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Preparation and Electrical Properties of Barium Titanate Film by Hydrothermal Method

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Abstract

High concentration of the reactant is helpful to the uniformity of the grain, high reaction temperature is useful to the formation of the grain and longer reaction time affects the grain size clearly. The higher concentration of the reactant barium ion and the higher the pH value (0·25 N-pH 11·6→4 N-pH 13·8) and added hydroxide ion to increase the alkalinity make the uniformity of the grain very clearly. The bigger and more uniform of grain makes its dielectric constant larger. But the non-uniform grain having bigger size cannot increase its dielectric constant.

Keywords: films, electrical properties, grainsize, perovskites.

1 Introduction

The hydrothermal method is an attractive technique for formation of perovskite-type ceramic. The ABO_3 thin-film can be synthesized on substrates of the B-site metal being reacted in an alkaline aqueous solution containing the A-site elements, through the autoclave at sealed conditions. The reaction can form well dense thin-film with good adherence on substrates. Because of its advantages such as simple instrumentation, lower preparation-temperature, without annealing for crystallization after deposition, and high purity of the products, this method is very worthy of developing.

Recently, dielectric barium titanate have been widely studied for application in capacitor, varistor and even random access memory (RAM) with developing ultra large scaled integrated curcuits (ULSI). Well-crystallized polycrystalline material that can be controlled grain size (0·1–1·2 μm) and film thickness (0·1–1·0 μm) by changing temperature, concentration and reaction time.

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Yoshimura *et al.*[1] have prepared the $BaTiO_3$ thin film by hydrothermal electrochemical method. Later it is discovered[2] that the barium titanate thin film on titanium substrates can be synthesized by hydrothermal synthesis. Kajiyoshi *et al.*[3] have investigated the microstructure of strontium titanate thin film grown by the hydrothermal–electrochemical method. Phase-pure $SrTiO_3$ had been obtained using $Sr(NO_3)_2$ or $Sr(OH)_2{\cdot}8H_2O$ as sources of strontium and hydrous and anhydrous TiO_2 as a source of titanium.[4] Slamovich *et al.*[5] had processed hydrothermally at 40–80°C by reacting thin layers of titanium organometallic liquid precursors in aqueous to obtain thin films of cubic $BaTiO_3$. $BaTiO_3$ films had been synthesized on Ti-covered Si substrates.[6] Functionally graded $SrTiO_3$–$BaTiO_3$ thin films prepared by the hydrothermal–electrochemical method under flowing solution has been studied.[7] But the effects of the preparatory conditions, such as reacting species, reactant concentration, reaction temperature and time, on the properties of the strontium titanate film formed, grain size and reaction rate, have not been studied.

In this study we investigate the mechanism of the formation of barium titanate, discuss the effects of process variables, such as temperature, alkaline earth metal ion concentration and reaction time in pure composition, on the grain size and electrical property of perovskite film. At the same time, the techniques of surface analyses and chemical analyses are used to understand the compositions of the thin film in order to prepare the corresponding chemical stoichiometric ratio of ceramic film in high dielectric constant.

2 Experimental

Titanium metal through polishing, washing by acid and then by acetone in an ultrasonic cleaner was put in the teflon clamp in an autoclave to react. The redistilled water before use should be boiled at least 5 min in order to avoid the absorption of carbon dioxide. The titanium substrate was put in the horizontal position to avoid the concentration

gradient in the vertical position. The flowchart for the experiment is shown in Fig. 1.

3 Results and Discussion

The reaction mechanism is proposed as follows:[6]

$Ti + 2H_2O \rightarrow TiO_2 + 2H_2\uparrow$

$TiO_2 + 2H_2O \rightarrow Ti(OH)_4(aq.)$

and $Ba^{2+} Ti(OH)_4(aq.) \rightarrow BaTiO_3(s) + 2H^+ + H_2O$

From the above mechanism the higher the pH value is, the easier formation of $BaTIO_3$ is and the high concentration of barium ion is helpful to the formation of $BaTiO_3$.

3.1 Analysis of microstructure

3.1.1 Effect of the concentration of barium hydroxide

At 110°C 0·25 N $Ba(OH)_2$ the particle size formed is not uniform and even no clear grain formed exists and on the surface there are flake-like up and down levels. Up to 1 N $Ba(OH)_2$ large particle formed becomes great grain but the quantity is very few. The particle size is 0·3 μm and the smaller particle is still flake-like up and down levels. For 4 N $Ba(OH)_2$ the particle formed is uniform grain and its size is 0·18 μm. The tendency in higher temperature is the same as that in the concentration (Fig. 2).

