A New Fabrication Technique of Thin Films of Perovskite-Type Compounds by Hydrothermal-Electrochemical Method

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Abstract

A new technique called "hydrothermal-electrochemical method" has been developed, which could be categorized into a variety of the extended hydrothermal method. The technique provides an easy fabrication of well-crystallized thin films of perovskite-type compounds at very low temperatures. Application of the hydrothermal-electrochemical method is demonstrated on the thin film preparation of polycrystalline barium titanate, $BaTiO_3$ on the titanium-deposited glass substrate. The reaction was carried out in 0.1 to 0.5N $Ba(OH)_2$ electrolytic solutions at temperatures of 100 to 200°C and under saturated vapor pressures, using the substrate for anode and a Pt plate for cathode, galvanostatically applying a constant current density up to 18 mA/cm^2. Surface of the $BaTiO_3$ film was lustrous and free from any visible defects. Thickness of the films ranged from 70 nm to 300 nm for $BaTiO_3$. The adhesion between $BaTiO_3$ and the substrate was so strong that no exfoliation was observed. Similar $BaTiO_3$ thin films with thickness less than 70 nm were also formed even in simple hydrothermal conditions without applying any electric current.

1. Introduction

Perovskite-Type compounds are known as important materials for the application in solid state electronic devices including capacitors, thermistors, sensors, piezoelectric actuators, and absorbers for electromagnetic wave. Conventional methods to fabricate thin films of these compounds could be divided into the dry process, such as vacuum deposition, sputtering, CVD, etc., and the wet process such as sol-gel. All these methods require higher temperatures than 500°C to obtain well-crystallized films of perovskite-type compounds. These methods essentially should have to avoid the reaction between the film and the substrate, which often comes into conflict with the crystallization at high temperatures.

It is well-known that the hydrothermal method can provide well-crystallized and equi-sized particles of barium titanate at relatively low temperatures.[1,2] Generally, the crystallization temperature in hydrothermal reaction is lower than those in other methods. Thus, it would be quite interesting to take advantage of the hydrothermal reaction in the thin film fabrication.

In contrast with the dry methods and the sol-gel method, the anodic oxidation is a typical method which utilizes positively the reaction with the substrate. This method belongs to the wet process and can provide, for example, thin films of amorphous niobium or tantalum oxides on respective metal substrates[3], which are used for the electrolytic capacitor. It was believed, however, that only simple oxides, mostly in amorphous state, could be fabricated by this method.

The authors aimed more positive use of the chemical reaction between the electrolytic solution and the substrate than the conventional method did. Concerns were paid on the participation of solute cations into the oxidation reaction of the metal substrate to form complex oxide. Past studies[4,5] on the preparation of $BaTiO_3$ and $LiNbO_3$ powders by the hydrothermal anodic oxidation were quite suggestive for developing a new technique of thin film fabrication. Recently, it was found that $BaTiO_3$ thin films could be formed on the Ti metal substrate in high temperature and high pressure $Ba(OH)_2$ electrolytic solutions.[6] The $BaTiO_3$ film exhibited two excellent properties, one was characterized by its dense and homogeneous body, and the other was its very low crystallization temperature. Since this technique utilizes the electrochemical reaction under hydrothermal conditions, it was named "hydrothermal-electrochemical method".

In this paper, the authors' recent study[7] on the formation of $BaTiO_3$ thin film on the Ti-deposited glass substrate is reviewed for introducing this new technique for fabricating thin films of the perovskite-type compounds.

2. Experimental

Titanium was deposited on a Pyrex glass substrate with dimensions of 38x18x1.7mm^3 by the rf-sputtering technique (RFS-200, ULVAC Co.). The sputtering conditions are given in Table 1. Purity of the titanium target was 99.5%. The temperature of the substrate was kept constant at approximately 200^{o}C.

