Electrochemical Synthesis of Ba- and Sr-Based Titanate Thin Films using Ti Electrode Prepared by RF Sputtering

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Abstract–Barium and strontium titanate films were electrochemically synthesized onto Ti thin film prepared by RF sputtering. Applied current waveform was modulated to investigate the film growth mechanism. Superimposed cathodic pulses accelerated the formation of titanate thin films, and both the electrode surface pH and (Ba^{2+}, Sr^{2+}) ion size had a strong influence on film formation. Titanate film formation mechanism was investigated with a scanning electron microscope, an X-ray diffractometer and an electrochemical quartz crystal microbalance (EQCM). *In-situ* mass change of Ti electrode during electrolysis indicated that electrochemical method sets a limit to film growth.

Key words: Barium Strontium Titanate, Electrochemical Method, Current Pulse Waveform, Electrochemical Quartz Crystal Microbalance, Film Growth

INTRODUCTION

Barium and strontium titanate thin films are considered as prospective candidates for charge storage DRAM capacitors because of their high dielectric constant [Baumert et al., 1998; Othsuka et al., 1985]. Thin films have been manufactured by radio frequency (RF) sputtering, chemical vapor deposition, and physical vapor deposition [Pasierb et al., 1998; Takeshima et al., 1997], which require high temperature during the film deposition [Tsuzuki et al., 1998]. Recently, low-temperature techniques such as electrochemical [Venigalla et al., 1995; Bendale et al., 1996], hydrothermal [Hoffmann et al., 1997; Xu et al., 1996; Seo and Kong, 2000; Seo and Kong, 2000], and hydrothermal-electrochemical [Kajiyoshi et al., 1996] methods have been developed to synthesize the crystalline titanate thin films such as $BaTiO_3$, $SrTiO_3$, $Ba_xSr_{(1-x)}TiO_3$ on Ti metal foil surface.

Based on the phase stability diagram in the system of Ba-Ti-H_2O, $BaTiO_3$ is predicted to be the stable phase above pH 12 [Bacsa et al., 1998]. Therefore, the electrochemical synthesis method requires a higher pH solution prepared by the addition of pH enhancer into barium hydroxide solution. Previous results [Bendale et al., 1996] showed that the addition of NaOH deteriorates the dielectric property of the synthesized film. An alternative method is required for maintaining the surface pH high during the film formation without adding pH enhancer.

Results of $BaTiO_3$ formation on the anodically grown titanium oxide indicated that the variations of Ti oxide thickness and the state of pre-existing Ti oxide film affect significantly the $BaTiO_3$ formation [Xu et al., 1996]. Since a thick anodic film hinders the electrochemical formation of homogeneous and uniform titanate film [Venigalla et al., 1995], the removal of natural oxide film prior to the electrochemical synthesis is very important. Conventional oxide removal methods, such as mechanical and/or chemical polishing, have a limitation in obtaining a uniform surface [Kajiyoshi et al.,

1995; Yoshimura et al., 1998]. In order to minimize the complexity caused by the presence of Ti natural oxide film and to determine the possibility of the preparation of thin film capacitor electrodes for electronic devices, sputtered Ti thin films were used as a substrate electrode instead of titanium foil.

In this work, Ti thin film grown by the RF sputtering was used as a substrate electrode, and the modulation of applied current waveform was adopted to investigate the effect of surface pH in the formation of titanate thin films.

EXPERIMENTAL

Glass substrates with dimensions of $10 \times 50 \times 1$ mm^3 were used to prepare titanium thin films. To remove organic impurities of the glass surface, glasses were ultrasonically cleaned in acetone solution for 15 min and, in D.I water for 10 min. 1 μm-thick Ti film was deposited on the glasses by RF magnetron sputtering equipment (Korea Vacuum Tech, KVS-T4560) and used as a working electrode. Platinum plate was used as a counter electrode and Ag/AgCl (sat. KCl) was used as a reference electrode. Electrolyte was prepared by using reagent grade $Ba(OH)_2 \cdot 8H_2O$ and $Sr(OH)_2 \cdot 8H_2O$, and electrodeposition was carried out at 85 °C.

