The Strategy to Fabricate the $MTiO_3$ (M = Sr, Ba) Thin Films by Laser Ablation

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$BaTiO_3$ and $SrTiO_3$ thin films were fabricated on $Pt/Ti/SiO_2/Si$ substrate by the pulsed laser deposition process. The dependence of the deposited film quality upon the partial oxygen pressure during the deposition process was importantly examined. Regardless of the oxygen pressure, the as-deposited films were not fully crystallized. However, the film deposited at low oxygen pressure became well crystallized after the annealing process. It was concluded, therefore, that the partial oxygen pressure is reduced as low as possible during the deposition process and then anneal the as-deposited samples at ambient pressure to fabricate the well crystallized $SrTiO_3$ and $BaTiO_3$ films by laser ablation.

Key Words : Thin film, Laser ablation, Ferroelectrics, Crystallization

Introduction

Pulsed laser deposition (PLD) is a relatively new technique that is used to prepare thin films of complicated multicomponent materials.[1-5] This technique is distinguished by a short pulse duration, a short wavelength, and a huge energy flux of the laser beam used for PLD. The deposition process is accomplished by sitting on the substrate of a plume of ionized and ejected material which is produced by high-intensity laser irradiation of a solid target. In spite of a few limitations of the technique, such as occurrence of particulates on the film surface and unevenness of thickness, laser ablation offers several advantages including: a) the film composition can be nearly identical to the target stoichiometry; b) deposition in a wide range of oxygen partial pressure; c) low crystallization temperatures due to high excitation energy of the photofragments in the laser produced plasma; d) high deposition rates; e) deposition of materials with high melting temperatures. Many ferroelectric ceramics have been successfully deposited using high power Nd:YAG or excimer lasers having pulse duration of approximately 10-25 ns with repetition rates up to several hundred hertz with energies approaching 500 mJ/pulse.[6-8] Especially many researchers have reported results on the characteristics of $BaTiO_3$ and $SrTiO_3$ thin films deposited by PLD on different substrates.[9-12] $BaTiO_3$ is one of the attractive material because of its diverse properties such as high dielectric constant, ferroelectric, electro-optical, and non-linear optical application since it shows the second harmonic generation chracteristics.[13-15] Therefore, a flood of research has been made on $BaTiO_3$ to improve its physical properties to apply for the ferroelectric devices such as FRAM, high dielectric capacitor, high frequency switch, etc. Recently, the superlattices artificially made with $BaTiO_3$ and $SrTiO_3$ have attracted much attention because the superlattices possess the potential to provide a new function or enhanced performance to existing devices by controll lattice strain, demensionality, and stacking periodicity. On the consequence, a number of papers concerning the growth of artificial superlattices of $BaTiO_3/SrTiO_3$ whose dielectric, ferroelectric, and electro-optic properties were improved, have been reported.[16-20] However, it is understood that the controll of the characteristics of the PLD-deposited $BaTiO_3$ and $SrTiO_3$ films has not been well established.[21] Among the diverse conditions to be controlled oxygen pressure in the chamber during the deposition process is one of the most important factor to determine the quality of the films.[22]

In this paper, $BaTiO_3$ and $SrTiO_3$ thin films are fabricated on $Pt/Ti/SiO_2/Si$ substrate by the PLD process. The optimum conditions to prepare the thin films were investigated. Especially, the dependence of the deposited film quality upon the partial oxygen pressure was importantly examined. After the optimum conditions are investigated, the multilayered $BaTiO_3/SrTiO_3$ superlattce films will be fabricated.

Experimental

The experimental setup of PLD process to deposit $BaTiO_3$ and $SrTiO_3$ films is shown in Figure 1. Epitaxial oxide films were deposited on (111) oriented $Pt/Ti/SiO_2/Si$ substrate equipped with a high vacuum chamber and a Nd:YAG laser (λ = 355 nm). A $BaTiO_3$ and $SrTiO_3$ targets prepared by solid state reaction with high purity $SrCO_3$, $BaCO_3$, and

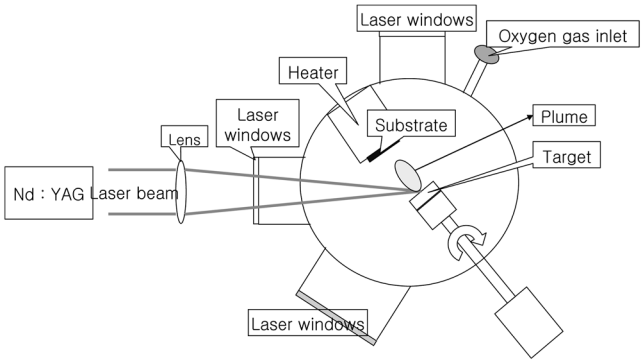

Figure 1. Experimental apparatus for the laser ablation of $BaTiO_3$/$SrTiO_3$ thin films.

