 etc.).

For further comparison, the experiment also proceeded by adding the same amount of $Ba(OH)_2$ in different NaOH solutions with Ti substrate. A $BaTiO_3$ film was obtained. It revealed by XRD examination that the relative crystal intensities of $BaTiO_3$/Ti obtained from the different NaOH solutions were proportional to the ratio of Ti-oxide/Ti obtained from the alkaline solution without the existence of alkali earth metal ion.

From this observation, the amount of $BaTiO_3$ formed was proportional to the amount of Ti-oxide formed from the previous the $BaTiO_3$ thin film. We postulate that the densified $BaTiO_3$ film was obtained by reaction of Ba^{2+} and formed Ti-oxide; that it was difficult for the Ti inside to make contact with OH^- and Ba^{2+}; and that $BaTiO_3$ thus cannot be formed in the inner layer.

After the reactive intermediate is formed, it could hydrolyze to give TiO_2 on the film surface. It was proposed that the mechanism of $BaTiO_3$ film could be written as [24]:

Table 2 The design matrix and experimental data of the Taguchi orthogonal array $L_{27}(3^{13})$

	A	B	$A \times B$	$A \times B$	C	$A \times C$	$A \times C$	$B \times$ C		D	$B \times C$	E		Relative crystal intensity, %
1	1	1	1	1	1	1	1	1	1	1	1	1	1	22, 26
2	1	1	1	1	2	2	2	2	2	2	2	2	2	35, 30
3	1	1	1	1	3	3	3	3	3	3	3	3	3	27, 27
4	1	2	2	2	1	1	1	2	2	2	3	3	3	28, 26
5	1	2	2	2	2	2	2	3	3	3	1	1	1	40, 46
6	1	2	2	2	3	3	3	1	1	1	2	2	2	24, 19
7	1	3	3	3	1	1	1	3	3	3	2	2	2	28, 25
8	1	3	3	3	2	2	2	1	1	1	3	3	3	28, 20
9	1	3	3	3	3	3	3	2	2	2	1‘	1	1	22, 24
10	2	1	2	3	1	2	3	1	2	3	1	2	3	33, 30
11	2	1	2	3	2	3	1	2	3	1	2	3	1	24, 32
12	2	1	2	3	3	1	2	3	1	2	3	1	2	38, 36
13	2	2	3	1	1	2	3	2	3	1	3	1	2	29, 24
14	2	2	3	1	2	3	1	3	1	2	1	2	3	36, 33
15	2	2	3	1	3	1	2	1	2	3	2	3	1	25, 24
16	2	3	1	2	1	2	3	3	1	2	2	3	1	26, 29
17	2	3	1	2	2	3	1	1	2	3	3	1	2	30, 27
18	2	3	1	2	3	1	2	2	3	1	1	2	3	25, 24
19	3	1	3	2	1	3	2	1	3	2	1	3	2	38, 26
20	3	1	3	2	2	1	3	2	1	3	2	1	3	30, 25
21	3	1	3	2	3	2	1	3	2	1	3	2	1	53, 53
22	3	2	1	3	1	3	2	2	1	3	3	2	1	42, 35
23	3	2	1	3	2	1	3	3	2	1	1	3	2	43, 35
24	3	2	1	3	3	2	1	1	3	2	2	1	3	32, 37
25	3	3	2	1	1	3	2	3	2	1	2	1	3	13, 13
26	3	3	2	1	2	1	3	1	3	2	3	2	1	28, 22
27	3	3	2	1	3	2	1	2	1	3	1	3	2	33, 30