Applied currents or potentials were modulated with potentiostat/galvanostat (PAR273A) and the resulting potential and current variations were measured with a high speed voltmeter (Keithley 2000). Simultaneous mass change of Ti film electrode during electrodeposition was *in-situ* measured with an electrochemical quartz crystal microbalance (EQCM, Seiko EG&G QCA917). Ti quartz electrode prepared by sputtering was purchased from Seiko EG&G.

Surface morphology and crystal structure of the synthesized thin films were investigated with a scanning electron microscope (SEM, Hitachi S-4200) and an X-ray diffractometer (XRD, Phillips DY616).

RESULTS AND DISCUSSION

Ti thin film prepared by RF sputtering on the glass substrate has been used as a substrate electrode. Fig. 1 shows the linear sweep

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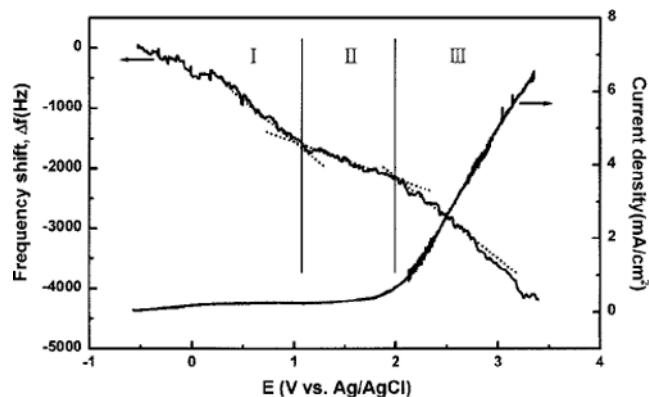†To whom correspondence should be addressed.
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Fig. 1. Linear sweep voltammogram and *in-situ* measurement of electrode mass change.

voltammogram (LSV) and the *in-situ* mass change of Ti electrode during electrodeposition in the solution of 0.5 M $Sr(OH)_2$ at 85 °C. As the potential increases, the anodic current increases slowly up to 1.6 V and increases rapidly above 1.6 V. Relevant anodic reactions are [Kajiyoshi et al., 1996],

$$Ti \rightarrow Ti^{4+} + 4e \xrightarrow{+H_2O} TiO_2 \tag{1}$$

$$4OH^- \rightarrow O_2 + 2H_2O + 4e \tag{2}$$

and the initial slow current increase is due to the oxide film formed by reaction (1). With the increase of potential, OH^- on Ti electrode participated in reaction (2) and the oxygen gas evolutions were detected. At the same time, OH^- reacted chemically with TiO_2 and the weight of Ti electrode was changed. The potential-frequency (p-f) curve of Fig. 1 shows an *in-situ* mass change of Ti film electrode which was measured by EQCM. Since the mass change of the electrode (ΔM) is directly related to frequency shift (Δf) (Sauerbrey equation) [Hori et al., 1983],

$$\Delta f = -C_f \Delta M, \text{ where } C_f = 935.7 \text{ Hz/}\mu g$$

Fig. 1 indicates that the weight of Ti electrode increases continuously with an increase of potential but the electrode mass-increase rate (i.e., the slope of the p-f curve) changes in the vicinity of 1.2 and 2.0 V. Despite a substantial difference in the amount of anodic current, the electrode mass-increase rate, ~2.09 $\mu g/V$, is comparable below 1.2 V (zone I) and above 2.0 V (zone III), but it decreases to 0.82 $\mu g/V$ at 1.2-2.0 V (zone II).

