Hydrothermal Formation and Growth of Single- and Double-Layer $BaTiO_3$ and $SrTiO_3$ Films on the Flexible Polymer Film Substrates from Sol−Gel Amorphous Titanium Oxide Films

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Polycrystalline single- and double-layer $BaTiO_3$ (BT) and $SrTiO_3$ (ST) films on flexible polymer films were synthesized by hydrothermal treatments of sol−gel amorphous titanium oxide films with $M(OH)_2$ (M = Ba, Sr) aqueous solutions from 60 to 150 °C. The amorphous titanium oxide films were prepared by a dip-coating method from a sol−gel precursor. The structure of the films formed under a variety of conditions characterized by X-ray diffraction (XRD) revealed that the polycrystalline cubic $MTiO_3$ (M = Ba, Sr) films were formed. The surface morphology of the films observed by scanning electron microscopy (SEM) indicated that the films were uniform. A model for the formation and growth of $MTiO_3$ films from amorphous titanium oxide films under hydrothermal conditions was proposed.

Introduction

Barium titanate ($BaTiO_3$) and strontium titanate ($SrTiO_3$) thin films have gained much attention in the electronics industry due to their application as capacitors.[1−5] A number of techniques such as sputtering[6−8] and vacuum evaporation[5,9] have been reported to prepare $BaTiO_3$ and $SrTiO_3$ films. However, most of these methods need high temperature to form ferroelectric films. Previous investigations have shown that $MTiO_3$ (M = Ba, Sr) films can be synthesized on titanium substrates in $M(OH)_2$ (M = Ba, Sr) aqueous solutions at temperatures less than 200 °C by hydrothermal and hydrothermal−electrochemical methods.[10−16] In contrast to the conventional solid state route, the hydrothermal and hydrothermal−electrochemical methods offer an inexpensive and environmentally friendly route to synthesize thin (or thick), shaped, sized, and oriented ceramic films and coatings in aqueous solutions in one step for a variety of applications.[10−14] It is generally accepted that a layer of titanium oxide formed on Ti substrate under the hydrothermal or hydrothermal−electrochemical condition acts as a precursor for the formation of $MTiO_3$. The hydrothermal−electrochemical method benefits from the electrochemical anodic oxidization of the metal substrate (e.g., Ti substrate) to form metal oxide film. The hydrothermal−electrochemical technique, therefore, provides the merits of enhanced purity, lower reaction temperature, and higher film growth rate.

Several groups have investigated the hydrothermal and hydrothermal-electrochemical synthesis of barium (strontium) titanate thin films on various substrates.[17−21] The hydrothermal synthesis of barium titanate thin films on Ti sputter-coated Si substrates at low temperatures has been reported.[17−19] Our group was the first to hydrothermally fabricate polycrystalline thin $BaTiO_3$ and $SrTiO_3$ films on Ti-deposited flexible polyphenylen sulfide (PPS) polymer films in $Ba(OH)_2$ and $Sr(OH)_2$ aqueous solutions, respectively.[20] Aksay and co-workers described an approach of fabrication crystalline $BaTiO_3$

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films by hydrothermal treatments of organometallic films prepared by titanium diisopropoxide bis(ethylacetoacetate) (TIBE) on polystyrene substrates in $Ba(OH)_2$ aqueous solutions at low temperatures.[21] Upon exposure to aqueous $Ba(OH)_2$ solutions, the hydrolysis of TIBE results in the formation of a network of titanium hydroxides or oxohydroxides, causing the nucleation and growth of $BaTiO_3$.