The preprocessed substrate and a platinum plate were then used for anode and cathode, respectively, for the electrochemical cell. Both electrodes were suspended with platinum lead wire in a teflon beaker containing 200ml $Ba(OH)_2$ electrolytic solution. Reagent grade of $Ba(OH)_2 \cdot 8H_2O$ (Wako Pure Chemicals Co.) was used for the preparation of the solutions. The cell was placed in an electrolytic autoclave and heated up to 200^{o}C under saturated vapor pressures. The autoclave and the cir-

Table 1. Sputtering conditions for Ti metal

Frequency	:	13.56 MHz
Input Power	:	150 watts
Ar Gas Pressure	:	5×10^{-3} torr
Target-Substrate Distance	:	50 mm
Sputtering Time	:	2 hrs
Pre-Sputtering Time	:	10 min
Thickness of the Ti film	:	1 um

cuit arrangement is illustrated in Fig. 1, where (A) Pt plate, (B) thermocouple, (C) stirrer and (D) Ti plate. Electric field was then applied between electrodes using a galvanostat (Type PAD 1K-0.2L, Kikusui Electronics Co.) so as to keep a constant current density up to 18 mA/cm^2. The treatment time for the electrochemical reaction was 10-60 min during which the voltage-time relation was recorded. After the treatment, the product was washed with redistilled water and ethanol, and then dried in a desiccator at room temperature for one day. Experiments using the same setup but without applying the electric current were also carried out.

Microstructure of the film was investigated by the scanning electron microscopy (ABT Co., SIGMA-V). The constituting phases of the film were studied using an X-ray diffractometer (Philips Co., PW1700) designed for the thin film analysis. On this diffractometer, a parallel beam enters into the specimen with very small glancing angle so that the penetration depth perpendicular to the surface becomes very small. In this study, Cu Kα was used at operating electricity of 40kV-55mA. Diffracted X-rays were monochromated by a graphite plate. Glancing angle was fixed at 0.5°. Sample spinner was not used since the film showed no preferency for orientation.

3. Results and discussion

The film consisted of $BaTiO_3$ single phase when it is processed at 200°C in 0.5N $Ba(OH)_2$ electrolyte for 30min. The

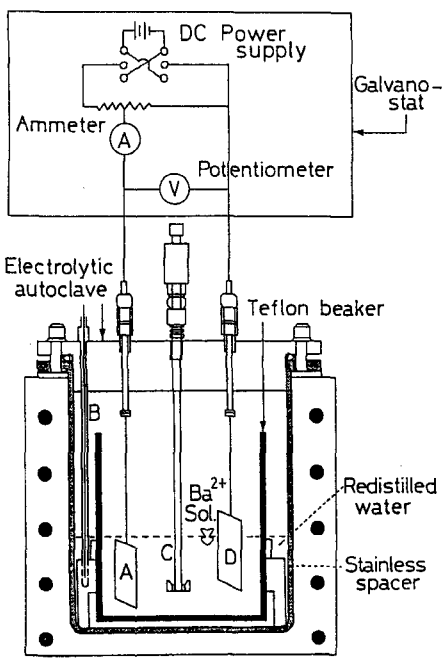

Fig. 1.

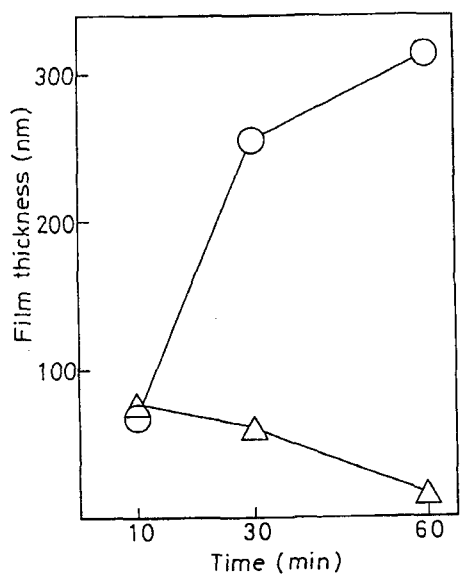

Fig. 2.

surface of the film was lustrous like a mirror and free from any visible defects. The films had various colors, blue, violet, gold, etc., depending on the experimental conditions. Thickness of the film was estimated from the weight change of the specimen prepared on the Ti metal substrate[6], and shown in Fig. 2. The thickness increased from 70 to 300nm with treatment time from 10 to 60 min for the specimens (O in Fig.2) processed at 200°C in 0.5N $Ba(OH)_2$ with the current density of approximately 15 mA/cm^2. Adhesion of the film on the substrate was so strong that no exfoliation was observed by scanning electron microscopy after scratching the surface by a knife edge.

