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Preparation and Properties of $(Ba_{0.7}Sr_{0.3})TiO_3$ Powders and Thin Films Using Precursor Solutions Formed from Alkoxide-hydroxide

Takashi Hayashi,[a]* Hiroshi Shinozaki[a] and Kyoichi Sasaki[b]

[a]Department of Materials Science and Ceramic Technology, Shonan Institute of Technology, 1-1-25 Tsujido-Nishikaigan, Fujisawa, Kanagawa 251-8511, Japan
[b]Electronics Department, Materials Division, Experimental Station, Former Research Associate at DuPont, Wilmington, DE 19898, USA

Abstract

$(Ba_{0.7}Sr_{0.3})TiO_3$ powders and thin films were prepared using alkoxide-hydroxide route. Solutions of Ba and Sr hydroxides dissolved in methanol were reacted with Ti-isopropoxide under conditions of stirring at room temperature for 15 h, and then dried under reduced pressure at ≦40°C to prepare precursors of $(Ba_{0.7}Sr_{0.3})TiO_3$ powder. The amorphous precursors were hydrolyzed at 100°C by introducing nitrogen gas containing water vapor. The hydrolyzed products were crystalline nanosize powders of $(Ba_{0.7}Sr_{0.3})TiO_3$. As-hydrolyzed $(Ba_{0.7}Sr_{0.3})TiO_3$ powders showed a good crystallinity with cubic phase. $(Ba_{0.7}Sr_{0.3})TiO_3$ thin films were also successfully prepared at 650°C on $Pt/Ti/SiO_2/Si$ substrates from precursor solutions obtained by the reaction of alkoxide with hydroxides. The $(Ba_{0.7}Sr_{0.3})TiO_3$ thin films exhibited the microstructure with fine grains as small as 20–60 nm. The dielectric constants of the thin films ranged from 600 to 800 at room temperature. © 1999 Elsevier Science Limited. All rights reserved

Keywords: films, powders: chemical preparation, sol-gel processes, dielectric properties, $(Ba_{0.7}Sr_{0.3})TiO_3$.

1 Introduction

$BaTiO_3$ and its related compounds have been extensively used in the preparation of high-permittivity capacitors, PTC resistors, transducers and ferroelectric memories. $BaTiO_3$ powders have been prepared by various methods such as coprecipitation,[1] oxalate,[2] sol-gel[3,4] and hydrothermal synthesis.[5] Homogeneous and high-purity fine powders can be prepared by these methods.

It would be preferable to use highly pure oxides or hydroxides[6] of Ba and Sr which are soluble in methanol, as Ba and Sr sources instead of the expensive and unstable Ba or Sr alkoxides. We previously reported[7,8] the preparation of $BaTiO_3$ powders by the hydrolysis of Ba–Ti solutions obtained by mixing titanium isopropoxide and a suspension or solution of barium hydroxide in methanol.

In this work, our objective is to develop a simple and economical low-temperature preparation process for $(Ba_{0.7}Sr_{0.3})TiO_3$ powders and thin films based on the reaction between methanol solutions of Ba and Sr hydroxides and Ti-alkoxide.

2 Experimental

$Ba(OH)_2.nH_2O$ (n61) and $Sr(OH)_2$ were dissolved in methanol. The concentrations of Ba and Sr hydroxides in methanol were determined using the titration technique and were adjusted to 0·5 and 0·25 mol l^{-1}, respectively. Figure 1 shows the flow chart for preparation of $(Ba_{0.7}Sr_{0.3})TiO_3$ powders and thin films using precursor solutions formed from alkoxide-hydroxides.

Solutions of barium and strontium hydroxides dissolved in methanol were mixed at a desired composition ratio, and then mixed with a stoichiometric amount of Ti-isopropoxide. The mixture solution was reacted under conditions of stirring at room temperature for 15 h.

