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In Situ Fabrication of $SrTiO_3$–$BaTiO_3$ Layered Thin Films by Hydrothermal-electrochemical Technique

Masahiro Yoshimura,* Wojciech L. Suchanek, Tomoaki Watanabe
and Bungo Sakurai

Center for Materials Design, Materials and Structures Laboratory, Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku, Yokohama 226-8503, Japan

Abstract

Layered thin films in the $BaTiO_3$–$SrTiO_3$ system have been fabricated by a hydrothermal-electrochemical method either in a closed autoclave or in a flow system using the titanium substrate and Ba- and Sr-hydroxides or acetates as sources of titanium, barium, and strontium, respectively. The synthesis conditions (temperature in the range of 120–200°C, current density of 1–20 mA/cm^2, flow rates of 1–50 cm^3/min, duration of 1–24 h) allowed an easy control of the microstructure of the titanate layers. $BaTiO_3$ layers could be deposited easily on $SrTiO_3$ layers at 150°C (1 h, 1 mA/cm^2) both in the closed autoclave and in the flowing solution. To deposit $SrTiO_3$ layers on $BaTiO_3$ layers, a current density of 10 mA/cm^2 or preceding water leaching of the $BaTiO_3$ surface were necessary. The multilayered nature of the $BaTiO_3$–$SrTiO_3$ films have been revealed by XRD, AFM, and XPS at various stages of their preparation. Based upon the experimental results, a growth mechanism of the $BaTiO_3$–$SrTiO_3$ double layers has been proposed. © 1999 Elsevier Science Limited. All rights reserved

Keywords: hydrothermal synthesis, $BaTiO_3$ and titanates.

1 Introduction

Attention of the researchers has recently been focused on the multilayered films in the $BaTiO_3$–$SrTiO_3$ system.[1–9] Demands to miniaturize and/or upgrade capacitors in integrated circuits necessitate fabrication of layered microstructures in order to reduce the leakage current several orders of magnitude, while keeping the high dielectric constant. [2–4] One of the possible applications of such thin films is as DRAM capacitors.[10] Another interesting application of the layered films in the $BaTiO_3$–$SrTiO_3$ system are functionally graded materials having different chemical composition across the film thickness, resulting in a desired gradient of properties across the material.[1,5,9,11] Such materials can find applications as tunable multilayer capacitors,[5] stress sensors,[11] etc. In addition, perfect multilayer, i.e. $BaTiO_3$/$SrTiO_3$ superlattice has been considered as one of the ideal candidates for ferroelectric nonvolatile memories.[12]

The previously prepared $BaTiO_3$–$SrTiO_3$ layered structures were fabricated by tape–casting,[5,11] dipcoating,[1] r.f. magnetron sputtering,[2–4] molecular beam epitaxy (MBE),[6,7] and pulsed laser deposition.[8] The MBE, pulsed laser deposition, and r.f. magnetron sputtering required high vacuum, and temperatures in the range of 500–750°C.[2–4,6–8] Both tape casting and dipcoating required heating of the films above 600°C.[1,5,11] Such heat treatments often result in cracking and/or peeling of the deposited layers, reaction of the film with the substrate, moreover, are energy-consuming. However, it is possible to prepare the $BaTiO_3$, $SrTiO_3$, or $(Ba,Sr)TiO_3$ thin films by hydrothermal-electrochemical method under mild conditions and temperatures not exceeding 200°C as reviewed in Ref. 13. $BaTiO_3$ thin films (400 nm thick) synthesized by hydrothermal-electrochemical technique exhibited dielectric constant of about 350 and dielectric losses of 7–10% at room temperature at 1 kHz, and minimum leakage current of 10^{-7}–10^{-8} A/cm^2 at 2 V.[14] Therefore, preparation of multilayered thin films in the $BaTiO_3$–$SrTiO_3$ system using this technique might result in novel microstructures and/or improved properties of the films, broadening applications of the hydrothermal-electrochemical

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*To whom correspondence should be addressed. Fax: + 81-45-924-5358; e-mail: yoshimu1@rlem.titech.ac.jp

processing. The layered thin films could be prepared in a closed autoclave or in a solution flow cell for hydrothermal-electrochemical synthesis which allows fabrication of layered thin films in only one experiment by simply changing the composition of the flowing solution and/or adjusting the processing conditions.[15]

The purpose of the research presented in this paper was: (1) preparation of single-phase thin films and double layers in the $BaTiO_3$–$SrTiO_3$ system by hydrothermal-electrochemical technique, either in a solution flow cell or in a closed autoclave, and (2) investigation of the processing conditions and the mechanism of growth of the $BaTiO_3$–$SrTiO_3$ layered thin films.