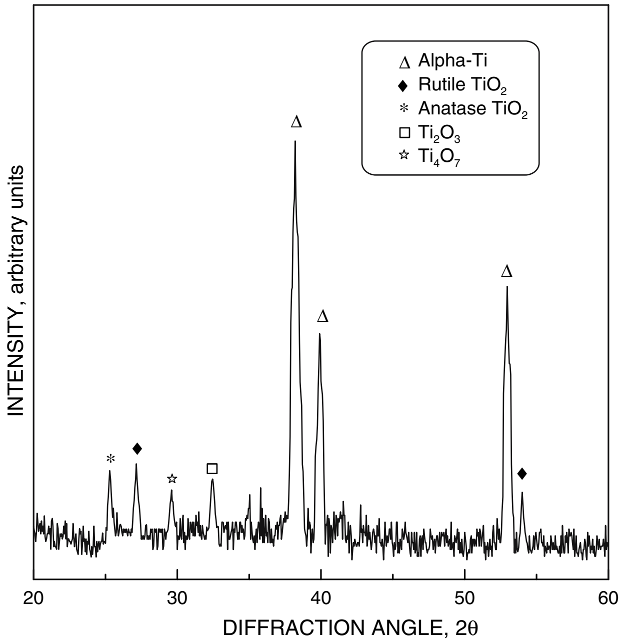

Fig. 1 The XRD patterns of the film obtained from Ti-substrate in a 2 M NaOH solution in an autoclave at 150 °C for 3 h

$$Ti + 4\ H_2O \rightarrow Ti(OH)_4 + 4\ H^+ + 4e^- \qquad (1)$$

$$Ba(OH)_2 \cdot 8H_2O + 2\ H^+ \rightarrow Ba^{2+} + 10\ H_2O \qquad (2)$$

$$Ti + 4\ OH^- \rightarrow TiO_2 + 2\ H_2O + \ 4e^- \qquad (3)$$

$$Ba^{2+} + Ti(OH)_4 \rightarrow BaTiO_3 + 2\ H^+ + H_2O \qquad (4)$$

The formation of TiO_2 and $Ti(OH)_4$, and that of $BaTiO_3$ are forward at high pH values.

Xu explained the formation mechanism of titanate film as, at a high OH^- concentration there is a tendency for highly densified and fine $Ti(OH)_4$ to form on the Ti substrate surface [25]. Only small pores exist, which make it difficult for the alkali earth metal ion to diffuse into the bulk of $Ti(OH)_4$. As a result, the produced titanate film is very thin.

Effects of preparatory variables

We utilized the reaction of Ba^{2+} with Ti metal to produce a barium titanate film on a Ti-substrate in a strongly alkaline solution. Reaction temperature, concentration of Ba^{2+}, and reaction time were again considered to investigate their effects on the relative crystal intensity of $BaTiO_3$ to Ti.

$BaTiO_3$-film could not be produced at reaction temperatures below 120 °C, even at high concentrations of Ba^{2+} up to 2 M. In addition, 2 M of Ba^{2+} solutions contained in a teflon container were subjected to Ti-substrate for 3 h at various temperatures, and the obtained films were examined by XRD, as shown in Fig. 2. Figure 2(a) shows the XRD patterns of the Ti metal substrate at 120 °C, and a $BaTiO_3$ phase was detected. Figure 2(b) shows the XRD pattern of the $BaTiO_3$ film obtained at 130–140 °C, revealing a visible $BaTiO_3$ phase. The XRD pattern of the $BaTiO_3$ film produced at 150–160 °C, has a strong relative intensity of $BaTiO_3$/Ti, as shown in Fig. 2(c). The relative crystal intensities of the $BaTiO_3$ films were increased with the increasing of the reaction temperature. From the comparison of films produced from various temperatures below 160 °C, films produced at a higher reaction temperature show stronger relative crystal intensity. On the contrary, it is clear that Fig. 2(d) shows the XRD patterns of $BaTiO_3$ film produced at 180–200 °C. It was found that the relative intensity of $BaTiO_3$/Ti was weaker than that of film produced at 150–160 °C, as shown in Fig. 2(c).

From the preliminary studies of temperature, the reaction temperature was set at a temperature range of 150–160 °C for the experimental design in the following section.

