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Effects of Lanthanides-Substitution on the Ferroelectric Properties of Bismuth Titanate Thin Films Prepared by MOCVD Process

Byong-Ho Kim and Dong-Kyun Kang†

Department of Materials Science and Engineering, Korea University, Seoul 136-713, Korea
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ABSTRACT

Ferroelectric lanthanides-substituted $Bi_4Ti_3O_{12}$ ($Bi_{4-x}Ln_xTi_3O_{12}$, BLnT) thin films approximately 200 nm in thickness were deposited by metal organic chemical vapor deposition onto $Pt(111)/Ti/SiO_2/Si(100)$ substrates. Many researchers reported that the lanthanides substitution for Bi in the pseudo-perovskite layer caused the distortion of TiO_6 octahedron in the a-b plane accompanied with a shift of the octahedron along the a-axis. In this study, the effect of lanthanides (Ln=Pr, Eu, Gd, Dy)-substitution and crystallization temperature on their ferroelectric properties of bismuth titanate ($Bi_4Ti_3O_{12}$, BIT) thin films were investigated. As BLnT thin films were substituted to lanthanide elements (Pr, Eu, Gd, Dy) with a smaller ionic radius, the remnant polarization ($2P_r$) values had a tendency to increase and made an exception of the Eu-substituted case because $Bi_{4-x}Eu_xTi_3O_{12}$ (BET) thin films had the smaller grain sizes than the others. In this study, we confirmed that better ferroelectric properties can be expected for films composed of larger grains in bismuth layered peroskite materials. The crystallinity of the thin films was improved and the average grain size increased as the crystallization temperature increased from 600 to 720°C. Moreover, the BLnT thin film capacitor is characterized by well-saturated polarization-electric field (P-E) curves with an increase in annealing temperature. The BLnT thin films exhibited no significant degradation of switching charge for at least up to 1.0×10^{11} switching cycles at a frequency of 1 MHz. From these results, we can suggest that the BLnT thin films are the suitable dielectric materials for ferroelectric random access memory applications.

Key words : Ferroelectric, Lanthanides-substituted, Randomly-oriented, Fatigue-free

1. Introduction

Attention to Aurivillius phases, which constitute a wide family of layered compounds, has increased because of their potential use in electronic and optic devices.[1] $Bi_4Ti_3O_{12}$ (BIT) and related materials of the Aurivillius family consists of a layered-structure of $(Bi_2O_2)^{2+}$ and $(A_2B_3O_{10})^{2-}$ pseudo-perovskite layers stacking along the c-axis direction. The electrical properties as well as the ferroelectricity of BIT show a strong anisotropic nature originating from the layered structure. In the structure, perovskite blocks, $(Bi_2Ti_3O_{10})^{2-}$, are interleaved with $(Bi_2O_2)^{2+}$ layers along the c-axis, and ferroelectricity arises mainly in the perovskite blocks. In contrast, it has been reported that the resistivity along the c-axis is two to three orders of magnitude higher than that in the a-b plane because the $(Bi_2O_2)^{2+}$ layer acts as an insulating layer.[2,3]

BIT-based materials have been extensively studied because of their large spontaneous polarization along the a-axis, low processing temperature, and high Curie temperature. However, BIT thin film shows serious degradation of ferroelectric properties after being subjected to ~10^6 read/write switching cycles.[4] In a previous study, to improve its relatively low remnant polarization and fatigue properties, some of the trivalent elements, such as La^{3+} and Nd^{3+}, were used to substitute Bi^{3+} at A-site.[5] Park *et al.*[6] found that $Bi_{3.25}La_{0.75}Ti_3O_{12}$ (BLT) thin film annealed at 650°C exhibits a large remnant polarization (P_r=12 μC/cm^2) and good fatigue characteristics even after 3×10^{10} switching cycles. It was also found that Nd doping of BIT film leads to a high P_r value of 25 μC/cm^2.[5] From these results, an enhanced remnant polarization and nearly fatigue free property were acquired. The remnant polarization of Nd-substituted $Bi_4Ti_3O_{12}$ is larger than that of La, and this was attributed to the smaller ion radius of Nd than that of La for the size of the A-cation significantly influencing the structural distortion. The origin of ferroelectric polarization in the Aurivillius phase was due to the large distortion of TiO_6 octahedra and the displacement of the Bi_2O_2 layers with respect to the perovskite structure. Considering that the substitution with smaller cation could cause considerably larger distortion and more internal stress, which might result in a larger remnant polarization, we attempted here to use Ln (Pr^{3+}, Eu^{3+}, Gd^{3+}, Dy^{3+}) as the candidate to substitute A-site Bi^{3+}.[7-9] Therefore, understanding the substitution technique known as "site engineering" is essential for improving its ferroelectric properties.[4]

A number of different methods have been developed to prepare Bi-layered perovskite thin films, including dry