After the reaction, in case of preparation of $(Ba_{0.7}Sr_{0.3})TiO_3$ powders, methanol was evaporated under reduced pressure at ≦40°C, whereupon the precursors were obtained as free-flowing white powders. The resulting amorphous precursors were

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*To whom correspondence should be addressed. Fax: + 81-446-36-1594; e-mail: hayashi@mate.shonan-it.ac.jp

slowly hydrolyzed and crystallized at about 100°C by introducing N_2 gas containing water vapor into the rotary evaporator rotating at 60 rpm. Some of the hydrolyzed powders were calcined at 900°C for 2 h, and were sintered at 1250, 1275 and 1300°C for 2 h.

On the other hand, in case of preparation of $(Ba_{0\cdot7}Sr_{0\cdot3})TiO_3$ thin films, the thin films were prepared using precursor solutions obtained by the reaction of alkoxides with hydroxides. The concentrations of $Ba(OH)_2$ and $Sr(OH)_2$ were adjusted to 0·13 mol l^{-1}, respectively. The thin films were prepared on $Pt(200\,nm)/Ti(50\,nm)/SiO_2/Si$ substrates by heating at 650°C for 4 h in oxygen, after heating at 150°C for 1·5 h in a flow of oxygen/water vapor mixed gas. Film thickness was controlled by repeating the cycle of spin coating and heating process. Gold electrodes of $3{\cdot}14 \times 10^{-4}$ cm^2 areas were sputter-deposited through a mask onto the surface of the thin films.

The precursors and the hydrolyzed products were characterized by thermogravimetric analysis (TGA)/differential thermal analysis (DTA), specific surface area (SSA), scanning electron microscope (SEM), infrared spectroscope (IR) and X-ray diffraction (XRD). The crystalline phase and the microstructure of thin films were examined by XRD and SEM, respectively.

The dielectric properties of $(Ba_{0\cdot7}Sr_{0\cdot3})TiO_3$ sintered bodies and thin films were measured at 1 kHz using an impedance analyzer.

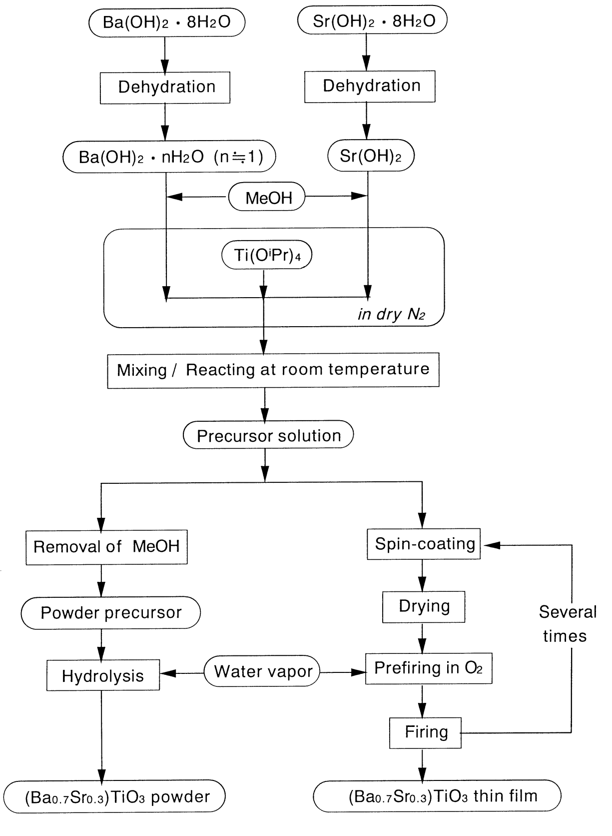

Fig. 1. Flow chart for preparation of $(Ba_{0\cdot7}Sr_{0\cdot3})TiO_3$ powders and thin films by spin-coating.

