Interfacial structure of multi-layered thin-films produced by pulsed laser deposition for use in small-scale ceramic capacitors

Takao Araki¹, Takanori Hino² and Masahiro Ohara³

¹ Professor, Institute for International Relation, Ehime University, Matsuyama Japan
² Associate Professor, Department of Environmental Materials Engineering, Niihama National College of Technology, Niihama, Japan
³ Professor, Department of Materials Science and Biotechnology, Graduate School of Science and Engineering, Ehime University, Matsuyama, Japan

E-mail: t-alucky@mb.pikara.ne.jp

Abstract. The aim of this study was to develop thin film capacitors with superior properties that could provide an alternative to materials currently used in conventional multi-layer ceramic capacitors fabricated by sintering. To this end, an artificial dielectric super lattice technique, incorporating pulsed laser deposition, was applied to improving the dielectric properties of thin film capacitors. This method permits the A-site atoms of a perovskite ABO₃ structure to be selected layer by layer at a nanoscopic scale; consequently, multi-layer BaTiO₃-SrTiO₃ thin films were produced on Pt(111)/Ti/SiO₂/Si(100) and SrTiO₃(111) substrates. Hetero-epitaxial grain growth was observed between BaTiO₃ and SrTiO₃, with the lattice mismatch between them introducing a compressive residual strain at the interface. The dielectric properties of these multi-layer thin-film capacitors were found to be superior to those of conventional solid-solution thin films once the thickness of the layers and the ratio of the two oxides were optimized.

1. Introduction

Barium titanate (BaTiO₃) is widely used as a dielectric material in a variety of everyday applications, including memory IC cards, chip capacitors and flash memory. Chip capacitors, otherwise known as multi-layer ceramic capacitors (MLCCs), are of particular importance as these are used in most compact electronic devices such as laptop computers, PDAs, and mobile phones. In the case of passive components, which include MLCCs, there is a high demand for an improvement in the dielectric constant and a reduction in the layer thickness in order to reduce their physical size. This is hindered, however, by the fact that a thickness of around 1 μm represents the technical limit for conventional powder metallurgy processes. The development of improved thin film technologies is therefore essential to the development of next-generation capacitors.

Although thinner dielectric layers can be easily produced by physical or chemical vapor deposition techniques, the dielectric characteristics of MLCCs formed in this way are usually not as good as those of bulk ceramics produced by powder metallurgy processes. These dielectric characteristics have been
somewhat improved through forming solid-solution films; but even so, equivalent properties are still far from being achieved.

The discovery that the strain induced by the formation of super lattice films improves their dielectric properties has prompted a considerable amount of research into this field [1-2]. Typically, these super lattice films are produced through layer-by-layer growth of artificial crystals at a nanoscopic scale [1-2]. In the present study, a pulsed laser deposition (PLD) technique was utilized to disintegrate bulk materials into atoms, which were then deposited on a suitable substrate to form super lattice films. In this way, multi-layer BaTiO$_3$-SrTiO$_3$ thin films were produced and their dielectric characteristics were evaluated.

2. Experimental procedure

The deposition targets were prepared by sintering compacts, which consisted of high purity BaTiO$_3$ (BTO onward) and SrTiO$_3$ (STO) powders. Single layer films of Ba$_{1-x}$Sr$_x$TiO$_3$ (BSTO) and multi-layer films of (BaTiO$_3$)$_{1-x}$(SrTiO)$_x$ (BTO-STO) were then fabricated by irradiating a KrF excimer laser onto the sintering targets, and ablating particles from the target onto the substrate [3-4]. The two types of single-crystal substrate were prepared as 1.0x1.0x0.5 mm$^3$ wafers of Pt(111)/Ti/SiO$_2$ (100) by DC sputtering onto a 1%Nb-doped single-crystal SrTiO$_3$ (111) substrate measuring 0.5x0.5x0.5 mm$^3$.