The variation of mass-increase rate with potential mentioned is the result of the reaction occurring on electrode surface including reactions (1) and (2). It can be interpreted with the $SrTiO_3$ formation since the X-ray diffractogram obtained after LSV confirms the formation of crystalline $SrTiO_3$. In the same electrolyte, Fig. 2 shows that $SrTiO_3$ crystalline film is formed at 0.3 V after 300 s. Since the main reaction occurring at 0.3 V is the formation of TiO_2, it indicates that TiO_2 was converted into $SrTiO_3$ crystal structure during electrolysis. Mass-increase rate change in Fig. 1 shows that the formation of $SrTiO_3$ film on Ti electrode is composed of two-step reactions. Initially, formed TiO_2 is transformed into a metastable oxide (or hydroxide) phase which Sr^{2+} in solution can be incorporated into. During this phase change, oxygen evolution starts and the partial dissolution of metastable phase causes the slight decrease in the mass-
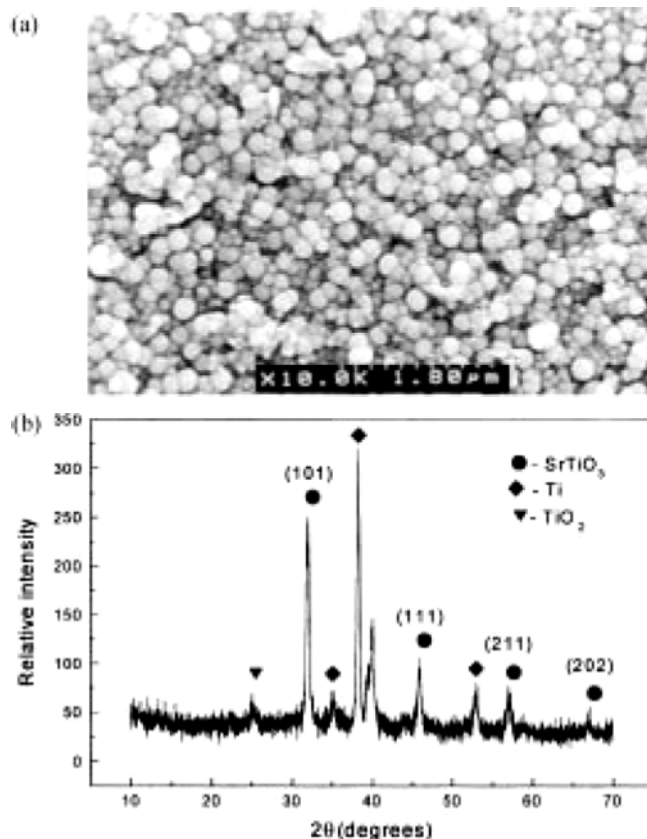
Fig. 2. $SrTiO_3$ film formed at 0.3 V after 300 s.
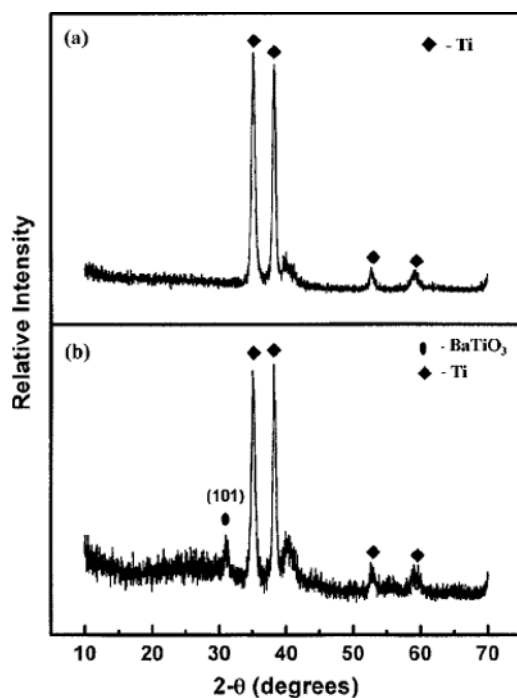(a) surface morphology, (b) X-ray diffraction pattern

Fig. 3. X-ray diffraction patterns when different current waveforms were applied to form $BaTiO_3$.
(a) constant current density (i_a=25 mA/cm² for 60 s), (b) current pulse waveform (i_c=-25 mA/cm², t_c=2 s; i_a=25 mA/cm², t_a=4 s for 90 s)

increase rate above 1.2 V. Electrode mass-increase rate in zone III is supposed to result from the formation of $SrTiO_3$ thin film on Ti electrode surface. After film formation, the diffusion of OH^- and H_2O to the Ti surface is retarded and TiO_2 formation at the interface between $SrTiO_3$ film and Ti electrode can be suppressed. On the other hand, O_2 evolution becomes a dominant reaction at the surface of strontium titanate films. Similar electrode mass-increase rate between below 1.2 and above 2.0 V is because of the faradaic efficiency for TiO_2 formation affecting the mass increase by $SrTiO_3$ formation decreases rapidly above 2.0 V. It will be discussed later in detail.