The sol−gel method has been used to fabricate various thin films. The synthesis of $BaTiO_3$ and $SrTiO_3$ films by sol−gel process has also been reported.[22−24] The sol−gel processing involves the formation of a metal-oxo-polymer network from molecular precursors such as alkoxides. Thin films can be formed from sol−gel-derived precursor by dip-coating or spin-coating methods with good chemical homogeneity. Since they are amorphous, a high-temperature treatment is needed to induce crystallization. However, the post-calcination process frequently gives rise to the degraded films due to the inhomogeneous crystallization, selective evaporation or deposition, and undesired chemical reactions. Hydrothermal treatment of sol−gel-derived titanium oxo-polymer films in $M(OH)_2$ (M = Ba, Sr) solutions to induce the formation of crystalline $MTiO_3$ (M = Ba, Sr) films could combine with the advantages both of hydrothermal and sol−gel process. Recently, Ying et al. reported the synthesis of nanocrystalline anatase TiO_2 particles via sol−gel precipitation of alkoxide, followed by hydrothermal treatment.[25]

In this paper, we demonstrated the feasibility of the preparation of crystalline $BaTiO_3$ and $SrTiO_3$ films on the flexible PPS polymer films through the hydrothermal treatment of sol−gel amorphous titanium oxide films.

Experimental Section

The Formation of Amorphous Titanium Oxide Films by Sol−Gel Method. Polyphenylen sulfide (PPS) sheet film with a thickness of 0.125 mm (Torelina 300, Toray Industries, Inc.) was cut into the size of 15 mm × 50 mm and used as a substrate. The substrate was chemically etched for 15 min by a mixed solution of chromic acid and sulfuric acid at 70 °C. Washed with water, the PPS sheet was ultrasonicated for 5 min each in acetone and water solutions. The sol−gel precursor used to produce the titanium oxide film was similar to that used by Selvaraj et al.[26] Titanium isopropoxide (0.2 mol, Aldrich Chemical Co.) was dissolved in 1 mol of anhydrous 2-propanol (Aldrich), to which 0.2 mol of di-2-propanolamine (Aldrich) and 0.4 mol of a water and 2-propanol solution (water/2-propanol = 1:2, v/v) were added. After being stirred at room temperature for 2 h, a transparent solution was obtained. The precursor solution was kept in a sealed container as a stock solution, which could be stable for several months. The sol−gel films on PPS substrates were prepared by a dip-coating method at the rate of 1 mm/s with diluted stock solution by 2-propanol (stock solution/2-propanol = 1:3 to 1:5, v/v). After being dried in air for at least 3 days to evaporate the organic solvent, the amorphous titanium oxide films on PPS substrates were formed.[27] Adjusting the dilution ratio of stock solution with 2-propanol could control the thickness of sol−gel-derived amorphous titanium oxide films. Typically, the thickness of amorphous titanium oxide film was about 1 μm for a dilution ratio of 1:4.

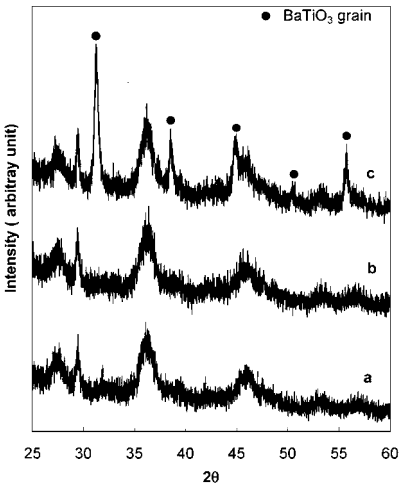

Figure 1. X-ray diffraction patterns of (a) a PPS substrate and a titanium oxide film on PPS substrate (b) before and (c) after hydrothermal treatment in 1.0 M $Ba(OH)_2$ aqueous solution 2 h at 150 °C.

Hydrothermal Treatment. For the hydrothermal experiments, a Teflon beaker containing the 200 mL the $Ba(OH)_2$ or $Sr(OH)_2$ electrolyte was placed in an autoclave cell. The $Ba(OH)_2$ and $Sr(OH)_2$ solutions were freshly prepared using $Ba(OH)_2 \cdot 8H_2O$ and $Sr(OH)_2 \cdot 8H_2O$ (guaranteed reagent) and distilled water. To remove the dissolved CO_2, the distilled water was boiled for about 5 min before being used. The titanium oxide film on the PPS substrate was fixed on a steel wire by a Teflon clamp and vertically hung in the electrolyte solution. The autoclave was sealed and heated to a specified temperature at a heating rate of 100 °C/h under the saturated vapor pressure, where the system was maintained for 2 h. After the hydrothermal treatment, samples were taken when the temperature of the autoclave cooled to the room temperature. The obtained barium titanate or strontium titanate films on the PPS substrates were immersed in pH 9, CO_2-free water adjusted with $NH_3 \cdot H_2O$ for 10 min under N_2 atmosphere for 10 min in order to remove the possible contamination of $BaCO_3$, then washed thoroughly with CO_2-free water, rinsed in ethanol, and dried under an N_2 atmosphere prior to characterization.