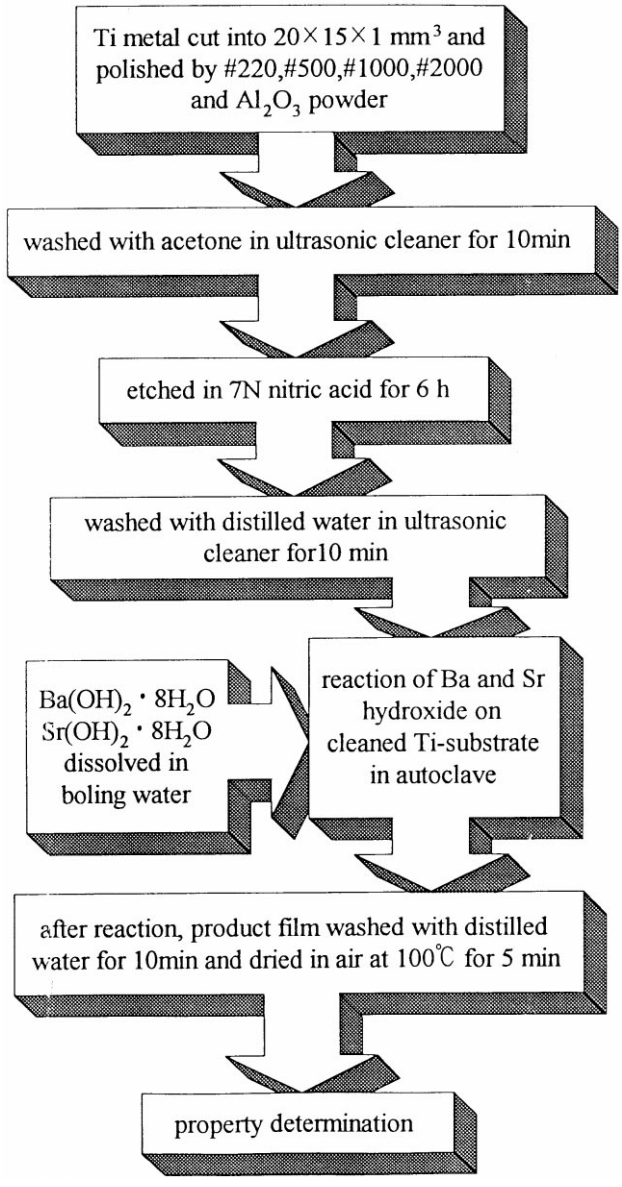

Fig. 1. Flowchart of the experiment.

3.1.2 Effect of temperature

For low concentration (0·25–0·5 N) of $Ba(OH)_2$, as the temperature increases the flake-like non-uniform

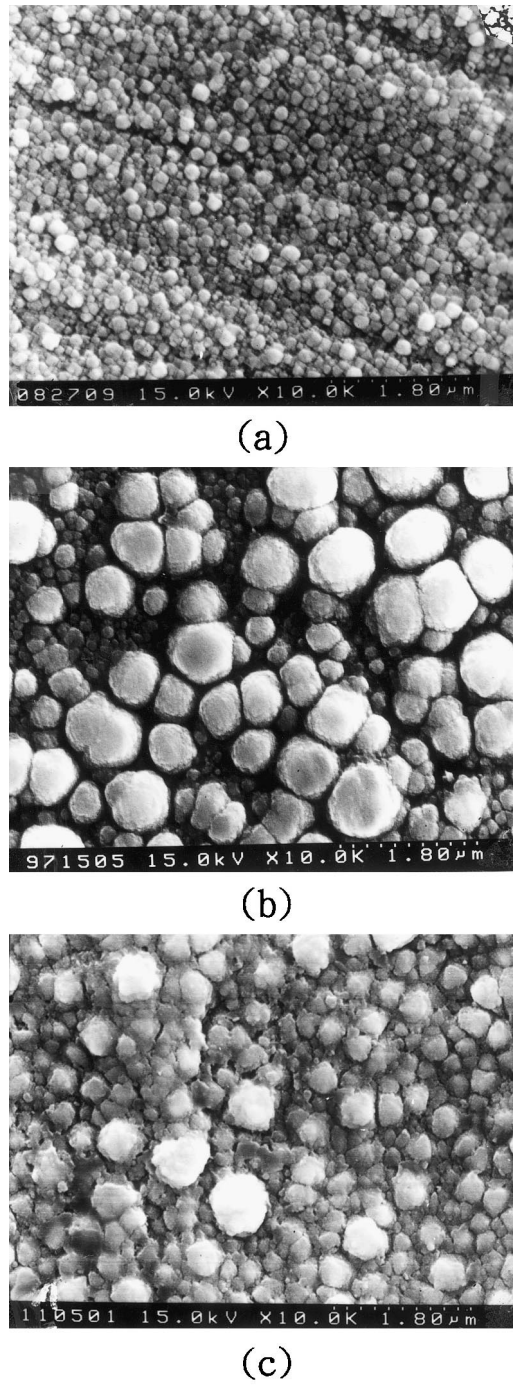

Fig. 2. (a) SEM for 4 N $Ba(OH)_2 \cdot 8H_2O$ at 130°C for 3 h (uniform grain); (b) SEM for 1 N $Ba(OH)_2 \cdot 8H_2O$ at 110°C for 20 h (great grain); (c) SEM for 0·5 N $Ba(OH)_2 \cdot 8H_2O$ at 130°C for 1 h (flake-like grain).