1. Formation of BaTiO₃ Film and SrTiO₃ Film

Two different current waveforms were used to synthesize $BaTiO_3$ and $SrTiO_3$ films. Fig. 3(a) shows an x-ray diffraction pattern obtained after constant anodic current density of 25 mA/cm² was ap-

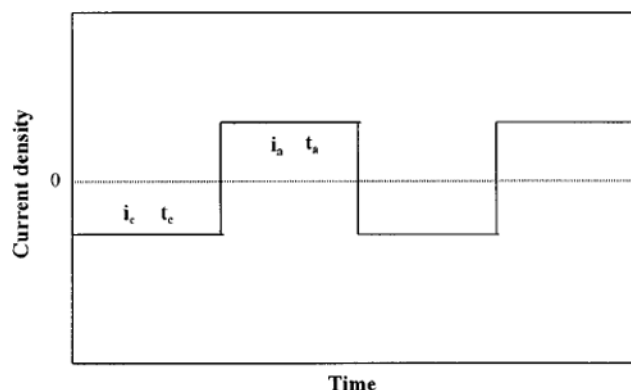
Fig. 5. Applied current pulse waveform (Variables: i_c, i_a, t_a, and t_c).

plied in 0.5 M Ba(OH)₂ solution for 60 s, and exhibits only Ti metal peaks. Fig. 4(b), which is the SEM picture of the corresponding film, indicates that the grain boundaries of Ti became smoother than as-deposited RF sputtered Ti films of Fig. 4(a). This may result from the formation of amorphous titanium oxides. However, when the pulse current waveform of Fig. 5 (total anodic time=60 s) was applied, sphere-like $BaTiO_3$ structure of Fig. 4(c) was synthesized and its crystallinity was verified by XRD [Fig. 3(b)]. Compared to the previous result [Bendale et al., 1996] that $BaTiO_3$ was formed with electrolysis time of longer than 300 s, the results mentioned above strongly support that cathodic pulses have the effect of increasing the rate of $BaTiO_3$ formation. Since hydroxide ions were generated from the reduction of water during cathodic pulses [Bard and Faulkner, 1980],
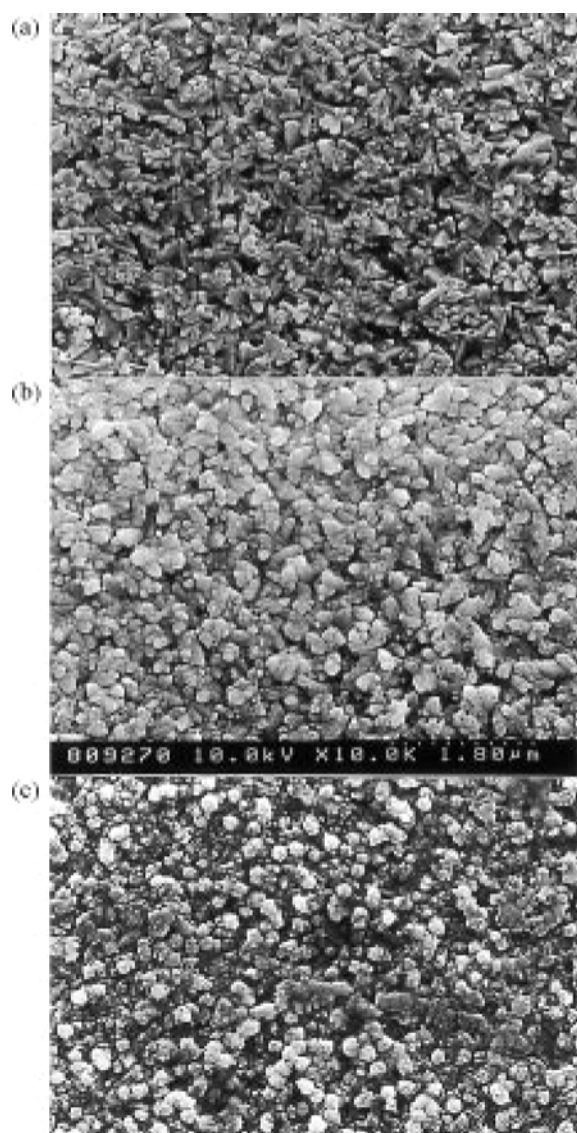