Characterization. The resultant structures were characterized by X-ray powder diffractometry (model MXP^{3VA}, MAC Science Co., Ltd., Tokyo, Japan) with Cu Kα radiation at 40 KV and 40 mA. Data were collected from 25 to 60° 2θ at a scan rate of 1°/min. The surface morphology of the grown films was investigated by scanning electron microscopy (SEM) (SEM, model S-4000, Hitachi, Tokyo, Japan).

Results and Discussion

Structural Characterization. Figure 1 shows the X-ray diffraction patterns of a $BaTiO_3$ film formed on a PPS substrate after the hydrothermal treatment of a sol−gel titanium oxide film on a PPS substrate in 1.0 M $Ba(OH)_2$ at 150 °C for 2 h, where the peaks of the BT crystallites are indexed (Figure 1C). All diffraction lines are well-defined without preferred orientations and show a single phase of cubic $BaTiO_3$ compared with JCPDS card no. 31-174. The formation of the cubic $BaTiO_3$ phase, observed in this work, is quite common in the hydrothermal treatment of titanium-loaded precursors in $Ba(OH)_2$ solution.[10−22] Figure 1a shows an XRD pattern of a PPS film, and Figure 1b shows the

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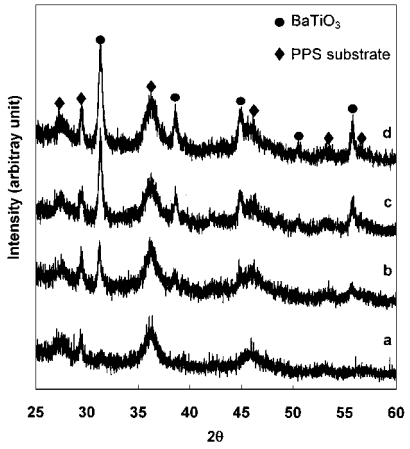

Figure 2. X-ray diffraction patterns of $BaTiO_3$ film samples prepared by hydrothermal treatment of titanium oxide films on PPS substrates at 150 °C and 2 h in different $Ba(OH)_2$ concentrations: (a) 0.01, (b) 0.1, (c) 0.25, and (d) 1.0 M $Ba(OH)_2$.

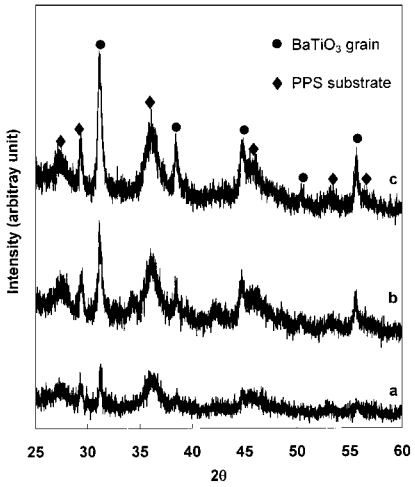

Figure 3. X-ray diffraction patterns of $BaTiO_3$ film samples prepared by hydrothermal treatment of titanium oxide films on PPS substrates in 1.0 M $Ba(OH)_2$ and 2 h at different temperatures: (a) 60, (b) 80, and (c) 150 °C.

typical XRD pattern of a titanium oxide film. It is confirmed that the sol−gel titanium oxide film is XRD-amorphous. The shape of the PPS substrate does not change after hydrothermal treatment, which indicates that the structure of PPS has no significant changes, probably because of the low reaction temperature and short reaction time. Similar results were observed on the hydrothermal fabrication of polycrystalline thin $BaTiO_3$ and $SrTiO_3$ films on the Ti-deposited PPS polymer films in $Ba(OH)_2$ and $Sr(OH)_2$ aqueous solutions.[20]