2 Experimental

2.1 Fabrication of $BaTiO_3$, $SrTiO_3$, and $Ba_xSr_{1\text{-}x}TiO_3$ single-phase, single-layer thin films

Reagent grade $Ba(OH)_2$, $Sr(OH)_2$, $Ba(CH_3COO)_2$, $Sr(CH_3COO)_2{\cdot}0{\cdot}5H_2O$ (all Wako Pure Chemical Industries Ltd., Japan), and polished titanium sheets (roughness 1–2 nm, purity 99·5%, Nilaco Corp., Japan) were used as sources of barium, strontium and titanium, respectively. The acetate solutions were used when the synthesis was carried out in the flow cell, the hydroxide solutions were used when the synthesis was carried out in the closed autoclave. Appropriate quantities of the hydroxides or acetates were dissolved in distilled and degassed water to yield 0·25 M solutions. The pH of each solution was adjusted to the value of 13 by 1 M-NaOH solution (Wako Pure Chemical Industries Ltd., Japan). During the experiments in the flow cell, acetate solutions were constantly bubbled with argon gas. Experiments have been carried out for 1 h at the temperatures of 120–200°C. In all cases galvanostatic conditions with constant current densities of 1–20 mA/cm^2 were applied. The titanium substrate served as positive electrode (anode). The synthesis in the flow cell was carried out under open or closed (recycled) flow. Solution flow rates were in the range of 1–50 cm^3/min.

2.2 Fabrication of $BaTiO_3$–$SrTiO_3$ double layers

Starting solutions were the same as those described in Section 2.1. The double layers were synthesized either in a closed autoclave (using appropriate hydroxides) or in a solution flow system (using appropriate acetates). Synthesis was carried out in two steps, at 150°C, under galvanostatic conditions. In the case of $BaTiO_3/SrTiO_3$ double layers (sequence of the layers: $BaTiO_3/SrTiO_3/Ti_{substrate}$) Sr-containing solution was used in Step 1 (duration of 1 h); in the following Step 2 (duration of 1 h) Ba-containing solution was used. The current density was kept constant at 1 mA/cm^2. When the synthesis was carried out in the solution flow system, transition from Step 1 to 2 occurred without cooling, just by changing the kind of flowing solution. In the case of $SrTiO_3/BaTiO_3$ double layers (sequence of the layers: $SrTiO_3/BaTiO_3/Ti_{substrate}$), Ba-containing solution was used in Step 1 (current density of 1 mA/cm^2, duration of 1 h); in the following Step 2 (current density of 1–10 mA/cm^2, duration of 1–24 h) Sr-containing solution was used. When the synthesis was carried out in the solution flow system, transition from Step 1 to 2 occurred without cooling, but with (or without) a 30 min-long surface treatment of the $BaTiO_3$ layer using distilled and degassed water (pH = 7). Solution flow rate was kept constant at 10 cm^3/min.

2.3 Characterization of the materials

Phase composition of the prepared films was characterized by X-ray diffraction (XRD, 40 kV-40 mA, CuK_α, MAC Science Co. Ltd., Tokyo, Japan). Surface morphology of the films were observed using atomic force microscopy (AFF, PicoSPM, model MS300, Molecular Imaging/Digital Instruments, USA). Depth profiles of the Sr, Ba, Ti, and O were obtained by either X-ray photoelectron spectroscopy (XPS, ESCA-3200, Shimazu Co. Ltd., Tokyo, Japan) or Auger Electron Spectroscopy (AES). Raman spectra were obtained using a laser Raman spectrometer (T64000 Atago-Jobin Yvon, France-Japan) working in a 'micro' mode. An Ar laser with a wavelength of 514·5 nm was used for excitation. The laser beam was focused to produce a 1–2 μm diameter spot. The double-layered films were characterized after each step of their fabrication.