3 Results and Discussion

3.1 $(Ba_{0\cdot7}Sr_{0\cdot3})TiO_3$ powders

Figure 2 shows TG and DTA curves of powder precursors and hydrolyzed products. The powder precursors were amorphous and showed weight loss of about 29% at ~1000°C by the TG curve, while in the hydrolyzed products, the weight loss at 1000°C was about 4% as determined by the TG curve. From IR spectra of the precursors, the presence of organic residues was confirmed. The hydrolysis of amorphous precursors of $(Ba_{0\cdot7}Sr_{0\cdot3})$ TiO_3 by introducing water vapor afforded a single phase crystalline $(Ba_{0\cdot7}Sr_{0\cdot3})TiO_3$ powders, as shown in Fig. 3. They had nearly the same compositions as those of the starting reactant solutions. Calcination at 900°C increased the crystallinity of the powders due to the development of grain growth.

SEM micrographs of as-hydrolyzed and calcined $(Ba_{0\cdot7}Sr_{0\cdot3})TiO_3$ powders are shown in Fig. 4. The as-hydrolyzed powders were weakly agglomerated and consisted of fine particles of 30–40 mn. On the other hand, the calcined powders were hard agglomerates that could not be broken up by ultrasonication.

Figure 5 shows XRD patterns of $(Ba_xSr_{1-x})TiO_3$ with various compositions. The XRD patterns of $(Ba_xSr_{1-x})TiO_3$ shifted to higher angles with increasing Sr content in $(Ba_xSr_{1-x})TiO_3$.

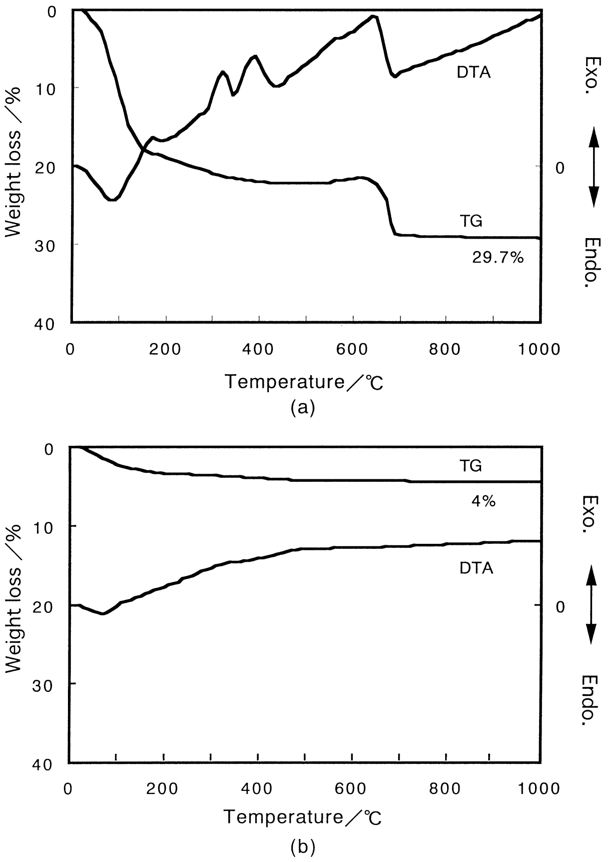

Fig. 2. TG/DTA curves of $(Ba_{0\cdot7}Sr_{0\cdot3})TiO_3$ powders. (a) precursor; (b) hydrolyzed product.

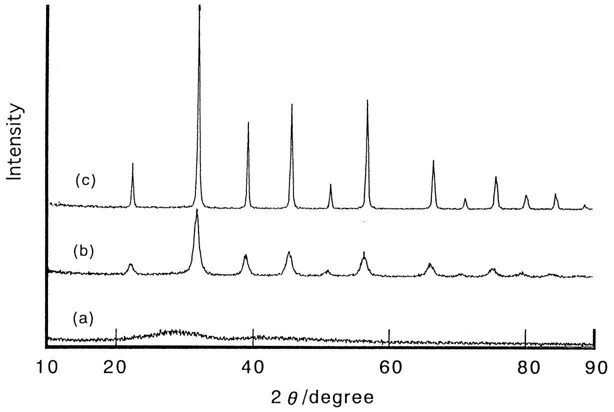

Fig. 3. XRD patterns of $(Ba_{0.7}Sr_{0.3})TiO_3$ powders. (a) Precursor; (b) as-hydrolyzed; (c) calcined at 900°C.