The observed cell voltage was almost constant in the range 5-10 V against the treatment time as shown in Fig. 3. The V-t diagram of $BaTiO_3$ thin film (O) prepared at 200°C in 0.5N $Ba(OH)_2$ was quite different from that obtained on the preparation of $BaTiO_3$ powders (Δ) in a similar experimental setup at 200°C but using 0.5N $Ba(NO_3)_2$ solution as the electrolyte.[4] In the latter, repetition of sudden drops in cell voltage was interpreted as due to the electrical and mechanical breakdown of the anodically formed TiO_2 film on the Ti metal plate, resulting in the formation of $BaTiO_3$ powder. Comparison of both V-t diagrams suggests that a rather different mechanism should be considered for the formation of thin films, which is now in progress.

X-ray diffractograms of the films are shown in Fig. 4. Crystals of $BaTiO_3$ showed no prefered orientation. Peak profile was sharp enough to prove the crystallinity of $BaTiO_3$, but not enough to identify its tetragonality. The structure of $BaTiO_3$ was thus supposed to be cubic. At room temperature, anatase (TiO_2) was observed instead of $BaTiO_3$. This indicates that heating up to 100-200°C is required to form a film of $BaTiO_3$.

The scanning electron micrograph of the fracture surface of the specimen processed at 200°C in 0.1N $Ba(OH)_2$ for 30min with 10mA/cm^2 is shown in Fig. 5. The thickest layer (c in Fig. 5) sputtered on the glass substrate (d) is the titanium one with columnar microstructure commonly found in sputtering. On top

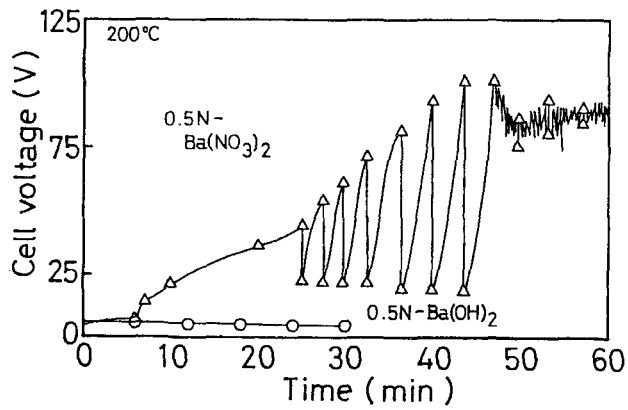

Fig. 3.

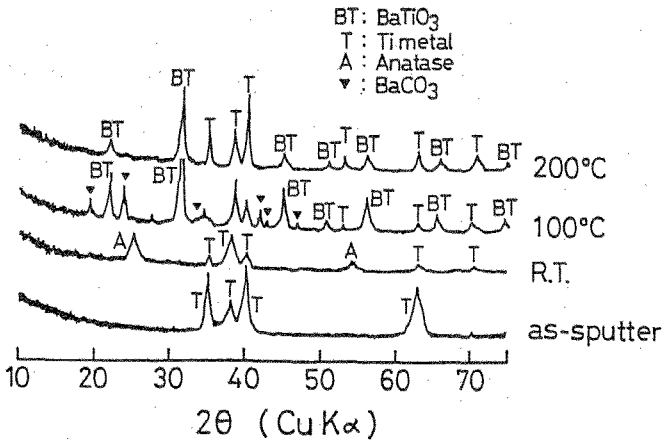

Fig. 4.