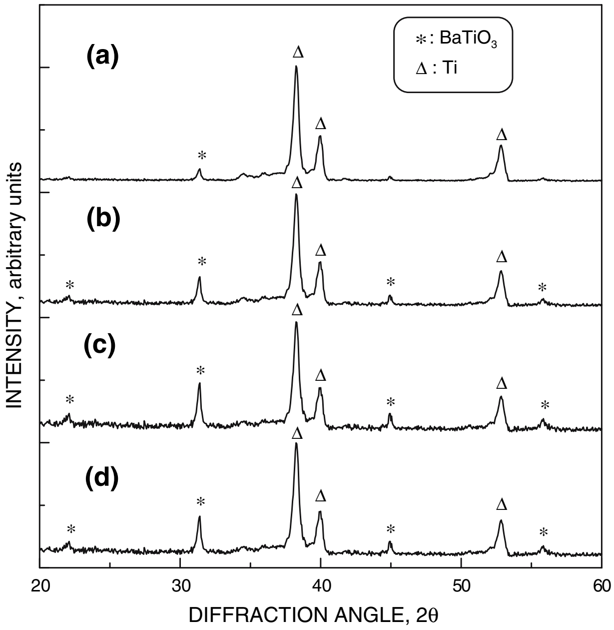

Fig. 2 The XRD patterns of the films prepared at various temperatures. (**a**) reaction temperature at 120 °C; (**b**) reaction temperature at 130–140 °C; (**c**) reaction temperature at 150–160 °C, and (**d**) reaction temperature at 180–200 °C

A $BaTiO_3$ film could be produced from 0.5 to 2 M $Ba(OH)_2$ solution with a temperature above 120 °C. At a lower concentration of $Ba(OH)_2$ (0.5 M) and lower reaction temperature (120–130 °C), the grain of the $BaTiO_3$ film was much more heterogeneous. However, it was very difficult to observe clear grain in a good condition, and then only in small aggregated grain on the substrate surface. It was found that the increase in $Ba(OH)_2$ concentration can conduct the formation of uniform grain $Ba(OH)_2$ film, and also found that at 1–2 M $Ba(OH)_2$, a homogeneous grain of $BaTiO_3$ film was examined. Particularly, the film synthesized at 150–160 °C, Ba^{2+} at 2 M, as well as having a reaction time of 3 h, was very homogeneous, with a uniform grain of about 0.2 μm, indicating that higher concentrations can promote the reaction of Ba^{2+} to react with $Ti(OH)_4$ to become $BaTiO_3$. Hence, a better grain distribution of $BaTiO_3$ was observed. In contrast, inhomogeneous grains containing abnormally grown grains accompanying small grains were observed, when the concentration of $Ba^{2+} > 2$ M.

We carried out the minimum setting for the reaction time of 2 h, a reaction temperature of 150–160 °C, and a Ba^{2+} concentration of 1 M, in order to obtain a film. The reaction time influenced the crystal growth and grain size. There was also an increase in the relative crystal intensity. However, the use of very long reaction times (i.e., 20 h) produced a film with an inhomogeneous distribution of grains and a tendency for aggregation was observed. Concomitantly, relative crystal intensity decreased as well.

The chosen preparatory conditions for the formation of barium titanate films were prepared at a certain temperature of 150–160 °C. A reaction time of 2–8 h, a Ba^{2+}-concentration of 0.5–2 M, the compositions of the $BaTiO_3$ films were usually uniform, the relative crystal intensities were about 0.1–0.5, grain sizes were 0.2–0.6 μm, film thickness was 0.1–0.6 μm, and dielectric constants were about 400–900.

Analysis of experimental results

Testing for significant factors and interactions

Bacsa et al. [24] revealed that the hydroxyl ion (OH^-) plays a vital role in the formation of the reactive intermediate, the titanium metal-hydroxy complex $Ti(OH)_4$, which causes the nucleophilic attack of the Ba^{2+} on $Ti(OH)_4$, and $BaTiO_3$ thin film is obtained, under hydrothermal conditions as well. Concomitantly, they also have found that $BaTiO_3$ is not formed at lower pH, and a high concentration of Ba and high pH favor the forward reaction.

Because the pH-value plays an important role in producing a perovskite thin film in this process, therefore, the pH-value was significantly affected by adding NaOH to the $Ba(OH)_2$ solution in this study. However, we were concerned with 4 factors: (1) the barium-concentration (factor A), (2) the NaOH concentration (factor B), (3) the reaction time (factor D), (4) the substrate surface treatment (factor E) as well as the interaction of the barium-concentration and the NaOH concentration ($A \times B$). The factors and levels for the experiment are given in Table 1.

The experiment was designed in an $L_{27}(3^{13})$ orthogonal array. The experimental layout and experimental results are given in Table 2. In Table 2, the $Ba(OH)_2$ solutions with different pH-values were prepared by utilizing three types of NaOH solutions. One with the lower pH-value (pH ≅ 11 at room temperature) was produced by dissolving only $Ba(OH)_2$ in water, another with the higher pH-value (pH ≅ 13 at room temperature) was producing by adding NaOH to the $Ba(OH)_2$ solution at a total concentration of NaOH at 1 M, and the other with the highest pH-value (pH ≅ 14 at room temperature) was producing by adding NaOH to the $Ba(OH)_2$ solution at a concentration of NaOH at 2 M.