3 Results and Discussion

3.1 $BaTiO_3$, $SrTiO_3$, and $Ba_xSr_{1\text{-}x}TiO_3$ single-phase, single-layer thin films

Under the investigated conditions, single-phase, single-layer $BaTiO_3$, $SrTiO_3$ or $Ba_xSr_{1\text{-}x}TiO_3$ thin films have been prepared when the current density did not exceed 1 mA/cm^2. XRD patterns of the films were typical for $BaTiO_3$, $SrTiO_3$ or $Ba_xSr_{1\text{-}x}TiO_3$, showing absence of carbonates and titanium oxides (Fig. 1). Results of synthesis carried out in the open and closed (recycled) flow were almost the same.[16,17] Depending upon the processing conditions, thickness and grain size of the films were between 20 and 300 nm. Effects of the processing conditions on microstructure of the $BaTiO_3$ and $SrTiO_3$ thin films have been discussed in detail in our earlier papers.[16,17]

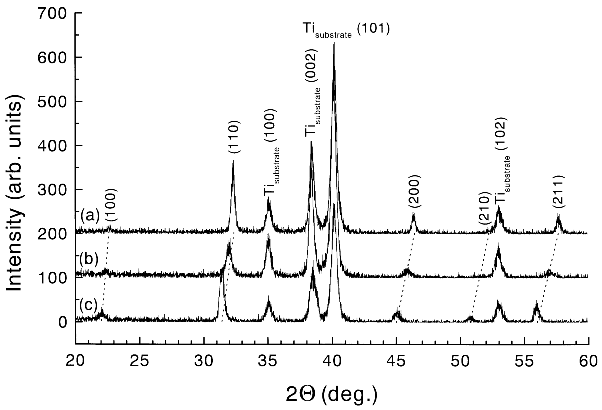

Fig. 1. XRD patterns of: (a) $SrTiO_3$, (b) $Ba_xS_{1\text{-}x}TiO_3$ ($x = 0{\cdot}75$ in the starting solution), and (c) $BaTiO_3$ single-phase thin films prepared in the flow cell by hydrothermal-electrochemical method. Temperature of 150°C, current density of $1\,mA/cm^2$, synthesis time of 1 h, and flow rate of $1\,cm^3/min$ were applied in all cases. Titanium-derived peaks are denoted as $Ti_{substrate}$. $BaTiO_3$- and $SrTiO_3$-derived (111) peaks overlap with Ti-derived (002) and (101) peaks, respectively.

3.2 Double layers in the $BaTiO_3$–$SrTiO_3$ system

Selected XRD patterns of single layers and double layers are presented in Fig. 2. They show distinct peaks derived from $SrTiO_3$ and $BaTiO_3$ layers. $Ba_xSr_{1\text{-}x}TiO_3$ solid solutions were not detected by the XRD, but we cannot preclude dissolution of small quantities of Ba in the $SrTiO_3$ layers or Sr in the $BaTiO_3$ layers. In fact, XPS data confirm the presence of Ba- or Sr-rich layers on the surface and respectively Sr- or Ba-rich layers, below (Fig. 3). Lack of sharp boundaries between the layers, revealed by the XPS analysis, could be ascribed to the surface roughness and/or formation of solid solutions. These data demonstrate that initially formed $SrTiO_3$ and $BaTiO_3$ layers have been covered by layers of $BaTiO_3$ and $SrTiO_3$, respectively. We want to emphasize that the $BaTiO_3/SrTiO_3$ and $SrTiO_3/BaTiO_3$ double layers synthesized in the flow cell have been fabricated in only one experiment, without cooling, just by changing the composition of the flowing solution. This is a serious advantage of the solution flow system for hydrothermal-electrochemical synthesis over the classical autoclaves, which must be cooled down for a relatively long time after synthesis of each layer, open and cleaned before the next experiment.

$BaTiO_3$ could be deposited easily on the $SrTiO_3$ layer to form a $BaTiO_3/SrTiO_3$ double layer. However, an additional surface treatment of the $BaTiO_3$ using pure water was necessary to deposit $SrTiO_3$ on $BaTiO_3$ to fabricate the $SrTiO_3/BaTiO_3$ double layer. The initially formed $BaTiO_3$ layer [Fig. 4(a)] remained almost unchanged when the synthesis was carried out without the intermediate (between Steps 1 and 2) water treatment [Fig. 4(b)]. It had been covered with the $SrTiO_3$ crystals when the intermediate water treatment was applied [Fig. 4(c)]. The positive effect of the water treatment of the $BaTiO_3$ layer seems to be due to the formation of TiO_2 (rutile) on the surface of $BaTiO_3$ after this intermediate step. Presence of rutile has been detected both by XRD and Raman spectroscopy.[18] The TiO_2 has been already reported to be formed on the surface of $BaTiO_3$ under quite similar experimental conditions.[19–22] The rutile layer seems to be responsible for easier deposition of $SrTiO_3$ crystals onto $BaTiO_3$ during the Step 2.