Table 1. Growth conditions for preparation of $BaTiO_3/SrTiO_3$ thin film by laser ablation

Nd:YAG laser	355 nm
Laser power	100 mW (BTO), 300 mW (STO)
Substrate temperature	300 °C
Target to substance distance	4.5 cm
Deposition time	40 min (BTO), 50 min (STO)
Oxygen pressure	0 mtorr~1 torr

TiO_2 powders (Sigma-Aldrich, USA) were attached on a rotating multitarget holder. $Pt/Ti/SiO_2/Si$ substrate was cleaned with acetone, methanol, isopropyl alcohol and finally deionized water. The loaded substrate was heated to reach the temperature within 300 °C-600 °C. The target-substrate distance was kept at 45 mm. The laser power was varied from 5 to 300 mW. The ablation process was continued for 5-60 minutes for each target. After selecting the optimum conditions of substrate temperature, laser power, and ablation time, oxygen pressure was examined by varing it from 0 to 1000 mtorr to investigate it's role on the deposited film quality. More detailed characteristic parameters of the ablation process are given in Table 1. Hereafter all deposition processes are performed at the given conditions in Table 1 except the oxygen partial pressure. Deposited $BaTiO_3$ and $SrTiO_3$ films were identified with Rigaku X-ray diffractometer after the deposition step and after the annealing step. Atomic concentration in $BaTiO_3$ film according to the penetration depth was examined by using Auger electron spectroscopy (AES) to investigate the oxygen content before and after the annealing process with the sputter rate of 74 nm/min. The deposited film thickness was investigated by examining the cross section of the film with the high-resolution scanning electron microscope (HR-SEM).

Results and Discussion

Figures 2a and 3a show the XRD patterns of as-deposited $SrTiO_3$ and $BaTiO_3$ films, respectively, depending upon the oxygen partial pressure. Sharp finger-print peaks identifying strontium titanate and barium titanate are not shown in the XRD figures, indicating that both samples are not fully crystallized at the given condition. As the oxygen pressure is increased very tiny peaks start to appear in $SrTiO_3$ film but not in $BaTiO_3$. Beyond the upper limit of the oxygen pressure of 1 torr, peaks were not increased further so the data were not shown here. The formation of $SrTiO_3$ crystalline phase superior to $BaTiO_3$ phase at oxygen pressure of 1 torr during the deposition process may be explained in terms of the lattice energy of M^{2+}-O. The ionic radius of Sr^{2+} with coordination number of 12 is 156 pm while that of Ba^{2+} is 175 pm. The bond distance of Sr-O in $SrTiO_3$ phase is 276 pm which is shorter than that of Ba-O (284 pm) in $BaTiO_3$ compound. The unit cell parameter is also small in $SrTiO_3$ crystal (*i.e.*, 3.9051 Å for $SrTiO_3$ and 4.0118 Å for $BaTiO_3$). The lattice energy in $SrTiO_3$ is, therefore, larger than that in $BaTiO_3$. Generally, the larger lattice energy means that the

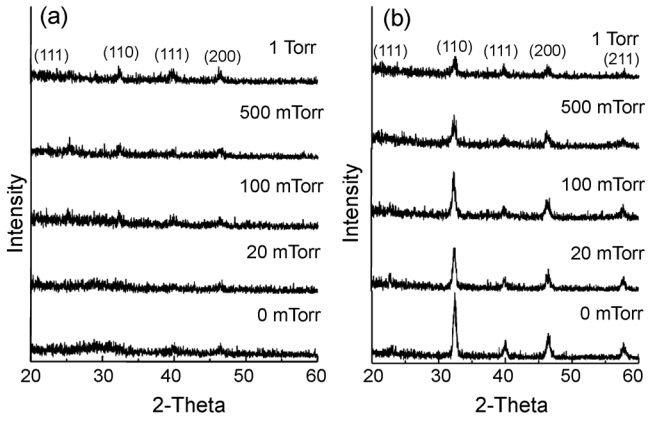

Figure 2. XRD pattern of $SrTiO_3$ depending on oxygen pressure (a) before the annealing process and (b) after the annealing process at 600 °C for 4 hrs.