Fig. 4. Surface morphology changes of Ti electrode with different current waveforms.
(a) as-deposited Ti films by RF sputtering, (b) anodic current only (25 mA/cm² for 60 s), (c) current pulse waveform (i_c=−25 mA/cm², t_c=2 s; i_a=25 mA/cm², t_a=4 s for 90 s)
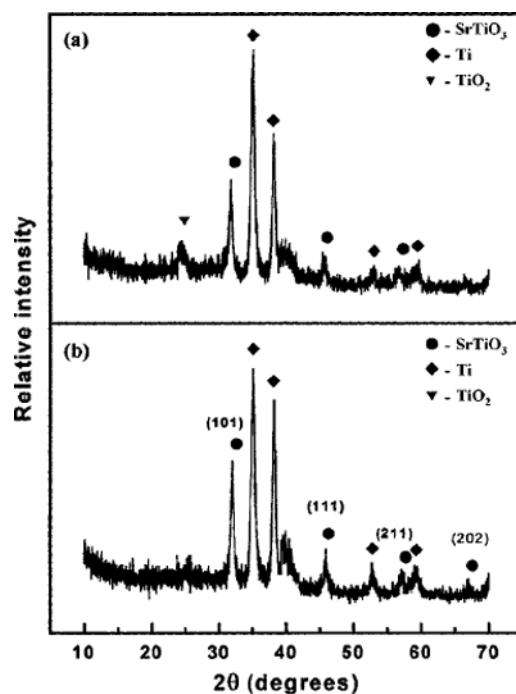

Fig. 6. X-ray diffraction patterns when different current waveforms were applied to form SrTiO₃.
(a) constant current density (i_a=25 mA/cm² for 60 s), (b) current pulse waveform (i_c=−25 mA/cm², t_c=2 s; i_a=25 mA/cm², t_a=4 s for 90 s)
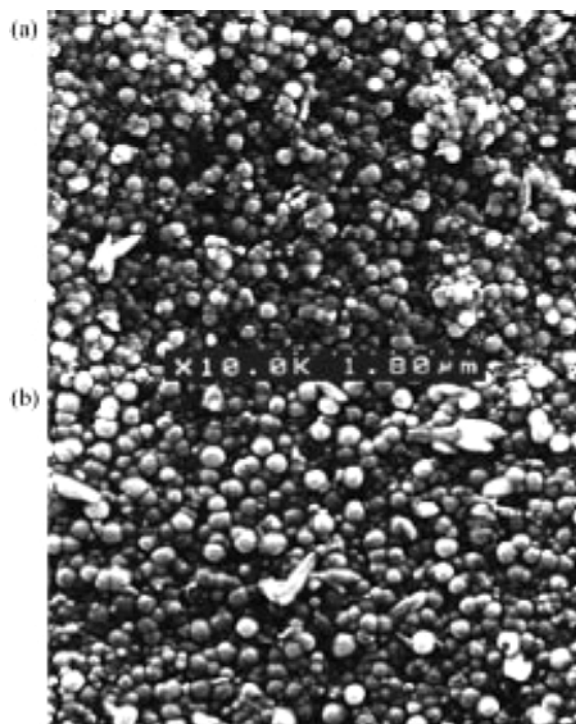
Fig. 7. Morphologies of electrodeposited SrTiO₃ films with different current waveforms.
(a) anodic current only (25 mA/cm² for 60 s), (b) current pulse waveform (i_c=−25 mA/cm², t_c=2 s; i_a=25 mA/cm², t_a=4 s for 90 s)

$$2H_2O+4e^- \rightarrow H_2+2OH^- \qquad (3)$$

a cathodic pulse increases the pH of Ti electrode surface and it functions favorably to transform TiO_2 formed during anodic pulses into $BaTiO_3$. That is, surface pH in the vicinity of the electrode has a greater influence on the formation of $BaTiO_3$ than bulk solution pH. However, both constant and pulse current waveforms result in the formation of $SrTiO_3$ for 60 s of total anodic time. Figs. 6 and 7 indicate that the crystallinity and average grain size of $SrTiO_3$ increase when pulse waveform is used.

Both $BaTiO_3$ and $SrTiO_3$ could be readily prepared by using cathodic pulses without adding a pH enhancer, such as NaOH, but the effect of cathodic pulses was significant in $BaTiO_3$ film formation.