The formation of BT films on PPS substrates has been investigated at a variety of operating conditions. The possibility of the formation of BT film follows the theoretical thermodynamic predictions by Lencka and Riman,[28,29] wherein the calculated stability of $BaTiO_3$ under hydrothermal conditions increases with pH by increasing barium concentration and with temperature. As shown in Figure 2a, the film processed in 0.01 M $Ba(OH)_2$ solution for 2 h at 150 °C fails to produce

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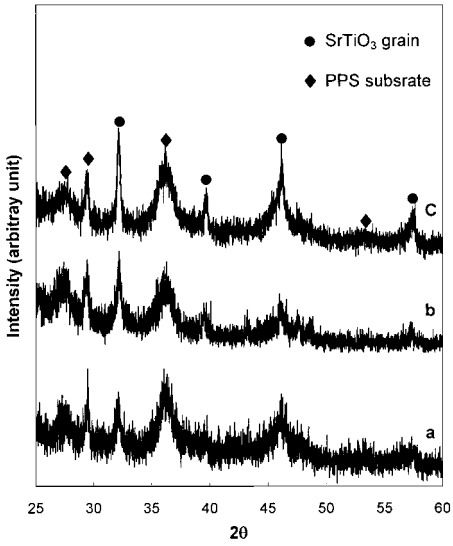

Figure 4. X-ray diffraction patterns of $SrTiO_3$ film samples prepared by hydrothermal treatment of titanium oxide films on PPS substrates in 1.0 M $Sr(OH)_2$ and 2 h at different temperatures: (a) 60, (b) 80, and (c) 150 °C.

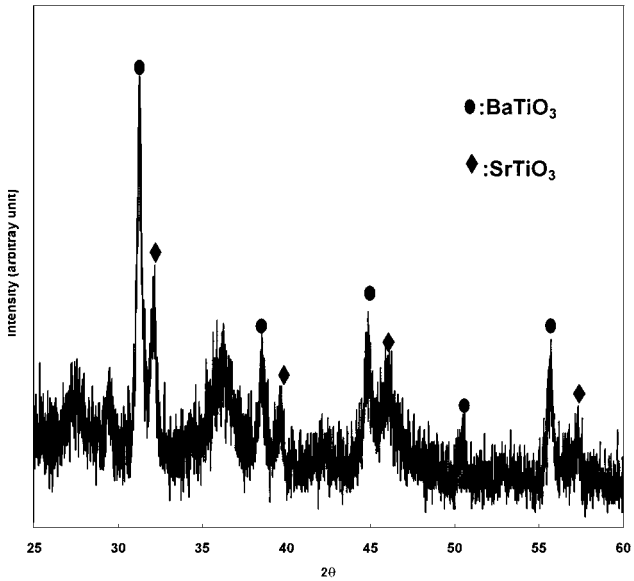

Figure 5. X-ray diffraction pattern of a double-layer ceramic film on a PPS substrate (BT/ST/PPS film). The BT and ST film were prepared by the hydrothermal treatment of the sol−gel titanium oxide films on PPS substrate and on ST film surface in 1.0 M $M(OH)_2$ (M = Ba, Sr) aqueous solution at 150 °C for 2 h, respectively.

crystalline BT film. By increasing the Ba concentration, the system moves into the thermodynamic stable region toward the formation of phase-pure $BaTiO_3$ films. Figure 2 shows that the crystalline BT patterns can be observed when the $Ba(OH)_2$ concentration is higher than 0.1 M. Hydrothermal treatment of the titanium oxide film on PPS in high $Ba(OH)_2$ concentration yields the high intensity of the XRD patterns (Figure 2d). Similar trends may be found in the literature regarding the formation of BT film by hydrothermal treatment of titanium oxide in $Ba(OH)_2$ solution. Poor BT XRD-patterns can be observed for an amorphous titanium oxide-coated PPS film hydrothermal treated at 60 °C in 1.0 M $Ba(OH)_2$ solution for 2 h (Figure 3a). The well-crystallized BT films could be formed at high temper-