compound is more stabilized. This stabilization energy is supposed to result in the difference in forming a little bit more crystallized film for $SrTiO_3$ than for $BaTiO_3$ at oxygen pressure of 1 torr. Although tiny peaks appear in $SrTiO_3$, the as-deposited samples of both compounds were formed pseudo-stable pyrochlore crystalline regardless of the oxygen partial pressure in the chamber. This result is consistent with that found in the as-deposited PZT film prepared by high-frequency magnetron sputtering on $Pt/Ti/SiO_2/Si$ substrate at 450 °C.[23] Samples annealed at 600 °C for 4 hours in atmospheric condition became well crystallized stable perovskites. Figures 2(b) and 3(b) are the XRD patterns of annealed $BaTiO_3$ and $SrTiO_3$ films. Peak positions are as same as those of bulk materials which means that films are well crystallized. Close investigation of the XRD pattern of $SrTiO_3$ indicates that the peaks come out sharper in the sample deposited at lower oxygen pressure. After the deposition process the $SrTiO_3$ film deposited at higher oxygen partial pressure forms weak crystallization while the one prepared at lower oxygen partial pressure does not crystallize at all (see Figure 2a). This tiny difference of crystallization during deposition precess seems to be the reason of the difference in crystallization after the annealing process. More crystallized as-deposited films do not allow oxygen to permeate inside the film, thereby inhibiting the formation of further crystallization inside the $SrTiO_3$ film during the annealing step. The sharpness of the XRD peak after the annealing as a function of the oxygen partial pressure during the deposition process clearly tells us that the less crystallized as-deposited $SrTiO_3$ phase becomes more crystallized during the annealing process (see Figure 2). Differently from $SrTiO_3$, the as-deposited $BaTiO_3$ film does not show any crystallized peak no matter how the oxygen partial pressure was changed. The poor crystallized as-deposited phase makes oxygen permeate easily inside the film, thereby forming the well crystallized $BaTiO_3$ film after the annealing process. The similar crystallized XRD pattern of $BaTiO_3$ films after the annealing process regardless of partial oxygen pressure during the deposition is originated

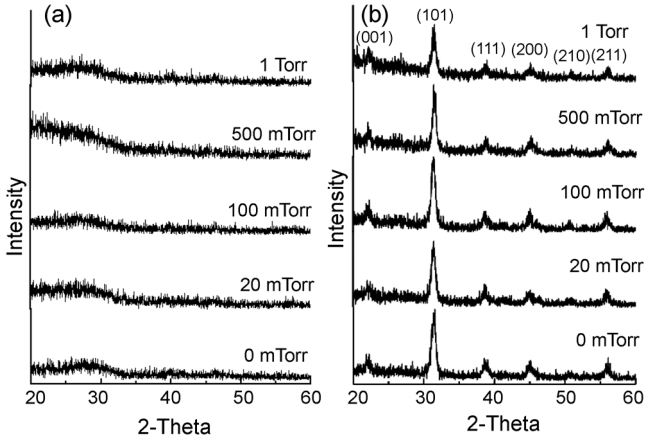

Figure 3. XRD pattern of $BaTiO_3$ depending on oxygen pressure (a) before the annealing process and (b) after the annealing process at 600 °C for 4 hrs.

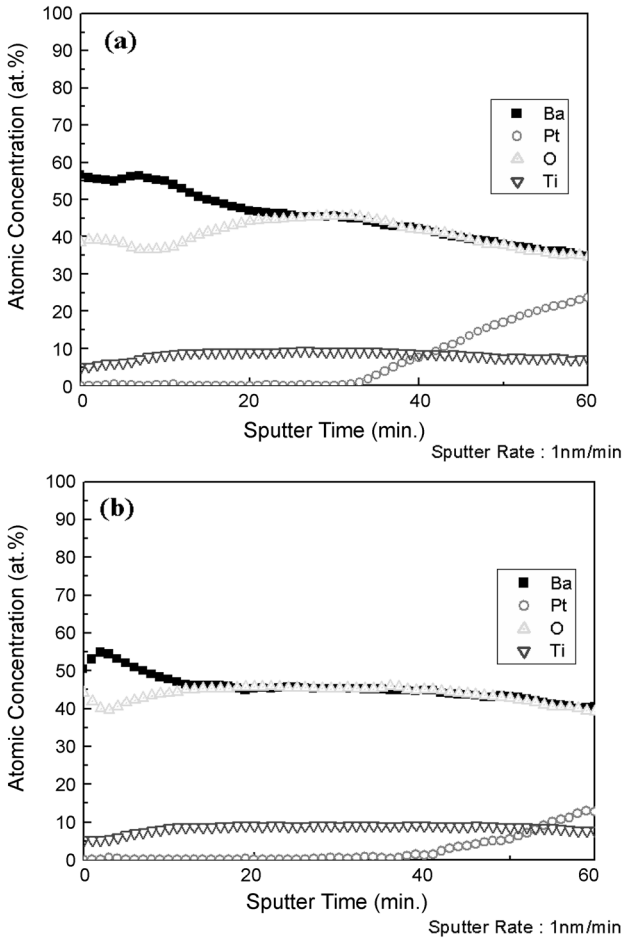

Figure 4. AES data of $BaTiO_3$ film (a) before the annealing process and (b) after the annealing process.

