# Properties of $MTiO_3$ (M = Sr, Ba) and $PbM'O_3$(M′ = Ti, Zr) Superlattice Thin Films Fabricated by Laser Ablation

**T. M. Lim, J. Y. Park, J. S. Han, P. G. Hwang, K. H. Lee,[†] K. W. Jung,[*] and D. Jung[*]**

*Department of Chemistry and Institute of Natural Basic Sciences, Wonkwang University, Iksan, Jeonbuk 570-749, Korea*
*[*]E-mail: djung@wonkwang.ac.kr*
*[†]Nanoscale Science and Technology Institute, Wonkwang University, Iksan, Jeonbuk 570-749, Korea*
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$BaTiO_3/SrTiO_3$ and $PbTiO_3/PbZrO_3$ superlattice thin films were fabricated on $Pt/Ti/SiO_2/Si$ substrate by the pulsed laser deposition process. The morphologies and physical properties of deposited films were characterized by using X-ray diffractometer, HR-SEM, and Impedance Analyzer. XRD data and SEM images of the films indicate that each layer was well deposited alternatively in the superlattice structure. The dielectric constant of $BaTiO_3/SrTiO_3$ superlattice thin film was higher than that of individual $BaTiO_3$ or $SrTiO_3$ film. Same result was obtained in the $PbTiO_3/PbZrO_3$ system. The dielectric constant of a superlattice film was getting higher as the number of layer is increased.

**Key Words**: Superlattice, Laser ablation, Ferroelectric

## Introduction

Ferroelectric materials are characterized as crystals that possess a spontaneous dipole. Generally, the dielectric constants of ferroelectric materials are much bigger than those of normal dielectric compounds. It is necessary to possess stronger dielectric properties when a material is applied for the phase shifters, tunable filters, capacitors, non-volatile ferroelectric random access memory (FeRAM) devices, dynamic random access memory (DRAM) devices and steerable antennas. Many scientists, therefore, have tried to increase the dielectric property of ferroelectric materials by substituting the pre-existing metals with various transition metals, and/or by developing new materials. Several compo-unds, for example, lead zirconate titanates [$Pb(Ti_{1-x}Zr_x)O_3$, PZT][1,2] and lead lanthanum zirconate titanates[$(Pb_{1-y}La_y)(Ti_{1-x}Zr_x)O_3$, PLZT][3] have been successfully developed through the substitutional method. Both compounds exhibit better dielectric property than the intrinsic $PbTiO_3$ does. In addition, a flood of research has been focused on the syntheses of new materials which exhibit higher dielectric constants. Auri- villius phase compounds such as $SrBi_2Ta_2O_9$ (SBT) and $SrBi_2Nb_2O_9$ (SBN) are the typical examples.[4-7]

As a new synthetic process for the application of ferroelectric materials, the superlattice structure form (see Figure 1) with two kinds of classical ferroelectric compounds in film type can be introduced. Superlattice structure framework is an artificial crystal which is designed to deposit the alternating layers with more than two different materials. A ferroelectric perovskite is deposited onto a substrate first time and then the second compound is deposited onto the surface of the first one, and again the first one onto the surface of the second one, and so on. The superlattice structure film is known to exhibit better physical properties compared to the individual materials.[8] For example, ferroelectric superlattice structure which is made of $BaTiO_3$ and $SrTiO_3$ shows higher voltage tunability and dielectric properties than $BaTiO_3$ only or $SrTiO_3$ only.[9-12] Dielectric property of a material depends on the amount of structural distortions in the compounds. Structural distortion is essentially formed when a material is deposited onto the surface of a different compound having a different unit cell size. The superlattice structure made by laser ablation method with $SrTiO_3$/ $BaTiO_3$ cannot be exceptional. The lattice parameters of $SrTiO_3$ and $BaTiO_3$ are 3.9051 Å and 3.9947 Å, respectively. The difference of their lattice parameter by about 0.1 Å causes the structural distortion when they are deposited alternatively, and the structural strain will increase as the film thickness is increased.