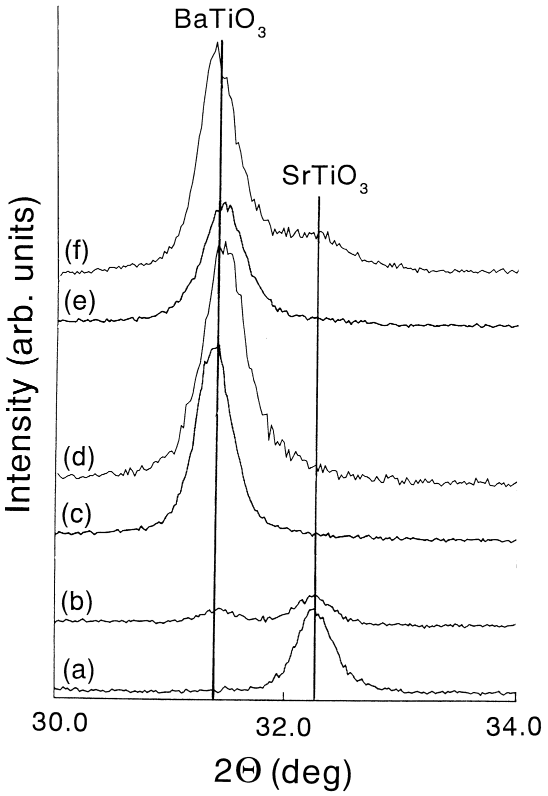

Fig. 2. XRD patterns showing the (110) peaks derived from (a) $SrTiO_3$ single-phase thin film, (b) $BaTiO_3/SrTiO_3$ double layer, (c) $BaTiO_3$ single-phase thin film; (d) $(SrTiO_3)/BaTiO_3$ double layer prepared in Step 2 by 24 h-long treatment in Sr-hydroxide at $1\,mA/cm^2$, without intermediate water treatment ($SrTiO_3$ was not detected in this case), (e) $SrTiO_3/BaTiO_3$ double layer prepared at $1\,mA/cm^2$ for 1 h in Step 2, with the intermediate water treatment; and (f) $SrTiO_3/BaTiO_3$ double layer prepared by applying current density of $10\,mA/cm^2$ for 1 h in Step 2.

Another way to deposit an $SrTiO_3$ layer on the $BaTiO_3$ layer was to apply current density of $10\,mA/cm^2$ [Fig. 2(f)]. Such experiments have been conducted in the closed autoclave. Unfortunately, because of the high current density, oxygen evolution caused several cracks in the films, making this way useless for practical applications. Longer synthesis time of 24 h at a current density of $1\,mA/cm^2$ did not allow deposition of the $SrTiO_3$ layers [Fig. 2(d)].

The processing in the solution flow cell may serve as an inexpensive and environmentally friendly way of fabrication of any layered thin films which can be synthesized by the hydrothermal-electrochemical techniques or other solution methods. It seems to be an important step in integration of the solution techniques with functional device technology, because the possibility of fabrication of a variety of materials and microstructures from solutions has been already demonstrated, as reviewed in Refs. 13, 16 and 23. Possibility of the solution recycling in a closed flow system during synthesis is another important point because it minimizes cost and the environmental load of the process.

3.3 Formation mechanism of the $BaTiO_3$–$SrTiO_3$ double layers

Based upon the experimental results described in the previous sections, we can speculate on the formation mechanism of the double layers in the $BaTiO_3$–$SrTiO_3$ system. The starting point of our considerations is the formation mechanism of single-phase $BaTiO_3$ and $SrTiO_3$ films on titanium substrate under hydrothermal-electrochemical conditions which has been already well established.[24–29] The mechanism includes dissolution of titanium from the substrate, formation of $Ti(OH)_n$ ions and subsequent reaction with cations (Ba^{2+}, Sr^{2+}) during the film nucleation stage.[27–29] Formation of the titanium oxide layer between the substrate and the