The films were characterized by XRD to detect perovskite phases. The relative crystal intensity, grain sizes, film thickness and dielectric constants were also determined. The significant factors and interaction can be tested via the method of analysis of variance. The analysis of variance is summarized in Table 3. The result of analysis of variance shows that the effect of NaOH concentration (factor B) and substrate surface treatment (factor E) are significant to 99 percent confidence.

Determination of the optimum combination of levels

Because the interaction ($A \times B$) is not significant, the discrete-type optimum combination of levels is produced by comprising the level effects of each factor. The average level (relative crystal intensity, μ) effects of each factor are given as follows:

$$\mu(A_1) = 27.6,\ \mu(A_2) = 29.2,\ \mu(A_3) = 32.7$$

$$\mu(B_1) = 32.5,\ \mu(B_2) = 32.1,\ \mu(B_3) = 24.8$$

$$\mu(D_1) = 27.4,\ \mu(D_2) = 31.1,\ \mu(D_3) = 30.7$$

$$\mu(E_1) = 28.3,\ \mu(E_2) = 33.8,\ \mu(E_3) = 27.3$$

Table 3 Analysis of variance for testing the significant factors

Source of variation	Sum of squares	Degree of freedom	Mean square	F_o	*P*-value
A	0.02414	2	0.01207	2.99	0.061
B	0.06714	2	0.03357	8.32	0.001
D	0.01623	2	0.00811	2.01	0.147
E	0.04330	2	0.02165	5.37	0.008
$A \times B$	0.03387	4	0.00847	2.10	0.098
Error	0.16534	41	0.00403		
Total	0.35002	53			

F_o: the computed F ratio.

P-value: the smallest level of significance that would lead to rejection of the null hypothesis

The discrete-type optimal combination of levels produced is $A_3B_1D_2E_2$.

Regression model

Based on fitting the experimental data, the regression model is constructed by using the least squares method. Referring to the factors *A*, *B*, *D* and *E* as well as the interaction of *A* and *B* ($A \times B$), the regression model is given as

$$\begin{aligned} Y &= -0.1656 + 0.0414A + 0.1544B + 0.1078D \\ &\quad + 0.2308E + 0.0097A^2 - 0.0344B^2 - 0.0228D^2 \\ &\quad - 0.0594E^2 - 0.0275A \times B \\ A &= 1,2,3;\ B = 1,2,3;\ D = 1,2,3;\ E = 1,2,3 \end{aligned}$$

where $A = 1$, 2 or 3, corresponding to level 1, 2 or 3 of factor *A*. In addition, *B*, *D* and *E* are the same as *A*. This regression model can be used for prediction, process optimization and process control. Based on the above regression model, we can search the continuous-type optimum combination levels by using the mathematical programing method. The continuous-type optimum combination levels are given by

$$A = 3.00,\ B = 1.07,\ D = 2.35,\ E = 2.01$$

These results are close to that of the discrete-type optimum combination levels.

Comparison of some representative films from the 27 test runs with the film obtained in the confirmatory experiment

This theory was confirmed in a confirmatory experiment of $A_3B_1D_2E_2$. In this experiment the Ba^{2+} concentration of the solution was set at 2 M, without additional NaOH, reaction temperature was 150–160 °C, reaction time was 5 h and the substrate surface was polished with 2 μm diamond paste. A crystal $BaTiO_3$ film was obtained with the properties described below.

The XRD patterns of some of the obtained films are shown in Fig. 3. Figure 3(a) is the film prepared from run 25 ($A_3B_3D_1E_1$) in Table 2, having a relative crystal intensity of 0.13 (intensity of (110) $BaTiO_3$ peaks in XRD spectrum/intensity of (001) Ti peak in XRD spectrum). Figure 3(b) is the film from run 21, having a relative crystal intensity of 0.53 ($A_3B_1D_1E_2$). Figure 3(c) shows the film from the control experiment of $A_3B_1D_2E_2$ with a relative crystal intensity of about 0.55.