Pulsed laser deposition(PLD) is a relatively new technique that is used to prepare thin films of complicated multicomponent materials.[13-17] 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

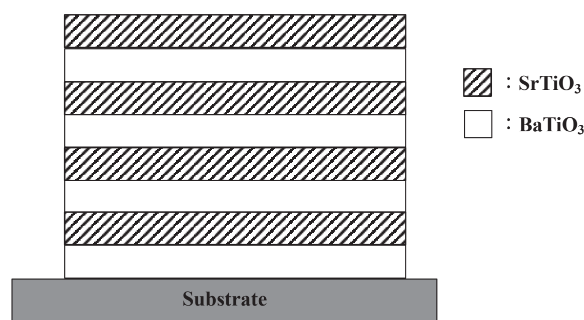


**Figure 1.** Simple diagram of a superlattice

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.[18-20] Especially many researchers have reported results on the characteristics of $BaTiO_3$ and $SrTiO_3$ thin films deposited by PLD on different substrates.[21-24] Recently, the superlattices artificially made by PLD process with $BaTiO_3$ and $SrTiO_3$ have attracted much attention On the consequence, a number of papers concerning the growth of artificial superlattices of $BaTiO_3$/$SrTiO_3$ having improved dielectric, ferroelectric, and electro-optic properties, have been reported.[25-30]

BT/ST and PT/PZ superlattice thin films are fabricated on Pt/Ti/$SiO_2$/Si substrate by the PLD process. In this paper, the optimum conditions to prepare the thin films were investigated and the dependence of ferroelectric properties on the number of deposited layers is characterized.

## Experimental

The experimental setup of PLD process to deposit $BaTiO_3$/$SrTiO_3$ and $PbTiO_3$/$PbZrO_3$ films is shown in Fig. 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 (l = 355 nm). A $BaTiO_3$ target was prepared by solid state reaction at 1100°C for 2 hrs with highly pure $BaCO_3$ and $TiO_2$ powders (Sigma-Aldrich, USA) with 1:1 molar ratio, and a SrTiO3 target with $SrCO_3$ and $TiO_2$ powders (Sigma-Aldrich, USA) with 1:1 molar ratio. Similarly $PbTiO_3$ and $PbZrO_3$ targets were synthesized with (PbO + $TiO_2$ with 1.1:1 molar ratio) and (PbO + $ZrO_2$ with 1.1:1 molar ratio) (Sigma-Aldrich, USA) at 900°C for 3 hrs, respectively. Extra 10% of PbO was added to compensate for it's evaporation at high temperature during solid state reaction. Prepared targets were attached on a rotating multitarget holder. The substrate consists of a 1500 Å for bottom electrode, a 100 Å Ti adhesion layer, and 3000 Å $SiO_2$ on a Si wafer. Platinum electrode was highly (111) oriented normal to the surface of the film. 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. Partial oxygen pressure in the chamber was varied from 0 to 1000 mtorr. 5-Layered and 10-layered BT/ST and PT/PZ superlattice films were prepared by depositing the first and second compound alternatively by rotating the multi-target holder back and forth. Deposited films were identified with X-ray diffractometer (Panalytical MRD). Microstructure, crystallographic orientation, and the thickness of the film were analyzed by examining the cross section of the film with the high-resolution scanning electron microscope (HR-SEM, Hitachi S-4800). The relative dielectric constants of the superlattice thin films were measured using an impedance analyzer (HP LCR meter 4284A) at 100 kHz and at room temperature. Top electrodes with the radius of 0.125 mm in size were prepared by depositing Pt by sputtering method and Pt (111) layer deposited onto Ti/$SiO_2$/Si substrate was used as a bottom electrode.

## Results and Discussion

The optimized conditions to deposit BT/ST and PT/PZ superlattice films were decided such as substrate temperature of 300°C partial oxygen pressure of 0 torr, laser power of 300 mW. Deposited samples were annealed at 600°C for 30 min at ambient

**Table 1.** Growth conditions for preparation of BT/ST and PT/PZ superlattice films by laser ablation

| Laser | Nd:YAG 355 nm |
|---|---|
| Laser power | 300 mW |
| Substrate temperature (℃) | 300 |
| Target-substrate distance | 4.5 cm |
| Deposition time | BT/ST : 10 min.<br>PT/PZ : 5 min. |
| Annealing condition | BT/ST : 600°Cfor 4 hours<br>PT/PZ : 600°Cfor 30 min. |
| Oxygen pressure | 0 mtorr |