The BSTO and BTO-STO films were each deposited onto individual substrates, which were heated to a temperature of 973 K in a O$_2$-8%O$_3$ atmosphere under gas pressures of 1 and 8 Pa. The laser was irradiated onto the rotating target at a fluency of 3.0 J/cm$^2$ and a repeated pulse frequency of 2 Hz. BTO-STO super lattice films were made to different layer thicknesses, while still maintaining a total film thickness of 200 nm, as shown Figure 1. The thickness of each BTO and STO layer was determined by the number of layers deposited and by the overall proportion of STO, i.e., x in (BaTiO$_3$)$_{1-x}$(SrTiO)$_x$; with films being produced to x values of 0.25, 0.50 and 0.75. The thickness of each layer was controlled by the number of laser pulses. The Ba$_{1-x}$Sr$_x$TiO$_3$ single-layer thin films were produced using targets made from powders of BTO and STO mixed to ratios of 0.00, 0.25, 0.50, 0.75 and 1.00. The thickness of all films produced was assessed by surface roughness measurement and atomic force microscopy (AFM), with the cyclic layer thickness being estimated from the satellite peaks obtained by X-ray diffraction (XRD).

The crystal structure of the films was also examined by XRD, using CuK$_\alpha$ radiation and a scan speed of 1°/min across a2θ angle range of 20° to 120°. Electrical measurements were conducted using a configuration of platinum/BTO film/STO substrate, the platinum electrodes being deposited by sputtering through a metal shadow mask with an area of 0.25 mm$^3$. The capacitance and dielectric loss tangent were measured by a LCR meter (HP4284A) at frequencies ranging from 100 Hz to 1 MHz and temperatures of between 250 to 400 K. Dielectric constants were calculated by the following equation:
Figure 2. XRD patterns of (a) BaTiO$_3$ film, (b) SrTiO$_3$/BaTiO$_3$ film and (c) BaTiO$_3$/SrTiO$_3$ film deposited on Pt/Ti/SiO$_2$ substrates.

\[ C_p = \varepsilon_0 \varepsilon_r \cdot S/t, \]

where \( C_p \) is the capacitance, \( \varepsilon_r \) is the dielectric constant, \( S \) is the electrode area, \( t \) is the thickness of film and \( \varepsilon_0 \) is the dielectric constant in a vacuum (8.854 x 10^{-12} \text{ F/m}).

### 3. Results and discussions

#### 3.1 Effect of build-up sequence on crystal grain growth

In the case of both the 100 nm thick STO film formed on a 100 nm thick BTO layer on a Pt(111)/Ti/SiO$_2$/Si substrate, and the 200 nm thick BTO film produced directly on the same substrate, the XRD peak intensity of BTO(111) was extremely low, as shown in Figure 2. On the other hand, with the 100 nm thick BTO film on a 100 nm thick STO layer, this BTO(111) diffraction can be clearly observed; thus providing a strong indication of epitaxial BTO grain growth on a Pt(111)/Ti/SiO$_2$/Si substrate. It is considered that this epitaxial grain growth occurs due to a relaxation of the lattice mismatch between the BTO(111) and Pt(111) by the formation of the STO layer between them. The lattice spacing of Pt(111) in the [1-10] direction is 0.5548 \text{ nm}, and that of BTO and STO are 0.5648 \text{ nm} and 0.5522 \text{ nm}, respectively. The lattice mismatch can therefore be calculated by Eq (2):

\[ \Delta f = (f_f-f_s)/(f_s), \]

where \( f_f \) is the lattice spacing of the film and \( f_s \) is the lattice spacing of the substrate.

The lattice mismatches between Pt and BTO, and between Pt and STO, are calculated to be 1.80 and 0.47 \%, respectively. Although the XRD peak of STO(111) normally observed at 20=39.9 is not evident in Figure 2, this is simply because the small lattice mismatch between STO(111) and Pt(111) means that it is obscured by the far more intense Pt(111) peak. The lattice mismatch between Pt(111) and BTO(111) in the [10-1] and [0-11] direction is 2.38 \%, whereas the mismatch of the BTO (111)/Pt(111) interface is 2.28 \% in the [1-10] direction and 2.86 \% in the [10-1] and [0-11] direction. The mismatch of the STO(111)/Pt(111) interface is the smallest amongst all of the material combinations tested in this study. However, the hetero-joining of materials of the same crystal structure has been known to produce epitaxial crystal growth, even with a large lattice mismatch [5]. It is therefore considered that the lattice spacing and crystal orientation of the STO(111) formed on Pt(111) promotes the formation of BTO(111), which has a relatively large lattice mismatch with the Pt substrate. Consequently, subsequent experiments utilized STO(111) single crystals produced by STO deposition as the substrate, in order to more precisely control the crystal growth of the deposited films.