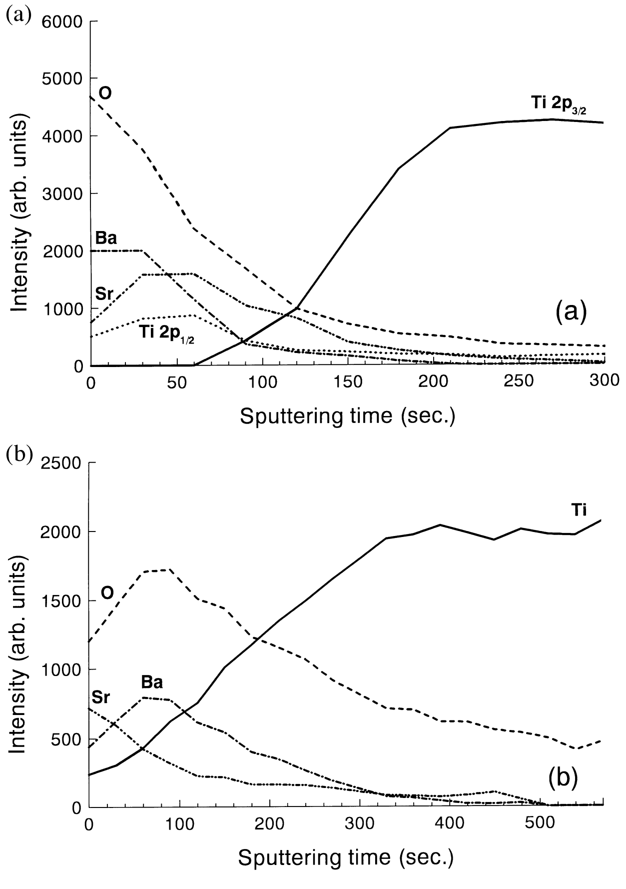

Fig. 3. Typical XPS depth profiles of Sr (3d), Ba (3d), Ti (2p), and (1s) for (a) $BaTiO_3/SrTiO_3$ double layer thin film; (b) $SrTiO_3/BaTiO_3$ double layer thin film.