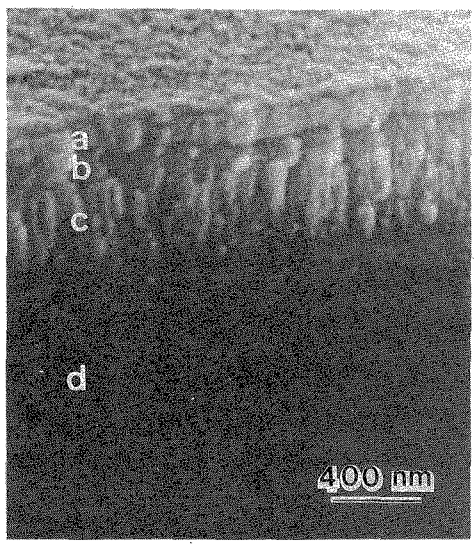

Fig. 5.

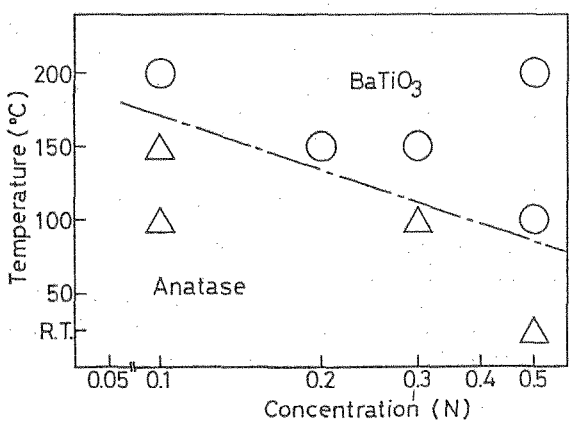

Fig. 6.

of the titanium layer, one can find in Fig. 5 two layers with thickness of approximately 150 (a) and 100 (b) nm, respectively. A detailed X-ray analysis is now undergoing, suggesting that the layer (a) near surface is $BaTiO_3$ and the second one (b) is a mixture of amorphous TiO_x and anatase.

Formation diagram of $BaTiO_3$ at a constant electric current density of $10mA/cm^2$ with treatment time of 60 min is shown in Fig. 6. It should be noted that this diagram only indicates the phases noticeable in the region approximately 0-100 nm from the surface, since the analysis was carried out by XRD with thin film attachment. Thus, the two-layer structure of the film as suggested above was not depicted in the figure. Formation temperature of $BaTiO_3$ decreased down to 100^oC with increasing Ba^{2+} concentration. It is rather surprising that well-crystallized $BaTiO_3$ thin films were formed at such low temperatures.

Thin films of $BaTiO_3$ were also formed using 0.5N $Ba(OH)_2$ solution in the temperature range between 100 and 200^oC without applying any electric current. The appearance and microstructure of the film were essentially the same as those formed with the aid of electric current, except that the thickness was relatively small. The thickness slightly decreased with the treatment time as shown in Fig. 2 (specimens denoted by △) , suggesting probable dissolution in solutions. These phenomena may indicate that applying the electric current is not essential for the $BaTiO_3$ film formation, but is effective in increasing the film thickness.

4. Concluding remarks

Smooth and dense thin films of $BaTiO_3$ with thickness less than 300 nm have been prepared on the Ti-deposited glass substrate by the hydrothermal-electrochemical method at temperatures of $100-200^oC$. Up to date, the authors also have succeeded in fabricating thin films of $SrTiO_3$ on Ti metal substrate[8], $LiNbO_3$ on Nb[9], $BaFeO_{3-x}$ on Fe[10] by the same method. They also succeeded in fabricating $BaTiO_3$ thin film on polyphenylen sulfide (PPS) film[11]. This is probably the first case in making ceramic thin film on polymer film substrate, as far as the authors concern. Although there still remains plenty of room for improvement, the hydrothermal-electrochemical method seems to offer a potential field for the thin film fabrication of various complex oxides.

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