#### 3.2 $\text{Ba}_{1-x}\text{Sr}_x\text{TiO}_3$ single layer thin film

With the single layer BSTO thin film deposited on a STO(111) substrate, only XRD peaks of BSTO(111) were observed; this clearly indicating epitaxial grain growth of the deposited layer from
the substrate. The lattice spacing of the (111) plane (d(111) value), as calculated from the diffraction angle of the BSTO(111) films, exhibited a linear relationship with regards to composition (x), as shown in Figure 3. For comparison, the lattice spacing of the (111) plane estimated from JCPDS cards for BTO and STO using Vegard’s law is also shown. From this, we can see that the difference between the two lines becomes larger with a reduction in x, indicating that the lattice mismatch between the BSTO film and STO substrate also becomes larger. However, even under such conditions, epitaxial crystal growth of BSTO from the STO(111) substrate is still maintained.

A compressive strain of about 0.5 GPa has previously been reported at the interface of a super lattice [6], which was found to lead to an increase in the dielectric constant. It is therefore expected that the use of a super lattice will show great potential for producing materials with unprecedented properties [7]. Since this compressive strain is introduced parallel to the (111) plane, it is increased when the crystal grows along the (100) plane. The fact that the BSTO crystal grew epitaxially, despite the large lattice mismatch, suggests that the lattice of the films is expanded by the compressive strain as a rhombohedral crystal in the <111> direction. To ascertain whether there is indeed any difference in the dielectric properties between the upper and lower electrodes, the electrical field was applied in a vertical direction relative to the substrate.

Figure 4 shows the temperature dependence of the dielectric constants of the BSTO single layer films. Of significance is the fact that the BSTO thin films do not appear to exhibit a maximum value around the phase transformation temperature of 393K, a phenomenon which is commonly seen in bulk BTO ceramics. This arises because the phase transition temperature of the BTO-STO ceramic system becomes lower with an increase in STO content, and thus the temperature at which a maximum occurs is reduced [8]. In practice, however, the temperature corresponding to a maximum dielectric constant in STO bulk ceramics has been reported to be as low as absolute zero [8-9]. The BSTO films produced in the present work show a very different behavior to their bulk phase with regards to the temperature dependence of their dielectric characteristics. For instance, in the case of the film with a composition of x=0.25, there is no change in the dielectric constant value of 320 with a change in temperature. This is attributed to the temperatures used in this experiment being well below the Curie temperature of BSTO, the point beyond which BSTO exhibits a characteristic positive temperature coefficient. The dielectric loss, tan δ, was found to increase at elevated temperatures, but was sufficiently low (~0.02) below room temperature. On the other hand, the frequency dependence of the dielectric constant did vary as the temperature increased. When the STO content of the film was increased, i.e. x=0.50, the

Figure 3. Temperature dependence of the dielectric constant and dielectric loss for (a) x=0.25, (b) x=0.50 and (c) x=0.75 in single layer Ba$_{1-x}$Sr$_x$TiO$_3$ films.
dielectric constant was found to increase with decreasing temperature. Moreover, for a given frequency, the dielectric constant of the x=0.75 film was smaller than that of the x=0.25 film. The dielectric constant of the bulk ceramic was greatest at x=0.60 and a temperature of about 210K [10] with the Ba$_{1-x}$Sr$_x$TiO$_3$ thin films exhibiting a similar tendency.

As shown in Figure 5, the dielectric constant at room temperature did moderately increase in relation to $x$ to a maximum at $x=0.50$, but abruptly decreased at higher $x$ values. Both the dielectric constant and dielectric loss were found to be dependent on frequency in the case of the STO thin-film, though this was not observed in the other thin-films. This same frequency dependence was also observed in the case of the STO thin film deposited on a STO(111) substrate, most likely due to the internal strain resulting from the small difference in d(111) shown in Figure 3. From this point of view, the fact that the BSTO thin film in which $x=0.0$ has the largest lattice mismatch means that it should have the highest dielectric constant; and yet the results obtained are quite contradictory. In the Ba$_{1-x}$Sr$_x$TiO$_3$ thin
film, a variation in the temperature dependence of the dielectric constant was observed with different levels of STO addition. Furthermore, such temperature dependence was seen only when \( x \) was greater than 0.5, as shown in Figure 4.

The results presented in this section indicate that the effect of STO addition on the dielectric characteristics of single layer BSTO films is dependent on the amount of STO addition (i.e. \( x \)). Given that STO addition in BTO-STO ceramics is known to reduce the influence of the phase transformation temperature, the results shown in Figure 4 and Figure 5 are believed to incorporate the effects of the phase transformation temperature changes on the dielectric characteristics.