Since pH of 0.5 M $Sr(OH)_2$ and 0.5 M $Ba(OH)_2$ is 11.2 and 13.1, respectively, at 85 °C, the concentrations of OH^- and cation (Ba^{2+} or Sr^{2+}) are higher in $Ba(OH)_2$ than in $Sr(OH)_2$ solution. When the effect of pH is solely considered, $BaTiO_3$ is expected to be formed more readily than $SrTiO_3$ because the rate of TiO_2 phase transformation into metastable phases is accelerated with increase in pH [Bendale et al., 1996]. However, contrary to expectations, comparison of Fig. 3a and 4b shows that $BaTiO_3$ was not formed for 60 s of electrolysis. In addition to the structural change of TiO_2 with pH, mobility of Ba^{2+} and Sr^{2+} ions inside solution and synthesized titanate films can be considered as an additional factor for film formation. Since the size of Ba^{2+} (0.143 nm) is bigger than Sr^{2+} (0.127 nm) [Schaffer et al., 1995], it is expected that Ba^{2+} moves slowly in solution, and the inward diffusion of Ba^{2+} into metastable phases can proceed slowly. Although intermediate titanium oxides are assumed
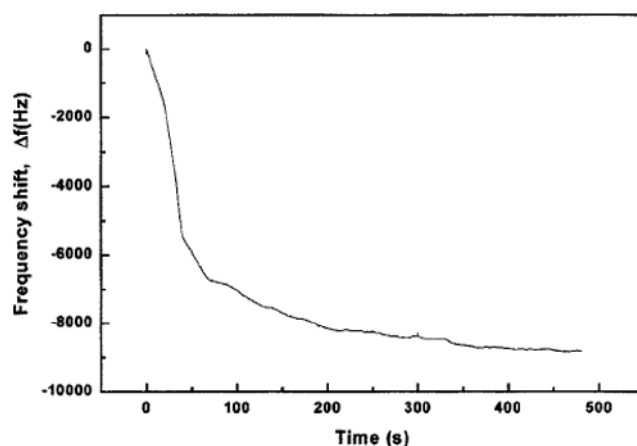
Fig. 8. Frequency (mass) change with respect to electrolysis time in the synthesis of SrTiO₃.

Table 1. Total faradaic efficiency* during different time span of electrolysis

Electrolysis time	Total faradaic efficiency
0-40 s	1.12%
40-180 s	0.32%
180-480 s	0.024%

*Assumption: Ti thin film was converted into $SrTiO_3$ only.

to be less stable in a high pH solution, low mobility of Ba^{2+} retards the rate of $BaTiO_3$ formation, while Sr^{2+} can be easily incorporated into metastable intermediate phases at relatively low pH.

Fig. 8 shows an *in-situ* mass change of Ti thin film electrode when constant current density of 25 mA/cm² is applied in 0.5 M $Sr(OH)_2$. Faradaic efficiencies obtained from the mass changes of Ti electrode are shown in Table 1. Faradaic efficiencies are defined as the mass of deposited materials during electrolysis divided by the theoretically deposited mass of materials. The mass of Ti film electrode has rapidly increased in the early stage, slowly increased after about 40 s, and remained constant after 400 s. Fig. 9 shows the mass and potential variations during initial 40 s of electrolysis. Rapid potential increase is due to the insulating TiO_2 formation by reaction (1),
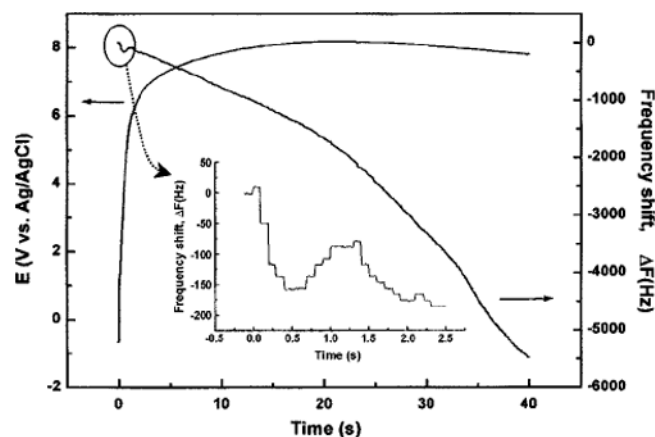

Fig. 9. Potential transient and frequency change during anodization of Ti in 0.5 M Sr(OH)₂ at 85 °C.