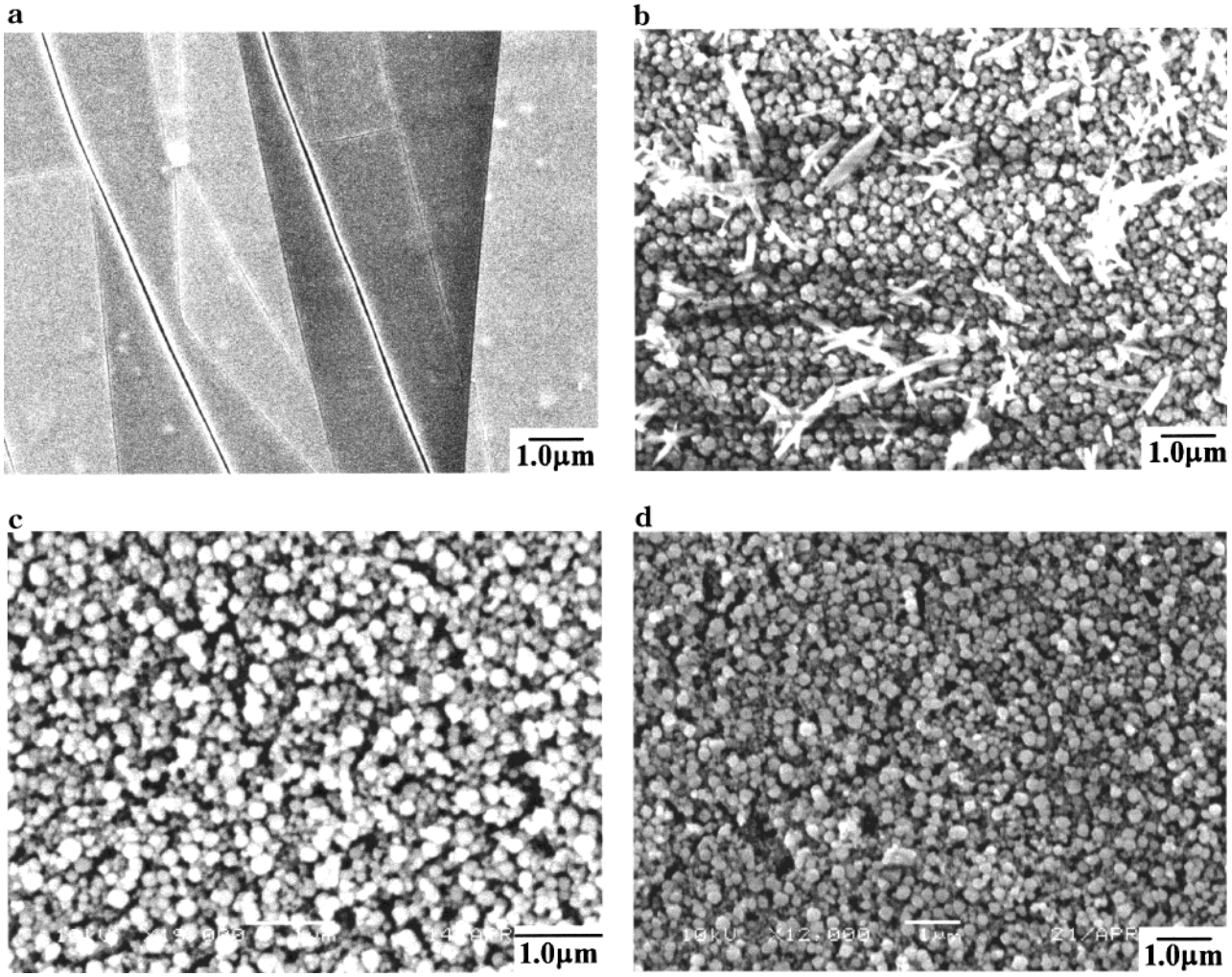

Figure 6. SEM images: (a) Typical titanium oxide film on PPS substrate before hydrothermal treatment. (b) $BaTiO_3$ film after hydrothermal treatment of a titanium oxide film on PPS substrate in 1.0 M $Ba(OH)_2$ solution 2 h at 150 °C. (c) $BaTiO_3$ film after hydrothermal treatment of a titanium oxide film on PPS substrate in 1.0 M $Ba(OH)_2$ solution 2 h at 80 °C. (d) $SrTiO_3$ films after hydrothermal treatment of a titanium oxide film on PPS substrate in 1.0 M $Sr(OH)_2$ solution 2 h at 150 °C.