3.3 (BaTiO\(_3\))\(_{1-x}\)(SrTiO\(_3\))\(_x\) multi-layer thin film

In the previous section, the factors influencing the dielectric characteristics of single layer films were found to be related to residual compressive strain at the material interface and the ratio of STO addition. This subsequently led to the idea that the use of multiple thin layers may have the potential to enhance this effect by increasing the number of hetero epitaxial interfaces. The PLD process used in this study can individually control the composition of each layer, and the number of artificial interfaces, simply by changing the thickness of each layer. Consequently, this section explores the possibility of improving the dielectric characteristics through the use of multi-layer (BaTiO\(_3\))\(_{1-x}\)(SrTiO\(_3\))\(_x\) thin films.

As shown in Figure 6, the XRD patterns of (BaTiO\(_3\))\(_{1-x}\)(SrTiO\(_3\))\(_x\) multi-layer thin-films with compositions of \( x = 0.25, 0.50 \) and 0.75 have a clearly discernible BSTO(111) main peak, and a number of satellite peaks, when the number of layers exceeds 10. The presence these higher-order satellite peaks adjacent to the main peak indicates the formation of a coherent film with a periodically modulated structure, in which there is a single in-plane lattice parameter throughout the entire film thickness \[11\]. This BTO-STO super lattice consisted of layers with two distinctly different lattice constants, and hence, a compressive stress was induced in the BTO layers by the STO layers\[12\].

In the BTO-STO multi-layer thin films, the diffraction angle of the main BSTO(111) peak was shifted to a higher angle and approached the main peak of STO(111) with increasing STO content. It should be noted that this STO(111) peak is the same as that of the single-layer STO thin films. The layer thickness of the super lattice was subsequently calculated from the diffraction angles of the main BSTO(111) peak and its satellite peaks according to Eq. (3).

\[
\Lambda = (m \lambda)/(2(\sin \theta_m - \sin \theta_0))
\]

Figure 6. XRD patterns of multi-layered Ba\(_{1-x}\)Sr\(_x\)TiO\(_3\) films with a stacking period of 20, the thickness of each layer being (a) [BTO(2.5 nm)/STO(7.5 nm)]\(_{20}\) cyclic layers (b) [BTO(5.0nm)/STO(5.0 nm)]\(_{20}\) cyclic layers and (c) [BTO(7.5 nm)/STO(2.5 nm)]\(_{20}\) cyclic layers.
From this, the cyclic layer thickness of the BTO-STO super lattice thin films were calculated to be (a) 9.0 nm, (b) 11.0 nm and (c) 10.7 nm, which were almost equivalent to the designed thickness of 10 nm.

Figure 7 shows the effect of the layer thickness on the dielectric constant and dielectric loss for multi-layer BSTO thin films with average compositions of $x=0.25$, $x=0.50$ and $x=0.75$. For reference, the values for single layer BTO and STO thin films are also shown in this figure. This clearly demonstrates that the dielectric constant for the multi-layer film in which $x=0.25$ is increased relative to a single layer film as a result of the multiple layers. Furthermore, the dielectric constant of the multi-layer film drastically increased when the cyclic thickness of STO and BTO was reduced below 7.5 nm and 2.5 nm, respectively; whilst a maximum value of 530 was obtained at BTO(3 nm)/STO (1nm). The dielectric loss, $\tan \delta$, remained at less than 0.02 regardless of the change in the average composition.

The dielectric constant at $x=0.50$ was observed to increase when the cyclic thickness was below BTO(10 nm)/STO(10 nm), whereas a maximum value of 560 was obtained at BTO(2 nm)/STO(2 nm).

Further reduction of the cyclic layer thickness reduced the dielectric constant; however, the dielectric constant obtained above BTO(5 nm)/STO(5 nm) was found to be smaller than that of a single thin film of $x=0.5$. Put simply, this means that the dielectric constant is reduced to a level comparable to that of a single layer film when the cyclic layer thickness is within a range of between 10 and 100 nm.

Furthermore, although the dielectric constant of a single layer film in which $x=0.50$ is larger than if $x=0.25$, as shown in Figure 5; the maximum dielectric constant obtained with a multi-layer thin film of $x=0.5$ was almost equivalent to that of $x=0.25$, with composition therefore having no observable effect.