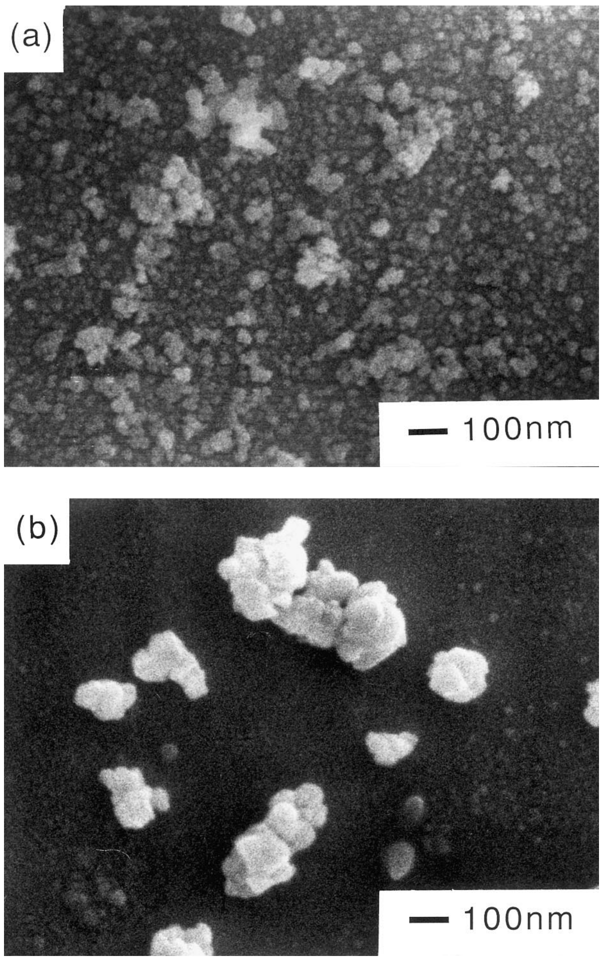

Fig. 4. SEM micrographs of $(Ba_{0.7}Sr_{0.3})TiO_3$ powders. (a) As-hydrolyzed; (b) calcined at 900°C.

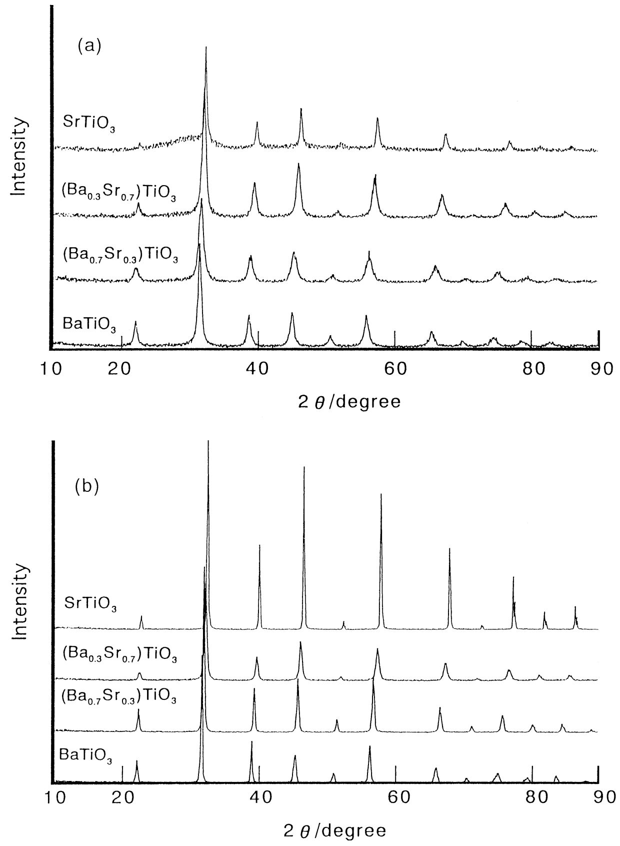

Fig. 5. XRD patterns of $(Ba_xSr_{1-x})TiO_3$ powders. (a) As-hydrolyzed; (b) calcined at 900°C.