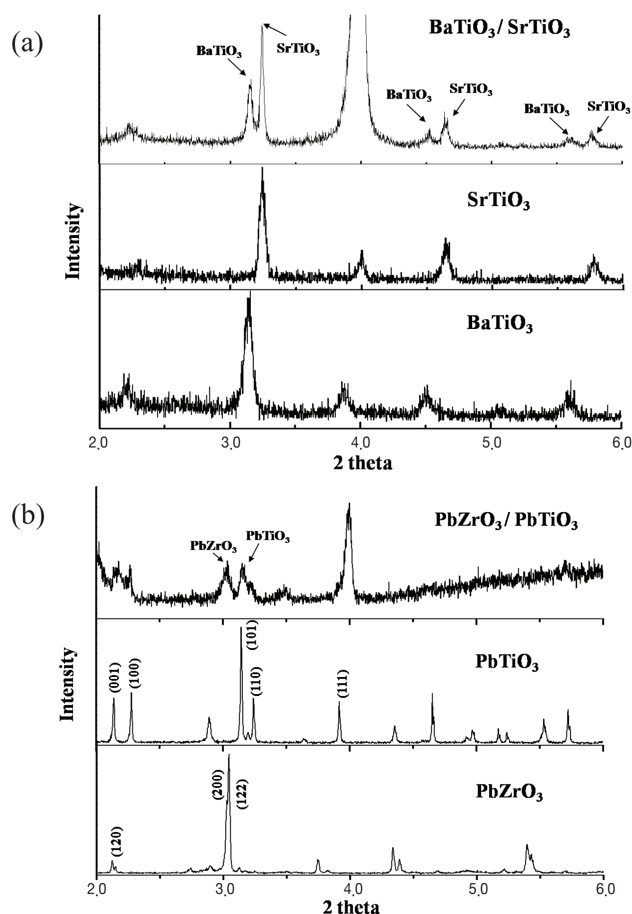


**Figure 2.** XRD pattern of (a) BT/ST and (b) PT/PZ superlattice

pressure. The detailed deposition conditions are illustrated in Table 1.

XRD pattern of BT/ST superlattice thin film is shown in Fig. 2. The split peaks tell us that alternating BTO and STO layers are well deposited. The stronger intensity in ST peaks compared with BT peaks is due to the later deposition of ST layer. The decrease of intensity and sharpness of the peaks in the superlattice film suggests that the crystallinity of the film is somewhat decreased because of the difference between the cell parameters of BT and ST. (The lattice parameters of cubic $SrTiO_3$ and $BaTiO_3$ are 3.9051 Å and 3.9947 Å, respectively.) The peak positions of $BaTiO_3$ in the superlattice are slightly shifted to high 2q, however those of $SrTiO_3$ in the superlattice are slightly shifted to low 2q. This means that the larger unit cell of $BaTiO_3$ is slightly decreased to adjust to the smaller cell of $SrTiO_3$, while the smaller cell of $SrTiO_3$ is slightly increased to adjust to the larger cell of $BaTiO_3$. Similar results were obtained from PZ/PT superlattice film.

Fig. 3 shows the SEM photographs of 10- and 5-layered BT/ST and PT/PZ superlattice films. $SrTiO_3$ and $BaTiO_3$ layers are well deposited alternatively. The thickness of each layer is about 50-60 nm which results in the total thickness of about 550 nm for 10 layers as shown in Fig. 3a. The 5-layered PT/PZ alternating film is about 120 nm thick, which means that the thickness of each layer is about 25 nm as shown in Fig. 3b. Si/$SiO_2$(300 nm)/Ti(10 nm)/ Pt(150 nm) substrate layers are clearly seen beneath the PT/PZ layer. The difference in the thickness between BT/ST and PT/PZ films is due to the longer time and the higher evaporating property in BT/ST. (The ablation time of each layer of BT/ST and PT/PZ are 20 min and 10 min, respectively.)