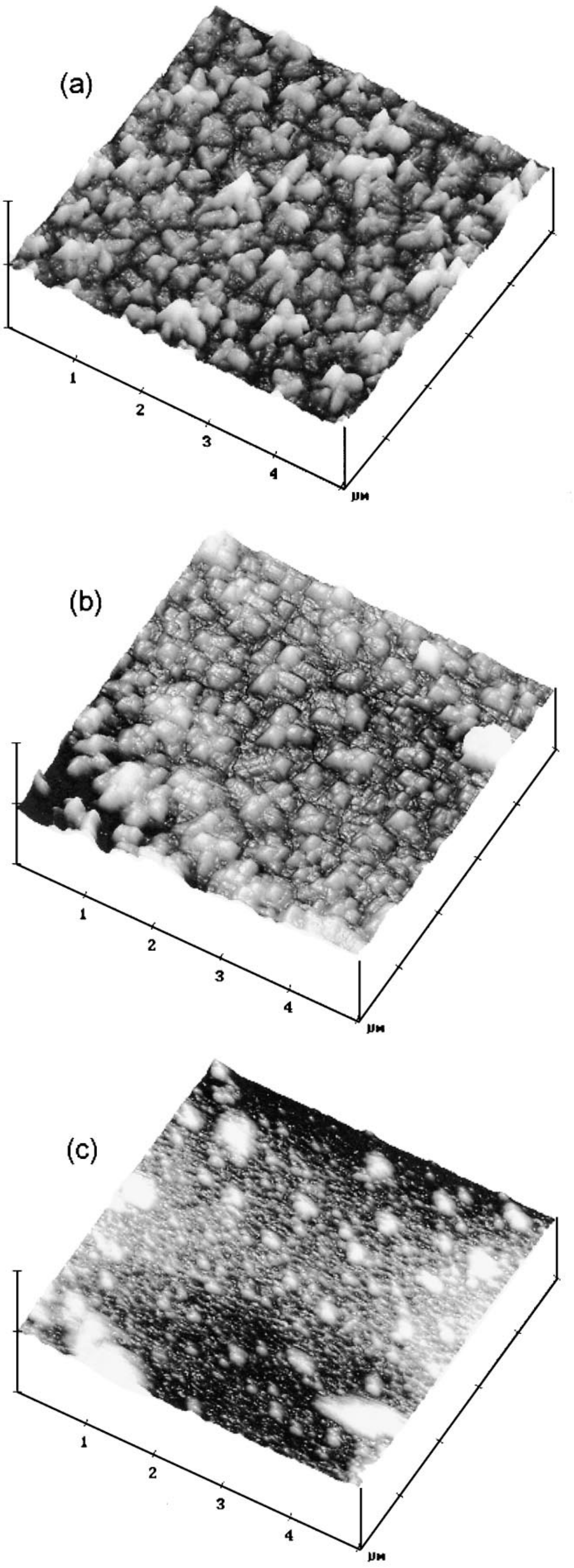

Fig. 4. AFM images of: (a) surface of the $BaTiO_3$ layer prepared in Step 1; (b) surface of the $(SrTiO_3)/BaTiO_3$ double layer after Step 2 without applying the intermediate H_2O treatment ($SrTiO_3$ was not detected in that case); (c) surface of the $SrTiO_3/BaTiO_3$ double layer after Step 2 with applying the intermediate H_2O treatment. Vertical scale: 1 μm/div.

film is a concurrent reaction under hydrothermal-electrochemical conditions and has been reported in the literature.[26,30,31] However, presence of this layer has not been clearly documented when the synthesis was carried out under only hydrothermal conditions, suggesting that formation of the titanium oxide layer is accelerated by the electrochemical treatment due to anodic oxidation. Growth of the dense titanate films is controlled by the transport of cations along the microcapillaries in the films to react on the substrate/film interface.[24–26] The general formation mechanism is the same in the case of SrTiO$_3$ films synthesized under hydrothermal-electrochemical conditions, as reviewed by Kajiyoshi and Yoshimura.[26]

The formation of the double layers in the BaTiO$_3$–SrTiO$_3$ system seems to involve two reaction sites: (a) on the surface of the films, i.e. on the solid/liquid interface which subsequently becomes the interface between the two titanate layers, and (b) on the substrate/film interface. However, the formation mechanism may be different for BaTiO$_3$/SrTiO$_3$ and SrTiO$_3$/BaTiO$_3$ double layers. Ionic exchange, according to eqn (1), has been proposed to explain the growth of BaTiO$_3$ layer on SrTiO$_3$ under hydrothermal conditions:[32]

$$\mathrm{SrTiO_3 + Ba^{2+} = BaTiO_3 + Sr^{2+}} \qquad (1)$$

ΔG of reaction (1) is negative, implying that reverse reaction is impossible.[32] Nevertheless, another growth mechanism which seems to occur first of all in the case of the SrTiO$_3$/BaTiO$_3$ double layers is also possible. It has been known that the perovskite crystals dissolve under hydrothermal conditions to form a titanium oxide layer on the surface, according to eqns (2) or (3):[21]

$$\mathrm{ATiO_3 + 2H^+ = A^{2+} + TiO_2 + H_2O} \qquad (2)$$

$$\mathrm{ATiO_3 + H_2O = A^{2+} + TiO_2 + 2OH^-} \qquad (3)$$

where A = Ba, Sr

Subsequently the TiO$_2$ layer on the surface of the ATiO$_3$ film can hydrolyze and may be turned to the titanate layer by the dissolution-precipitation mechanism for example according to the reactions (4) and (5):[27,29]

$$\mathrm{TiO_2 + 2H_2O = Ti(OH)_4} \qquad (4)$$

$$\mathrm{B^{2+} + Ti(OH)_4 = BTiO_3 + 2H^+ + H_2O} \qquad (5)$$

where B = Sr, Ba

Once a dense BTiO$_3$ layer is formed on an ATiO$_3$ layer, transport of the ions may occur by diffusion through the layers. B^{2+} ions diffuse through the BTiO$_3$ layer to react on the BTiO$_3$/ATiO$_3$ interface [site (a)], and A^{2+} ions diffuse through the ATiO$_3$ layer to react on the ATiO$_3$/Ti interface [site (b)] according to the summary eqns (6) and (7):[26]

$$\mathrm{Ti + A^{2+} + 6OH^- = ATiO_3 + 3H_2O + 4e^-} \qquad (6)$$

$$\mathrm{Ti + B^{2+} + 6OH^- = BTiO_3 + 3H_2O + 4e^-} \qquad (7)$$

The fact that the presence of the surface rutile layer stimulates deposition of a SrTiO$_3$ layer on the BaTiO$_3$ layer suggests that the dissolution of the surface titanate layer may be essential for formation of the SrTiO$_3$/BaTiO$_3$ double layers. In the case of the BaTiO$_3$/SrTiO$_3$ double layers, the experimental data suggest rather that BaTiO$_3$ is deposited on the SrTiO$_3$ layer by the mechanism described by eqn (1) i.e. by ionic exchange while the thickness of the SrTiO$_3$ layer remains constant due to conversion of underlying Ti and Ti-oxide layers into the SrTiO$_3$ (Fig. 5). In other words the reaction sites (a) and (b) move during the synthesis towards the substrate and the process starts to be controlled by the diffusion through both layers. In the case of the SrTiO$_3$/BaTiO$_3$ double layers, the mechanism described by eqns (2)–(5) is more likely.