which leads to the increase of electrode mass (i. e., decrease of frequency). After 0.5 s of electrolysis, potential increases slowly, but the electrode mass decreases, as indicated in Fig. 9. Such a mass variation supports that TiO_2 formed in the incipient stage was partially dissolved as it transformed into the metastable phase in highly alkaline solution. This is in accordance with the observation shown in Fig. 1. In the domain of showing the nucleation and growth of $SrTiO_3$ (0-40 s), its faradaic efficiency reaches 1.12%. However, after the film has been formed, the increase in electrode mass decreases rapidly, and most of the applied current is consumed by reaction (2), not contributing to the growth of $SrTiO_3$ film. As the result, the faradaic efficiency at 180 s is about 0.32% with increasing the film thickness, and the faradaic efficiency drops finally to 0.024%. The reason for a rapid decrease in faradaic efficiency is assumed to be that the access of H_2O and OH^- required for film growth at $TiO_2/SrTiO_3$ interface is significantly suppressed by initially formed films, and thus film stops growing [Kajiyoshi et al., 1995].

2. $Ba_xSr_{(1-x)}TiO_3$ Formation

$Ba_xSr_{(1-x)}TiO_3$ thin films were synthesized by using a constant

anodic current under various mole ratios of $Ba(OH)_2$ to $Sr(OH)_2$. Although the concentration of Ba^{2+} is higher than that of Sr^{2+} because of the higher solubility of $Ba(OH)_2$, Ba/Sr ratio in the film formed on Ti is always lower than that in solution [Kajiyoshi et al., 1996]. Fig. 10 shows the 2θ changes of $Ba_xSr_{(1-x)}TiO_3$ (101) plane according to the making-up changes of solution. It reveals that the pulse waveform has no great effect on the crystallinity. In a mixed solution of $Ba(OH)_2$ and $Sr(OH)_2$, the solution pH is lower than a single $Ba(OH)_2$ solution but higher than a single $Sr(OH)_2$ solution. Since the rate of Sr^{2+} inclusion is faster as described earlier, it is supposed that the observed behavior is quite dependent on Sr^{2+}, but independent of Ba^{2+}. The effect of cathodic pulses was minimized for the same reason.

Deposited film thickness is measured by partially removing $Ba_xSr_{(1-x)}TiO_3$ film, and Fig. 11 shows the boundaries between the substrate and deposited film. Fig. 12 is a capacitance-frequency curve, showing that the capacitance of the $Ba_xSr_{(1-x)}TiO_3$ film decreases rapidly with frequency. Dielectric constant of film is estimated to be 150 when the film thickness is 700 nm and electrode area is 0.1 cm^2. Its dielectric property is similar to the previous results obtained by electrochemical hydrothermal method [Bacsa et al., 1996].
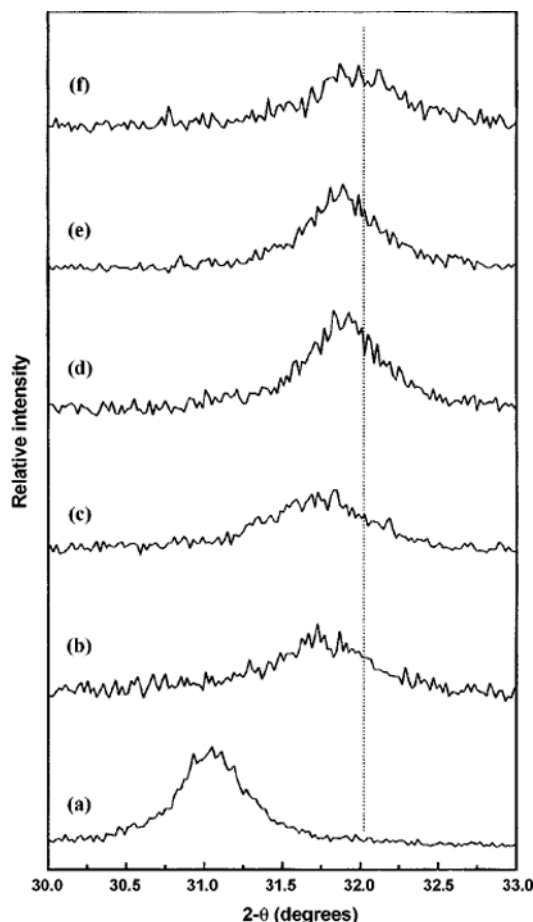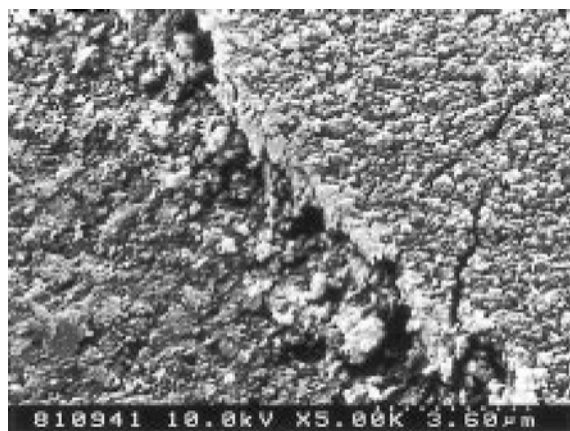