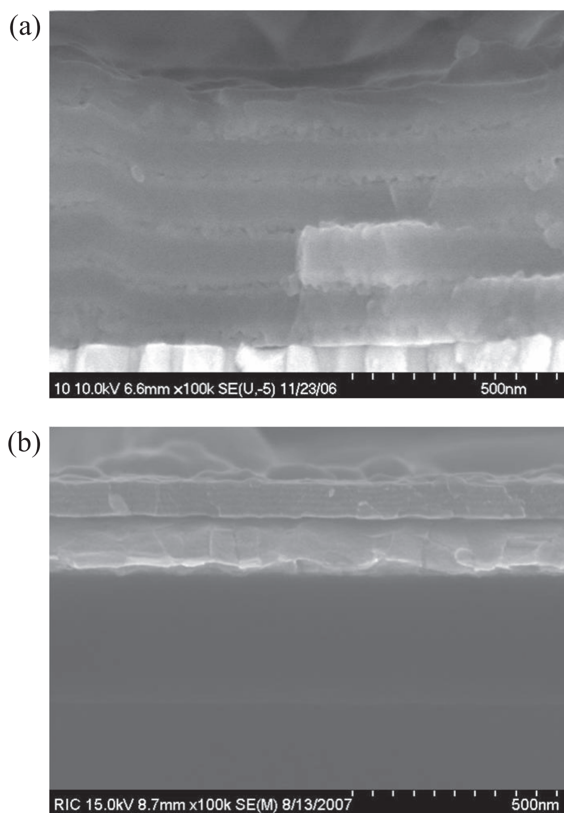


**Figure 3.** SEM images of (a) 10-layered BT/ST superlattice and (b) 5-layered PT/PZ superlattice

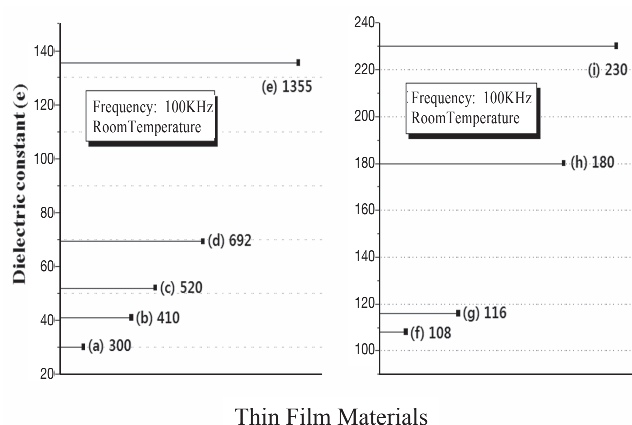


**Figure 4.** Relative dielectric constant of various hetero epitaxial (a) $BaTiO_3$*, (b) $SrTiO_3$*, (C) $(Ba_{0.5}Sr_{0.5})TiO_3$*, (d) 5-layered BT/ST superlattice, (e) 10-layered BT/ST superlattice, (f) $PbZrO_3$, (g) $PbTiO_3$, (h) 5-layered PT/PZ superlattice, and (i) 10-layered PT/PZ superlattice films. *cited from ref.[30]

The dielectric constant data of the films were collected by measuring capacitance values of the films at 100 kHz at room temperature through the following equation:

$$\varepsilon_r = \frac{\varepsilon}{\varepsilon_o} = \frac{Cd}{A\varepsilon_o}$$

$\varepsilon_r$ : dielectric constant (relative permittivity)
$C$ : capacitance
$\varepsilon_o$ : absolute permitivity
$d$ : thickness of the film
$\varepsilon$ : permitivity
$A$ : area of the film

The dielectric constant calculated from the capacitance data of films are increased with increasing the number of alternating layer in each superlattice film, as shown in Fig. 4. The dielectric constant of a 10-layered film is higher than that of origi- nal single perovskite by more than two times. This result is consistent with the conclusion[28-29] that the dielectric constant- increases with increasing the number of layer in the superlattice since the structural distortion is essentially formed when a material is deposited onto the surface of a different compound.

## Conclusions

The superlattice film constructed with BT/ST or PT/PZ was fabricated by laser ablation method. XRD data and SEM images confirm that the superlattice film was well deposited. The alternatively deposited films constructed by two different perov- skites show improved dielectric property compared with the original single perovskite. The increased dielectric constant in the superlattice film is due to the lowered symmetry of the film which is originated from the structural distortion during deposition with two compounds having different cell parameters.

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