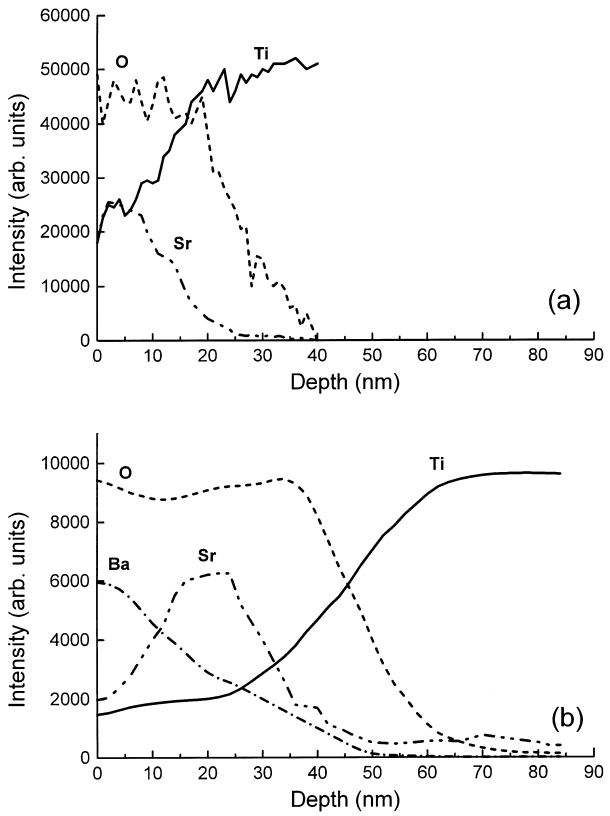

Fig. 5. Depth profiles of Sr, Ba, Ti, and O for (a) SrTiO$_3$ single-phase, single-layer thin film prepared in Step 1 (measured by XPS); and (b) BaTiO$_3$/SrTiO$_3$ double layer thin film prepared in the following Step 2 (measured by AES). Current density of 1 mA/cm^2 was applied for 1 h in each step.

Under the experimental conditions, solubility of the first $BaTiO_3$ layer may be not sufficient to produce the Ti-oxide layer on the surface. Therefore, the rutile layer has to be formed by the additional treatment in H_2O. It seems that the rutile layer is subsequently converted into the $SrTiO_3$ layer.

4 Summary

Single and double layers in the $BaTiO_3$–$SrTiO_3$ system have been synthesized under hydrothermal-electrochemical conditions at 120–200°C using either closed autoclave or solution flow cell. Purity and uniformity of the films were confirmed by XRD and micro-Raman spectroscopy. The $BaTiO_3$/$SrTiO_3$ and $SrTiO_3$/$BaTiO_3$ double layers have been characterized by XRD, XPS (AES), AFM and Raman spectroscopy after all preparation stages. $BaTiO_3$ layers could be easily deposited on $SrTiO_3$ layers at 150°C (1 h, 1 mA/cm^2). To deposit $SrTiO_3$ layers on $BaTiO_3$ layers without serious cracks in the films, water leaching of the $BaTiO_3$ surface (150°C, 30 min) with subsequent formation of TiO_2 (rutile) was necessary. The formation of the double layers in this system seems to involve two reaction sites: one on the surface of the films, i.e. on the solid/liquid interface which subsequently becomes the interface between the two titanate layers, and the second one on the substrate/films interface. Ionic exchange has been proposed as a formation mechanism of the $BaTiO_3$/$SrTiO_3$ double layers. Solubility of the first titanate layer on the surface, with subsequent formation of TiO_2, seems to be essential for successful deposition of $SrTiO_3$ on $BaTiO_3$. This processing route may serve as an inexpensive and environmentally friendly way of fabrication of layered thin films in the $SrTiO_3$–$BaTiO_3$ system as well as other multilayered materials.

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