atures (Figure 3a,b). Our results confirm that temperature and concentration of $Ba(OH)_2$ have a strong effect on the kinetics for the nucleation and growth of BT grain. Increasing the temperature and concentration of $Ba(OH)_2$ could enhance the mass transport of ionic species and the particle nucleation rate, thereby favoring the nucleation and growth of BT.

We also hydrothermally treated the titanium oxide-coated PPS films with $Sr(OH)_2$ solutions, employing experimental conditions similar to those used in the fabrication of $BaTiO_3$ films. Typical XRD patterns are shown in Figure 4 for the ST films fabricated by the hydrothermal treatment of titanium oxide films on PPS substrates in 1.0 M $Sr(OH)_2$ aqueous solution for 2 h at temperatures from 60 to 150 °C. It shows that the final products are associated with cubic strontium titanate (JCPDS card no. 35-0734). Because of the similarity of the chemical properties of $Sr(OH)_2$ with $Ba(OH)_2$, there is no significant difference regarding the process of the formation of ST films in comparison with the formation of BT discussed above.

After one layer of ST (or BT) film is formed, another layer of BT (or ST) film can be produced by simply dip-coating with another layer of sol−gel titanium oxide film, following a hydrothermal treatment. Figure 5 shows a typical X-ray diffraction pattern of a double-layer ceramic film on a PPS substrate (BT/ST/PPS film). A ST film was first prepared by the hydrothermal treatment of sol−gel titanium oxide films on PPS substrate in 1.0 M $Sr(OH)_2$ aqueous solution at 150 °C for 2 h, after dip-coating another layer of the sol−gel titanium oxide film on the ST film surface. The second BT layer was produced by the hydrothermal treatment of the sol−gel titanium oxide film on the ST film surface in 1.0 M $Ba(OH)_2$ aqueous solution at 150 °C for 2 h. Finally, the double-layer films with BT/ST/PPS type were fabricated. The peaks of BT and ST crystallites are indexed in Figure 5. All diffraction lines are well-defined and separated between the BT index and ST index, indicating that this is a double-layer film.

Film Morphology. Figure 6a shows the SEM image of a titanium oxide film on PPS substrate with the thickness about 1 μm prepared by sol−gel process. The surface of the film is uniform, containing the random distributed cracks. Figure 6b show a typical SEM image of BT film after hydrothermal treatment of a titanium oxide film on a PPS substrate in 1.0 M $Ba(OH)_2$ solution at 150 °C for 2 h. Crystal $BaCO_3$ can be formed on the top of $BaTiO_3$ grains. Various factors may contribute to the formation of $BaCO_3$. The CO_2 might be introduced

with starting solution, the thermal decomposition of organic components available in the sol−gel-derived film, and the PPS polymer substrate under hydrothermal conditions. It was reported that such $BaCO_3$ contamination could be avoided by washing with CO_2-free, ammoniated water at pH 9,[14−16] but we found that the kind of washing could not completely remove the $BaCO_3$ contamination on the top of the $BaTiO_3$ grains. Incubated in pH 9, CO_2-free water under N_2 atmosphere for 10 min, then washed thoroughly with CO_2-free water, rinsed in ethanol, and dried under N_2 atmosphere, the $BaCO_3$ contamination could be extensively removed. Thermodynamically, $BaTiO_3$ can be dissolved under such a condition, but the dissolution of $BaCO_3$ is expected to be much easier in a short incubation time.