![Figure 7](image-url)

**Figure 7.** Dielectric constants and dielectric loss at a frequency of 10kHz at room temperature for (a) $x=0.25$, (b) $x=0.50$ and (c) $x=0.75$ for multi-layered $(\text{BaTiO}_3)_{1-x}(\text{SrTiO}_3)_x$ films.
Other factors with the potential to induce strain may have influenced these results, although the detailed mechanism of these is not well understood currently. Nevertheless, the effect of strain induced by the multiplication of layers has been said to be enhanced as the cyclic layer thickness decreases. It has also been reported that a maximal dielectric constant is obtained when the cyclic layer thickness is 0.8 nm [9] or 0.45 nm [10], with an orientation of (001) [9] and (111) [10], respectively. In both of these cases, a substrate temperature of about 873 K was.

In the present work, the maximal dielectric constants of 530 for $x=0.25$ and 560 for $x=0.5$ were almost equivalent to those value reported in the literature, but their corresponding cyclic layer thicknesses were notably different. The reason for this is considered to be the difference in the substrate temperature used, which at 973 K was 100 K higher than that used in the aforementioned studies. This increased temperature is likely to result in greater diffusion of elements across the interface of each layer, which would subsequently affect the dielectric constant.

The dielectric constant of the multi-layer films in which $x=0.75$ was larger than that of the single layer thin films in which $x=0.75$. Moreover, the dielectric constant drastically increased when the cyclic thickness was reduced below BTO (2.5 nm)/STO (7.5 nm); the maximum value of 550 being obtained with the lowest thickness, i.e. BTO (1 nm)/STO (3 nm).

4. Conclusions

Three types of layered (Ba,Sr)TiO$_3$ thin films were fabricated by pulsed laser deposition and their dielectric characteristics were examined in detail. The findings can be summarized as follows:

1. In the case of a single layer BaTiO$_3$ (BTO) thin film deposited on SrTiO$_3$ (STO) film, a BaTiO$_3$ (111) diffraction peak was clearly observed. This indicates an epitaxial crystal relationship exists between BaTiO$_3$ films and Pt(111) substrates, which results from the relaxation of the lattice mismatch between them that is induced by the SrTiO$_3$ layer.

2. The dielectric constant of Ba$_{1-x}$Sr$_x$TiO$_3$ single layer thin films is dependent on the STO composition, $x$. The largest dielectric constant was obtained when $x=0.5$; increasing at low temperatures when $x\geq 0.5$, but showing no temperature dependency when $x<0.5$.

3. Examination of multi-layer (BaTiO$_3$)$_{1-x}$(SrTiO$_3$)$_x$ thin films by XRD showed clear evidence of a main peak attributable to (BaTiO$_3$)$_{1-x}$(SrTiO$_3$)$_x$(111), and additional satellite peaks, when the number of layers exceeded 10. The cyclic layer thickness of this super lattice was estimated from the diffraction angles to be approximately 10 nm, which corresponds well with the result expected from the conditions of pulsed laser deposition used.

4. In the (BaTiO$_3$)$_{1-x}$(SrTiO$_3$)$_x$ multi-layer thin films, the dielectric constant was found to improve with an increasing number of cyclic layers. A (BaTiO$_3$)$_{1-x}$(SrTiO$_3$)$_x$ multi-layer thin film with a cyclic layer thickness of 2 nm, 50 layers and $x=0.50$, i.e. [BTO(2 nm)/STO (2 nm)]$_{50}$ cyclic layers, $x=0.50$, exhibited the maximal dielectric constant of 560.

References

[1] Hino T et al 1999 J. Soc. Mat. Sci. 48 777
[2] Hino T et al 2003 Vacuum 70 47
[3] Tabata H, Tanaka H and Kawai T 1994 Appl. Phys. Lett. 65 1970
[4] Koinuma H, Aiyer H N and Matsumoto Y 2000 Sci. Tech. Adv. Mat. 1 1
[5] Yang G Z et al 1997 Phy. Lett. 14 478
[6] Wiener-Avnear N 1994 Appl. Phys. Lett. 65 1784
[7] Abe K and Komatsu S 1995 J. Appl. Phy. 77, 6461
[8] Haeni J H et al 2004 Nature 430 758
[9] Muller D A et al 2004 Nature 430 657
[10] Koinuma H 2001 The oxide electronics (Tokyo: Baifukan) p137 [in Japanese]
[11] Hino T et al 2007 J. Laser Micro/Nanoengineering 2 166
[12] Harigai T et al 2009 Thin Solid Films 609 13