The dielectric constants of the films obtained from run 25 and run 21, and the optimal experiment were measured at various frequencies, with results as shown in Fig. 4. Clearly, higher relative crystal intensity results in a higher dielectric constant. The dielectric constant of the film obtained in the control experiment was about 915 at 1 MHz.

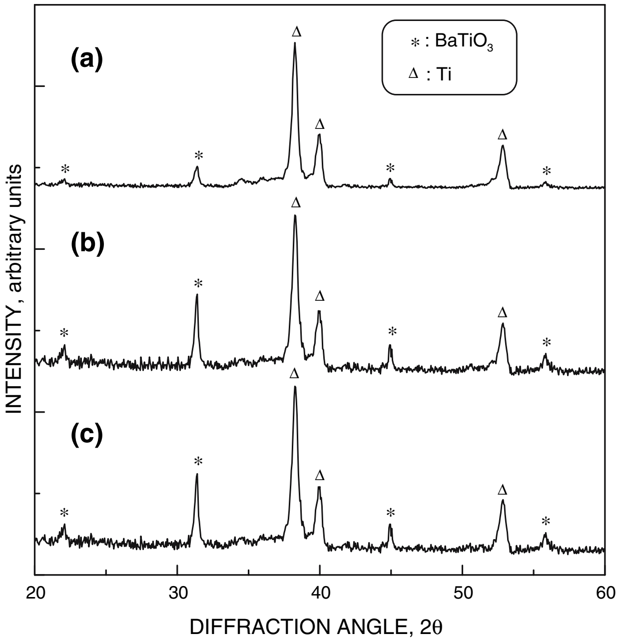

Fig. 3 The XRD patterns of the obtained films. (**a**) the film prepared from run 25 ($A_3B_3D_1E_1$) in Table 2 ; (**b**) the film prepared from run 21 ($A_3B_1D_1E_2$) in Table 2, and (**c**) the film obtained from the control experiment of $A_3B_1D_2E_2$

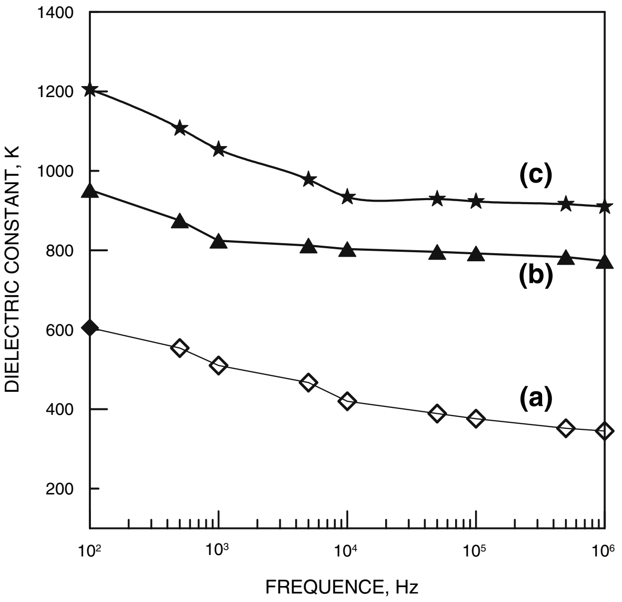

Fig. 4 Dielectric constant of $BaTiO_3$ film. (**a**) the film of run 25 in Table 2; (**b**) the film of run 21 in Table 2, and (**c**) the confirmation experiment film

Conclusions

Polycrystal barium titanate films were obtained from Ba^{2+} in strongly alkaline solution at a low temperature by hydrothermal reaction with a Ti substrate. The interface relationship between film and substrate was investigated, revealing that Ba^{2+} ions diffused into the $Ti(OH)_4$ gel, resulting in a homogeneous film. In order to minimize the number of experiments required to identify the critical process variables that control the film characteristics, a fractional factorial design was implemented.

The effects of such preparatory conditions as the Ba^{2+} concentration of the solution, NaOH concentration, reaction time and the substrate surface treatment were systematically studied using a 3-level orthogonal array design at 150–160 °C. Results indicate that NaOH concentration and surface characteristic are the key variables influencing the relative crystal intensity and dielectric constants of the obtained films. By combining the optimal settings for the variables ($A_3B_1D_2E_2$), a polycrystalline $BaTiO_3$-film with a relative intensity of 0.55, and high dielectric constant of about 915 at 1 MHz could be obtained.

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