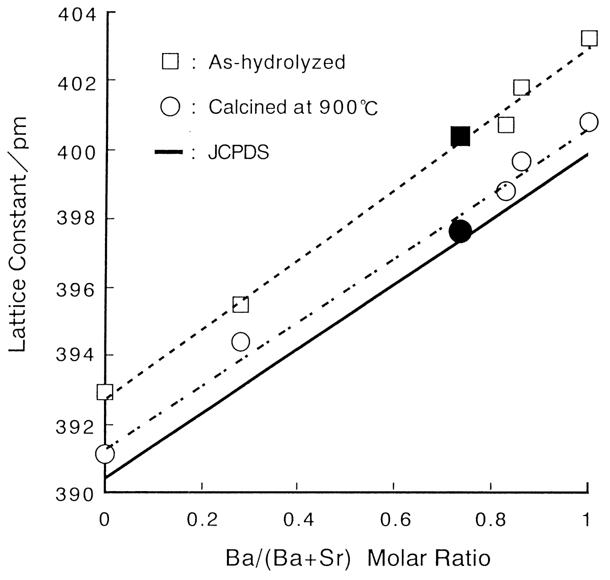

Fig. 6. Lattice constant versus molar ratio (Ba/(Ba + Sr)) of $(Ba_xSr_{1-x})TiO_3$. ■, ●: $(Ba_{0.7}Sr_{0.3})TiO_3$.

Lattice constants were calculated for as-hydrolyzed $(Ba_xSr_{1-x})TiO_3$ powders and those calcined at 900°C, and the relation between lattice constants and molar ratios of Ba/Ba + Sr is shown in Fig. 6. The lattice constants of both powders decreased with the increase in Sr content. The lattice constants of the calcined powders were in fair agreement with the JCPDS data. However, the lattice constants of the as-hydrolyzed powders were higher than those of the calcined powders, suggesting that the crystal structure in the latter may be expanded probably due to the presence of OH- groups.