Figure 6c shows the SEM image of the BT film after hydrothermal treatment of a titanium oxide film on PPS substrate in 1.0 M $Ba(OH)_2$ solution at 80 °C and 2 h. Increasing the reaction temperature causes the average grain size to increase from 0.15 μm for the film prepared at 80 °C to about 0.35 μm for the film prepared at 150 °C. Figure 6d shows the $SrTiO_3$ films after hydrothermal treatment of a titanium oxide film on PPS substrate in 1.0 M $Sr(OH)_2$ solution at 150 °C and 2 h. In view of the similar chemical behaviors of $Sr(OH)_2$ and $Ba(OH)_2$, the morphology of $SrTiO_3$ and $BaTiO_3$ films prepared by this method is similar. It worthwhile to mention that these films look porous and the adhesion of the BT film to PPS substrate actually highly depends on the substrate pretreatment, probably because the PPS substrate intrinsically is a hydrophobic polymer material. Previous work showed that very dense BT films could be prepared by hydrothermal treatment of the thin Ti films coated on a Pt surface that was first sputtered onto PPS substrate in $Ba(OH)_2$ solutions.[20] These BT films exhibited good adhesion to the Pt-coated PPS substrates. It is suggested that using a buffer layer on PPS substrates (such as Pt-coated PPS) or other substrates probably could produce dense BT films by this method. Various research is being carried out in this group along this route. Recent work shows that a dense BT film on a Si substrate with good adhesion can be prepared by this method.

Discussion of the Film Formation Process. The dissolution−crystallization mechanism has frequently been used to illustrate the nucleation and growth procedures of $BaTiO_3$ and $SrTiO_3$ on Ti metal substrates and Ti-coated substrate prepared by hydrothermal or hydrothermal−electrochemical methods.[10−13] Several models or suggestions have been proposed to explain the phenomena appearing in the formation of $BaTiO_3$ by the hydrothermal treatment of TiO_2 particles and Ti-loaded polymers in $Ba(OH)_2$ aqueous solution. Hertl synthesized $BaTiO_3$ powders by hydrothermal treatment of crystalline TiO_2 nanoparticles with aqueous $Ba(OH)_2$.[30] He used a model combining diffusional and topochemical growth of $BaTiO_3$ on TiO_2 particles to explain the reaction kinetic. The rate-limiting step was the Ba^{2+} ions diffused into TiO_2 particles by this model. Riman et al. used the heterogeneous nucleation suggestion to explain the hydrothermal growth of $BaTiO_3$ particles from titanium-containing cation-exchange resin.[31] Aksay and co-workers used a method similar to the dissolution−crystallization mechanism to describe the formation of $BaTiO_3$ films by hydrothermal treatment of the titanium organometallic films on polystyrene substrates in $Ba(OH)_2$ aqueous solutions.[21] However, we think that it is necessary to address the procedures for the formation of BT film by hydrothermal treatment of Ti-loaded polymer in detail.