Fig. 11. $Ba_xSr_{1-x}TiO_3$ films prepared with 1 : 3 ratio of $Ba(OH)_2$ to $Sr(OH)_2$ (Electrolysis time=600 s). Films were partially removed.

Fig. 10. X-ray diffractograms of $Ba_xSr_{(1-x)}TiO_3$ (101) with different solution compositions and current waveforms (Ba : Sr means the ratio of $Ba(OH)_2$ to $Sr(OH)_2$ in electrolyte. Electrolysis time=300 s).
(a) $BaTiO_3$, (b) $Ba_xSr_{(1-x)}TiO_3$ (Ba : Sr=1 : 1, pulse waveform), (c) $Ba_xSr_{(1-x)}TiO_3$ (Ba : Sr=1 : 1, anodic only), (d) $Ba_xSr_{(1-x)}TiO_3$ (Ba : Sr=1 : 3, pulse waveform), (e) $Ba_xSr_{(1-x)}TiO_3$ (Ba : Sr= 1 : 3, anodic only), (f) $SrTiO_3$
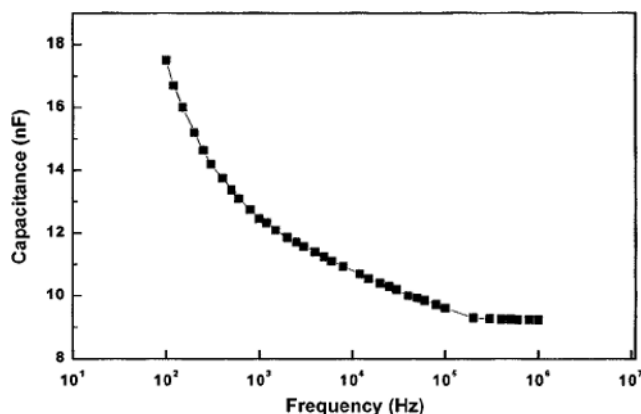

Fig. 12. Capacitance of $Ba_xSr_{(1-x)}TiO_3$ films prepared with 1 : 3 ratio of $Ba(OH)_2$ to $Sr(OH)_2$ vs. frequency (Electrolysis time=600 s).

CONCLUSIONS

In this work, Ba- and Sr-based titanate thin films were electrochemically synthesized and the film growth mechanism was investigated. Substrate Ti electrode was prepared by RF magnetron sputtering. Mass change during the titanate film growth suggested a two-step reaction mechanism: the formation of TiO_2 and the following insertion of Ba^{2+}, Sr^{2+} into metastable Ti oxides or Ti hydroxide phases. Superimposed cathodic pulses accelerated the formation of titanate films by increasing the surface pH of Ti electrode. Mobility of Ba^{2+} and Sr^{2+} ions inside both solution and synthesized titanate films has a significant effect on film growth. As the thickness of titanate film increases, OH^- and Ba^{2+} diffusion is severely blocked to the Ti/(Ba, Sr)TiO_3 film interface and the growth of film is finally stopped. Its dielectric property is commensurate with the film property prepared by other low temperature solution methods. (Ba, Sr)TiO_3 thin compact films were successfully prepared onto the Ti thin film prepared by RF magnetron sputtering, and these results provide another route to the manufacturing of thin film dielectric materials for capacitors.

ACKNOWLEDGEMENT

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