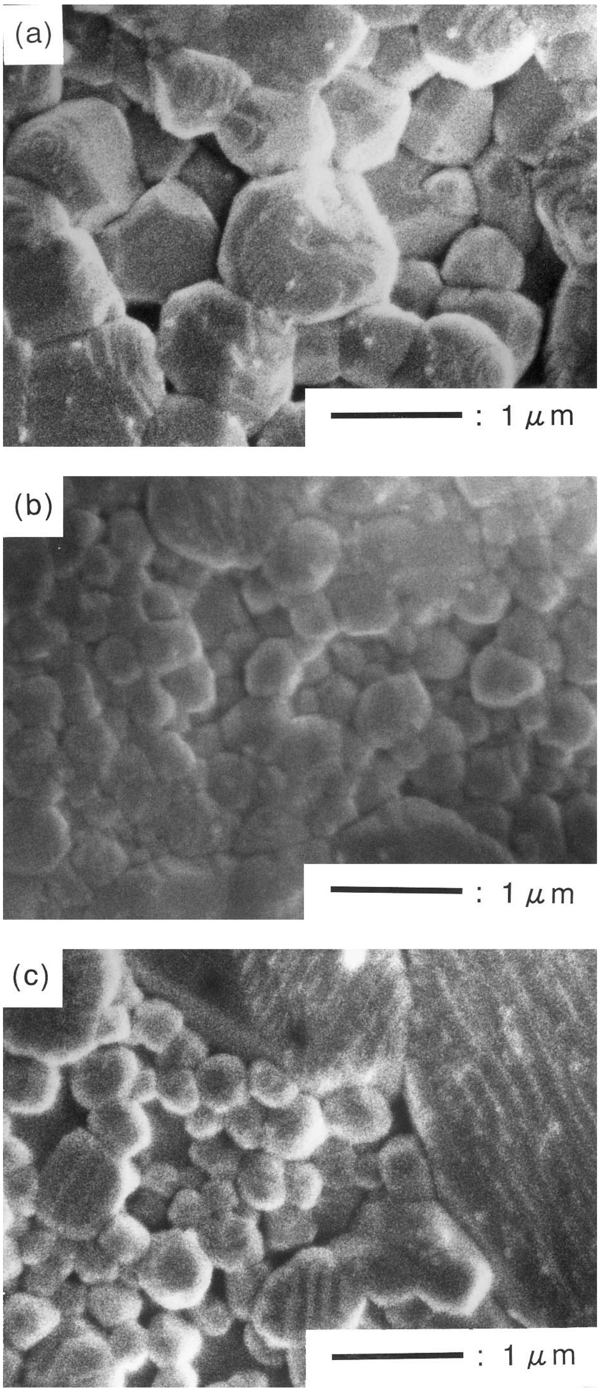

Fig. 7. SEM micrographs of sintered $(Ba_{0.7}Sr_{0.3})TiO_3$ bodies. (a) 1250°C; (b) 1275°C; (c) 1300°C.

3.2 Microstructure and dielectric properties of $(Ba_{0.7}Sr_{0.3})TiO_3$ sintered bodies

SEM micrographs of $(Ba_{0.7}Sr_{0.3})TiO_3$ bodies sintered at 1250, 1275 and 1300°C are shown in Fig. 7. Both samples sintered at 1250 and 1275°C exhibited relatively homogeneous microstructures with small grain sizes of 0·3–0·6 μm and relative density of approximately 97%. However, at the sintering temperature of 1300°C, exaggerated grain growth occurred, resulting in a nonuniform microstructure with grains as large as 10 μm. The relative density of sintered bodies increased with the increase in sintering temperatures from 1250 to 1275°C. However, at 1300°C, the relative density decreased, associated with exaggerated grain growth. Figure 8 shows the temperature dependence of the dielectric constant of $(Ba_{0.7}Sr_{0.3})TiO_3$ sintered bodies. The dielectric constant at 20°C of $(Ba_{0.7}Sr_{0.3})TiO_3$

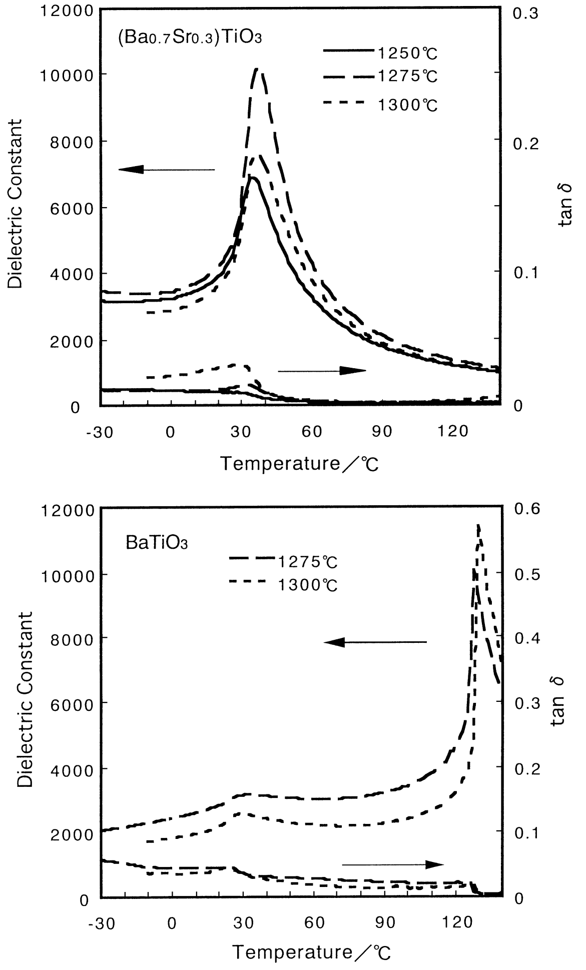

Fig. 8. Temperature dependence of dielectric constants of sintered bodies of $(Ba_{0.7}Sr_{0.3})TiO_3$ and $BaTiO_3$.