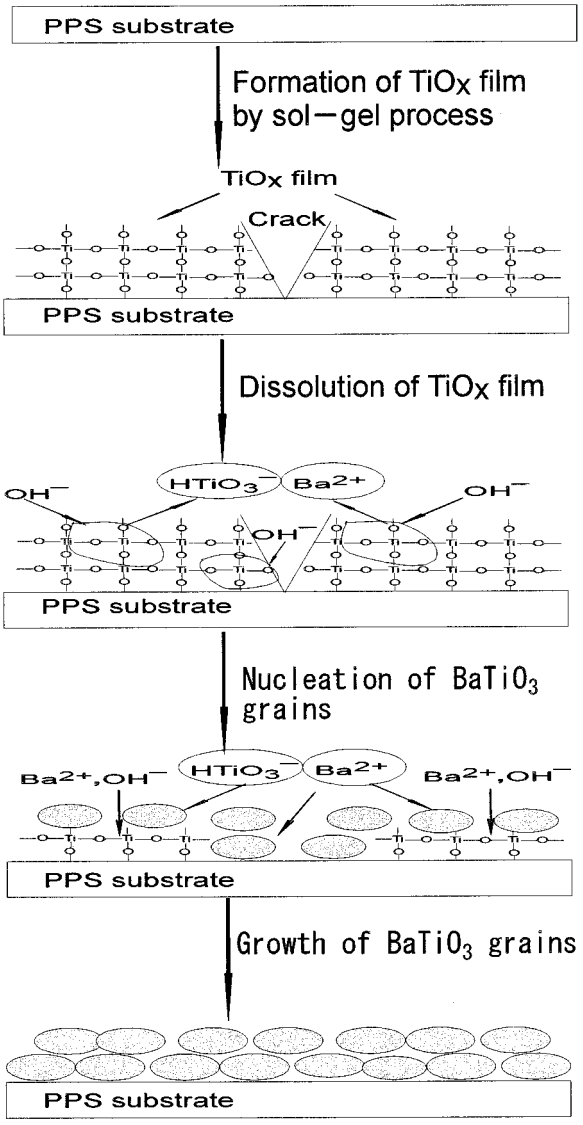

Figure 7. Schematic illustration of the hydrothermal synthesis processes of $BaTiO_3$ film prepared by hydrothermal treatment of titanium oxide films on PPS substrates.

On the basis of the experimental results, the possible procedures of the formation of BT film by the technique introduced here might be represented by a scheme like that shown in Figure 7. The dissolution−crystallization mechanism could also be used to explain the nucleation and growth procedures of BT films on amorphous titanium oxide (TiOx) films coated on PPS polymer substrates by a hydrothermal method. Upon exposure to aqueous $Ba(OH)_2$, the TiOx film dissolves in alkaline solution to form titanium hydroxyl species (probably $HTiO_3^-$ ions[32]). Simultaneously, the dissolved TiO_3^- ions

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react with the Ba^{2+} to form supersaturating particles and precipitate on the TiOx surface. The heterogeneous nucleation of BT crystals from solution continues until the surface is fully covered with BT grains. Fine pores and small fissures presented among the BT grains indicate that the dissolution of the titanium oxide film causes the film formation (Figure 6). Figure 6 also implies that the grain growth is controlled by a heterogeneous nucleation process. The dissolution of the amorphous TiOx film and the precipitation of BT precipitates can be very fast in highly concentrated alkaline media. Aksay reported that the formation of BT from a titanium organometallic precursor could appear after only 15 s in 1.0 M $Ba(OH)_2$ at 70 °C, as characterized by IR experiments.[21] We also reported that the formation of BT on Ti metal substrates by a hydrothermal−electrochemical method benefited from the anodic formation of amorphous titanium oxide, which could be quickly dissolved into concentrated alkaline solutions.[33] In contrast to the amorphous titanium oxide, the kinetic of the dissolution of crystalline TiO_2 particles in alkaline solution is quite low so that the hydrothermal formation of $BaTiO_3$ from crystalline TiO_2 nanoparticles takes a long reaction time.[30]

While $BaTiO_3$ crystals nucleate on the film surface, the Ba^{2+} and OH^- ions could permeate to the inner TiOx film surface via cracks contained in the TiOx film and fissures between the formed BT grains. The driving force for the Ba^{2+} and OH^- ions diffusion may be from the concentration difference between the solution and the substrate. The inward diffusion of Ba^{2+} and OH^- ions brings a new cycle of the dissolution−crystallization process on the BT/TiOx surface, which make the BT film thicken throughout the depth of the TiOx film to form BT.

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Summary

Amorphous titanium oxide film on polymer substrate prepared by sol−gel process was used successfully as a precursor in the hydrothermal synthesis of $BaTiO_3$ and $SrTiO_3$ films. BT (and ST) film could be mineralized at 60 °C in 1.0 M $Ba(OH)_2$ (and $Sr(OH)_2$) and 2 h. High temperature and $Ba(OH)_2$ (or $Sr(OH)_2$) concentration favored the formation of well-crystallized films. The mineralization of BT and ST from the amorphous titanium oxide on PPS substrate was very fast in comparison to the transformation from crystalline TiO_2 nanoparticles. The post-treatments of products were necessary in order to remove the $BaCO_3$ and $SrCO_3$ impurities, which inevitably contaminated the surface of BT and ST. Double-layer films on PPS substrate could be simply fabricated based on the method introduced in this paper. A dissolution−crystallization mechanism was suitable for the explanation of the formation and growth of BT and ST films by this technique. This method could be extended to prepare other ceramic films on various substrates based on the combination of sol−gel process with hydrothermal treatment.

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