grain decreases. Near to 200°C the grain becomes clear uniform at 0·2 μm. For high concentration (2–4 N) of $Ba(OH)_2$, at 110–130°C the grain is from non-uniform into uniform at 0·2 μm, at 130–150°C the grain becomes larger at 0·3 μm and at 150–200°C the grain is much larger at 0·4 μm but starts to become non-uniform again.

3.1.3 Effect of reaction time

As the reaction time increases, the grain size also becomes larger. Over 20 h in reaction time the grain can attain a maximum 1 μm.

3.2 Analysis of film thickness

The AES depth profile and α-step surface profile for 1 N $Ba(OH)_2{\cdot}8H_2O$ at 110°C for 1 h were shown in Figs 3 and 4, respectively. The gravimetric method is also used to measure the film thickness. From the above results there are relationships between film thickness and grain size. The larger the grain is, the thicker the film is.

3.3 Crystalline analysis

There are no phases of impurity except α-Ti and cubic $BaTiO_3$ in the XRD analysis (Fig. 5). In order to compare the crystalline analysis easily, one uses the ratio of the main peak of Ti to $BaTiO_3$ as the standard. Basically, the higher concentration of the reactant, the higher reaction temperature and the longer reaction time are very helpful to the increasing of crystalline property and the completeness of the grain also has the tendency of increasing crystallization. But too high concentration of reactant, too high reaction temperature and too long reaction time will decrease crystallization due to side reaction.

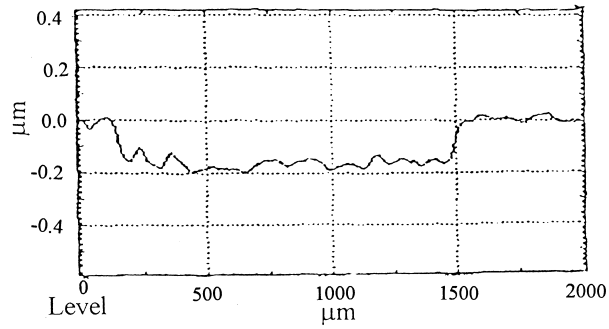

Fig. 4. α-step surface profile for 1 N $Ba(OH)_2{\cdot}8H_2O$ at 110°C for 1 h.

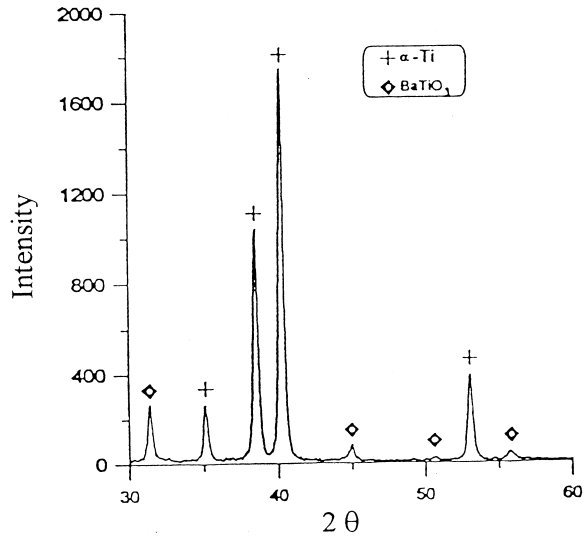

Fig. 5. XRD pattern for 1 N $Ba(OH)_2{\cdot}8H_2O$ at 110°C for 20 h.