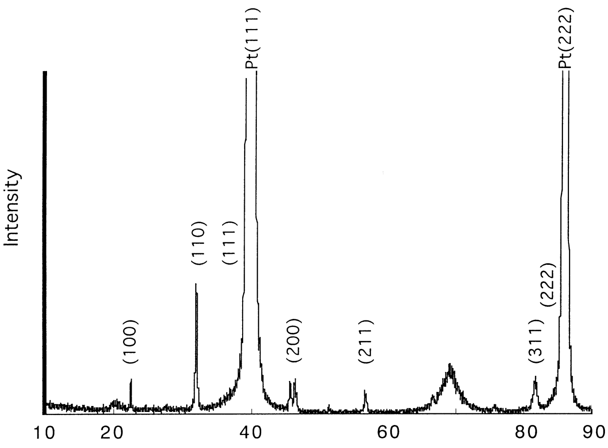

Fig. 9. XRD pattern of $(Ba_{0.7}Sr_{0.3})TiO_3$ thin film.

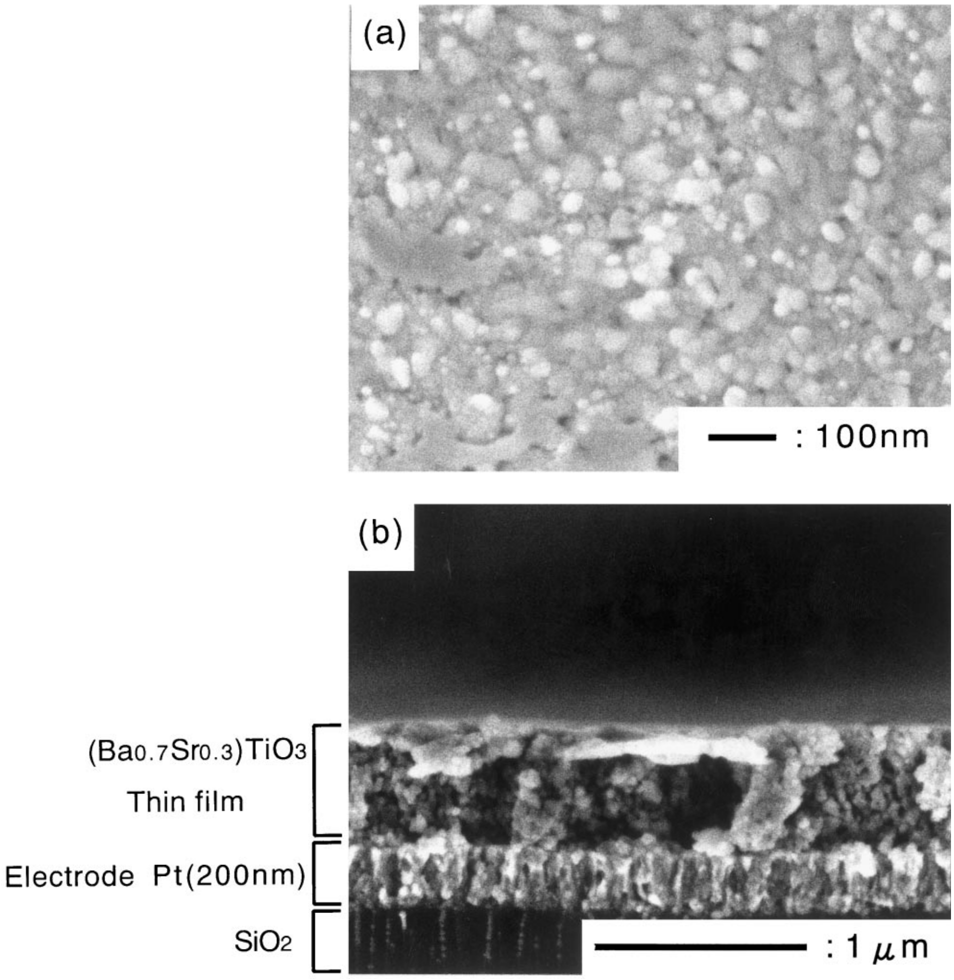

Fig. 10. SEM photographs of surface and cross-section of $(Ba_{0\cdot7}Sr_{0\cdot3})TiO_3$ thin films prepared at 650°C for 4 h on Pt(200 nm)/Ti(50 nm)/SiO_2/Si substrate. (a) Surface; (b) cross-section.

sintered bodies increased with the increase in sintering temperatures from 1250 to 1275°C. The dielectric constant and tan δ were approximately 4000 and 1%, respectively, at room temperature. But, the dielectric constant decreased at the sintering temperature of 1300°C. This result can be explained by the change in the microstructure and density of the sintered bodies. The Curie temperature of $BaTiO_3$ was shifted by Sr doping, as reported by Smolenskii *et al.*[9]

3.3 $(Ba_{0\cdot7}Sr_{0\cdot3})TiO_3$ thin films

Figure 9 shows XRD pattern of $(Ba_{0\cdot7}Sr_{0\cdot3})TiO_3$ thin film prepared at 650°C for 4 h on Pt(200 nm)/Ti(50 nm)/SiO_2/Si substrates. It was confirmed from XRD result that crystalline $(Ba_{0\cdot7}Sr_{0\cdot3})TiO_3$ thin films could be prepared at 650°C. Figure 10 shows SEM micrographs of the surface of $(Ba_{0\cdot7}Sr_{0\cdot3})$ TiO_3 thin film and a typical cross section. The thin films showed grain microstructure with fine grains as small as 20 to 60 nm.