from the poor crystallized as-deposited samples at any oxygen pressure (see Figure 3). The oxygen content in- and outside the film during the deposition process is, therefore, concluded to play an important role to crystallize the $BaTiO_3$ and $SrTiO_3$ films after the annealing.

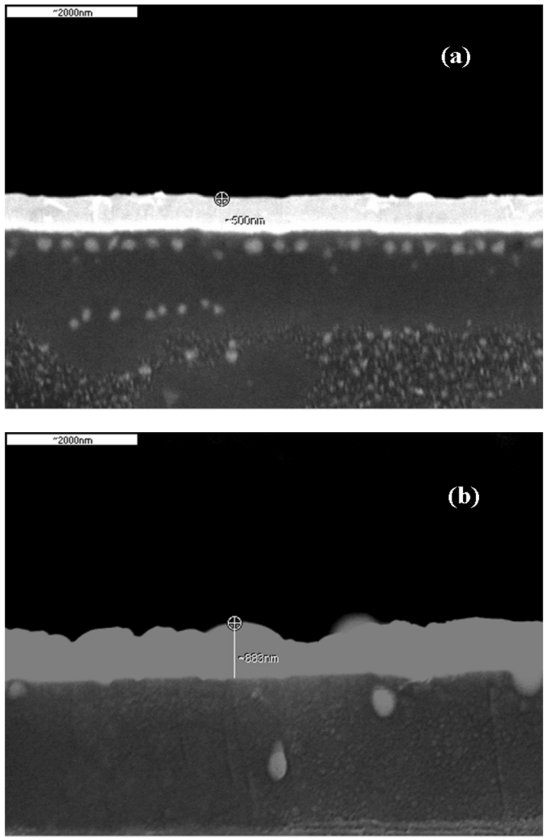

Figure 5. SEM photographs of cross section of (a) $SrTiO_3$ and (b) $BaTiO_3$ thin films.

Auger electron spectroscopy (AES) data of $BaTiO_3$ film before and after the annealing process, demonstrated in Figure 4(a) and Figure 4(b), clearly show the oxygen content of the samples before and after the annealing process. Oxygen content to the barium content ratio is relatively low until 30 nm from the surface of the as-deposited film, while that is higher in the annealed sample. The AES data tells us that stoichiometric amount of oxygen penetrates into the film and construct the crystalline $BaTiO_3$ during the annealing process. The annealing process is inevitable to crystallize both $BaTiO_3$ and $SrTiO_3$ phases. So far the appropriate process to fabricate the $BaTiO_3$ and $SrTiO_3$ thin films by laser ablation method is to reduce the partial oxygen pressure in the chamber as much as possible during the deposition process, and then anneal the deposited samples at 600 ^oC for 4 hours in atmospheric condition. The cross section images of high resolution scanning electron microscopy (HR-SEM) of $SrTiO_3$ and $BaTiO_3$ films fabricated by previously discussed processes are shown in Figure 5(a) and Figure 5(b), respectively. Both samples are well deposited on the substrate without major structural defect although unevenness of thickness is shown which is the inherent disadvantage of PLD method. Shortly after, multi-layered $BaTiO_3/SrTiO_3$ superlattice samples will be prepared based on the suggested processes and the samples will be characterized.

Conclusions

$BaTiO_3$ and $SrTiO_3$ thin films were fabricated on Pt/Ti/SiO_2/Si substrate by the PLD process. The optimum conditions to prepare the thin films were investigated. Especially the dependence of the deposited film quality upon the partial oxygen pressure was importantly examined. Before the annealing step, $SrTiO_3$ and $BaTiO_3$ films were not fully crystallized regardless of the partial oxygen pressure in the chamber. The crystallization could be accomplished only after the annealing process. The quality of the films after the annealing process looked better when they were deposited at lower oxygen pressure, specially in $SrTiO_3$. The appropriate method to fabricate the $SrTiO_3$ and $BaTiO_3$ films by laser ablation process is, therefore, concluded as follows; (a) partial oxygen pressure is kept as low as possible during the deposition process: (b) anneal the as-deposited samples at 600 ^oC in ambient pressure. This result can be applied for preparing metal oxide films with laser ablation method.

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