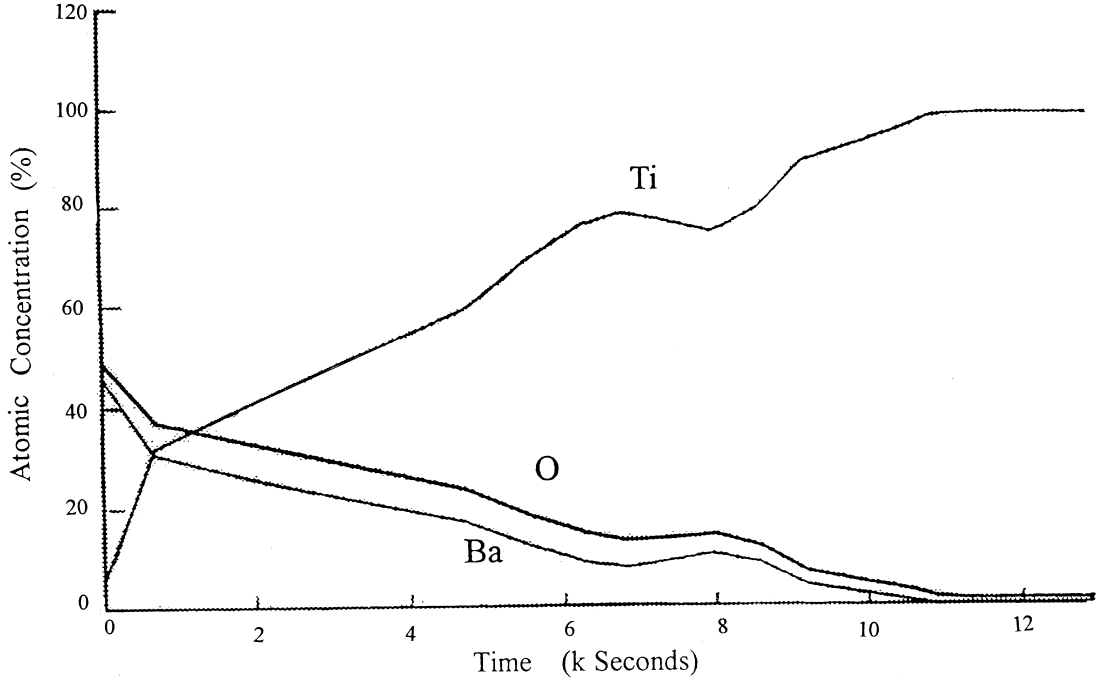

Fig. 3. AES depth profile for 1 N $Ba(OH)_2{\cdot}8H_2O$ at 110°C for 1 h.

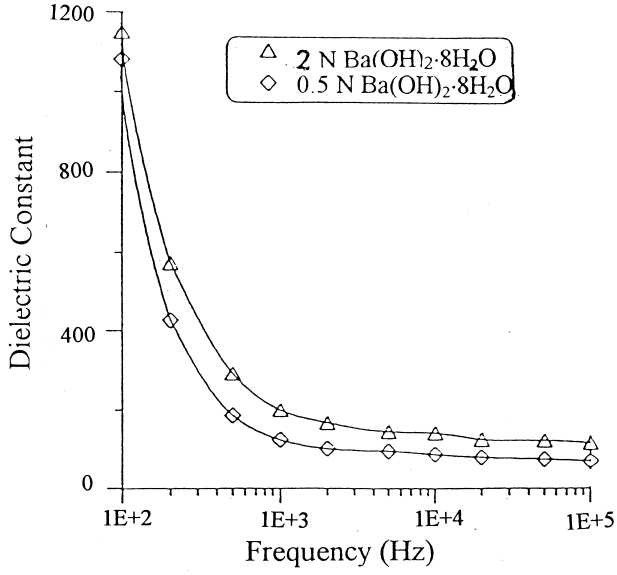

Fig. 6. Dielectric constant versus frequency for 0·5 and 2 N $Ba(OH)_2 \cdot 8H_2O$ at 130°C for 3 h.

3.4 Analysis of electrical property

The dielectric constant versus frequency for 0·5 N and 2 N $Ba(OH)_2 \cdot 8H_2O$ at 130°C for 3 h were shown in Fig. 6, it is indicated from Fig. 6 that the dielectric constant decreases as the frequency increases. For the completeness of crystallinity the dielectric constant is bigger and the larger grain size is helpful to increase its dielectric constant. But the effect of non-uniform grain is not clear. The value of the dielectric constant is the order of 10^2 to 10^3.

4 Conclusion

1. High concentration of the reactant is helpful to the uniformity of the grain, high reaction temperature is useful to the formation of the grain and longer reaction time affects the grain size clearly.
2. The higher concentration of the reactant barium ion, the higher the pH value (0·25 N-pH 11·6→4 N-pH 13·8) and the more hydroxide ion for increasing the alkalinity make the uniformity of the grain very clearly.
3. Using barium nitrate or barium acetate as the source of barium ion and sodium hydroxide as the source of alkalinity, the particle formed is better in uniformity and has no flake-like grains, but is smaller in the grain size and worse in the crystallinity. This is due to the effect of diverse ions to make worse in electrical property and there is no better in its microstructure.
4. The bigger and more uniform of grain makes its dielectric constant larger. But the non-uniform grain having bigger size can not increase its dielectric constant.

Acknowledgements

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