The dielectric constant and tan δ of the thin films ranged from 600 to 800 and from 4 to 7%, respectively, at room temperature. These values are within those reported by several investigator.[10–12] However, the dielectric constants of the thin films are lower than those of sintered ceramics. This may be attributable to microstructural heterogeneties, variations in crystalline quality, mechanical stress, space charge effects and intrinsic size effects.

4 Conclusions

Precursors of $(Ba_{0\cdot7}Sr_{0\cdot3})TiO_3$ powders have been prepared using the reaction between methanol solutions of Ba and Sr hydroxides and Ti-isopropoxide. By vapor-phase hydrolysis of the precursors, crystalline nanosize $(Ba_{0\cdot7}Sr_{0\cdot3})TiO_3$ powders with homogeneous composition have been successfully prepared at 100°C. $(Ba_{0\cdot7}Sr_{0\cdot3})TiO_3$ thin films could be also prepared by spin-coating using the precursor solutions of alkoxide and hydroxides. The lattice constants of the calcined powders were in fair agreement with JCPDS data. However, the lattice constants of the as-hydrolyzed powders were higher than those of the calcined powders. $(Ba_{0\cdot7}Sr_{0\cdot3})TiO_3$ bodies sintered at 1275°C showed a relatively homogeneous microstructure with grain sizes of 0·3–0·6 μm and a relative density of approximately 97%. They exhibited a dielectric constant of approximately 4000 and a tan δ of 1% at room temperature. On the other hand, the dielectric constant and tan δ of $(Ba_{0\cdot7}Sr_{0\cdot3})TiO_3$ thin films, which exhibited grain microstructure with fine grains of 20–60 nn, ranged from 600 to 800 and from 4 to 7%, respectively.

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