†Corresponding author : Dong-Kyun Kang
E-mail : adonis1128@empal.com
Tel : +82-2-921-9237 Fax : +82-2-928-3584

methods, such as sputter deposition,[10] laser ablation deposition and Pulsed Laser Deposition (PLD),[11] and chemical methods, such as sol-gel deposition,[12] Metalorganic Decomposition (MOD),[13] and Metal Organic Chemical Vapor Deposition (MOCVD).[14] Among these different methods, MOCVD, whose characteristic features include good step coverage, a high deposition rate, the ability to deposit high quality films, good control of the composition, and uniformity over a large area, is particularly attractive. However, the conventional bubbler type MOCVD of oxides leads to poor quality composition and a discontinuous growth rate, because of the decomposition of the precursors in the hot container. To overcome these problems, liquid source delivery MOCVD has been developed. The major advantage of using a single-mixture liquid source, as compared to a solid source, is that the stoichiometry of the deposited film can be controlled by precisely adjusting the ratio of the individual components in the liquid cocktail source.[15]

In this study, the fabrication and properties of the lanthanide-substituted BIT (BLnT) thin films were prepared by the liquid delivery Metal Organic Chemical Vapor Deposition (MOCVD) technique. The effect of different substitution levels on the ferroelectric properties was investigated. The mechanisms behind the substitution effects on the ferroelectric properties are also discussed.

2. Experimental Procedure

Ferroelectric BLnT thin films with thickness of about 200 nm were deposited on Pt(111)/Ti/SiO_2/Si(100) substrate by means of the liquid delivery metal organic chemical vapor deposition process. Triphenyl bismuth [$Bi(ph)_3$, 99%, Strem Chemicals], tris (2,2,6,6-tetramethyl-3,5-heptanedionato) lanthanide ion metal [$Ln(TMHD)_3$, 99%, Strem Chemicals] and di (iso-propoxide) bis (2,2,6,6-tetramethyl-3,5-heptanedionato) titanium [$Ti(O^iPr)_2(TMHD)_2$, 98%, Strem Chemicals], were used as starting materials for Bi, Ln and Ti, respectively. The precursors were dissolved together in n-butyl acetate (99.5%, Aldrich) to form one stock solution.

The typical deposition conditions are summarized in Table 1. A single mixture solution, the so-called cocktail source, of $Bi(ph)_3$, $Ln(TMHD)_3$ and $Ti(O^iPr)_2(TMHD)_2$ precursors was prepared to be used in liquid delivery MOCVD.

Table 1. MOCVD Process Conditions Used to Deposit BLnT Thin Films

Deposition parameters	Range investigated
Substrate temperature	540-600°C
Total reactor pressure	3-6 Torr
Vaporizer temperature	200-220°C
Stock solution concentration [Bi : Ln : Ti]	0.05 : 0.01 : 0.05 (M)
Carrier gas (Ar) flow rate	200 sccm
Oxidizing gas (O_2) flow rate	200 sccm

BLnT thin films were deposited on a Pt(111)/Ti/SiO_2/Si(100) substrate. Thereafter, the films were annealed at various temperatures in oxygen ambient for 1 h in order to enhance the electrical properties of the thin film. To investigate the ferroelectric properties of the films, platinum top electrodes with a diameter of 200 μm were deposited on the film surface via sputter technique using a shadow mask, and then the films were post-annealed in oxygen ambient for 30 min at same temperatures. The thermal stability of the BLnT precursors was confirmed by TG analysis. The XRD (X-Ray Diffraction; Rigaku, DMAX2500, 30 kV, 30 mA) patterns of the films were recorded to investigate the crystallographic structure of the films in the 2θ range of 10-70° using filtered CuKα radiation. The microstructure of the layered perovskite phase and the thickness of the thin films were analyzed by SEM (Scanning Electron Microscopy; Hitachi, S-4300, 15.0 kV). The electrical properties and reliability of the thin films were measured at room temperature using a standardized ferroelectric tester (Radiant Technologies Inc, RT66A).

3. Results and Discussion

3.1. Crystalline Phases and Preferred Orientations of BLnT Thin Films

Fig. 1 shows the XRD patterns of the BLnT thin films fabricated by the MOCVD process with different annealing temperatures ranging from 600 to 720°C. The peaks were indexed according to the standard powder diffraction data for $Bi_4Ti_3O_{12}$. The BLnT thin films were crystallized into a layered perovskite phase after annealing. Annealing above 600°C resulted in the production of well-crystallized BLnT films. As the annealing temperature of the films was increased from 600 to 720°C, the peaks in the XRD patterns became sharper. The obtained BLnT thin films exhibited a polycrystalline structure with no pyrochlore phase or preferred orientation. The correlation of the diffraction peaks of the BLnT thin films with those of $Bi_4Ti_3O_{12}$ (BIT) implies that the Ln substitution does not affect the layered perovskite structure of BIT. This indicates that the Ln^{3+} ions in the BLnT films do not form a pyrochlore phase, but dissolve into the pseudo-perovskite structure, and that Ln^{3+} ions can readily substitute for Bi^{3+} ions in this pseudo-perovskite structure.[16] Furthermore, the (117) peak is the strongest in patterns of films annealed at temperatures higher than 640°C, as shown in Fig. 1. This indicates that BLnT thin fims annealed at temperatures higher than 640°C were more randomly oriented.

3.2. Surface Morphology of BLnT Thin Films

Fig. 2 shows surface SEM micrographs of various BLnT thin films annealed at 720°C for 1 h in an oxygen atmosphere. The surface morphology is very sensitive to the annealing temperature. The surface of the BLnT thin films annealed at 600°C consisted of small grains and had a flat surface morphology. The surface of the BLnT thin films

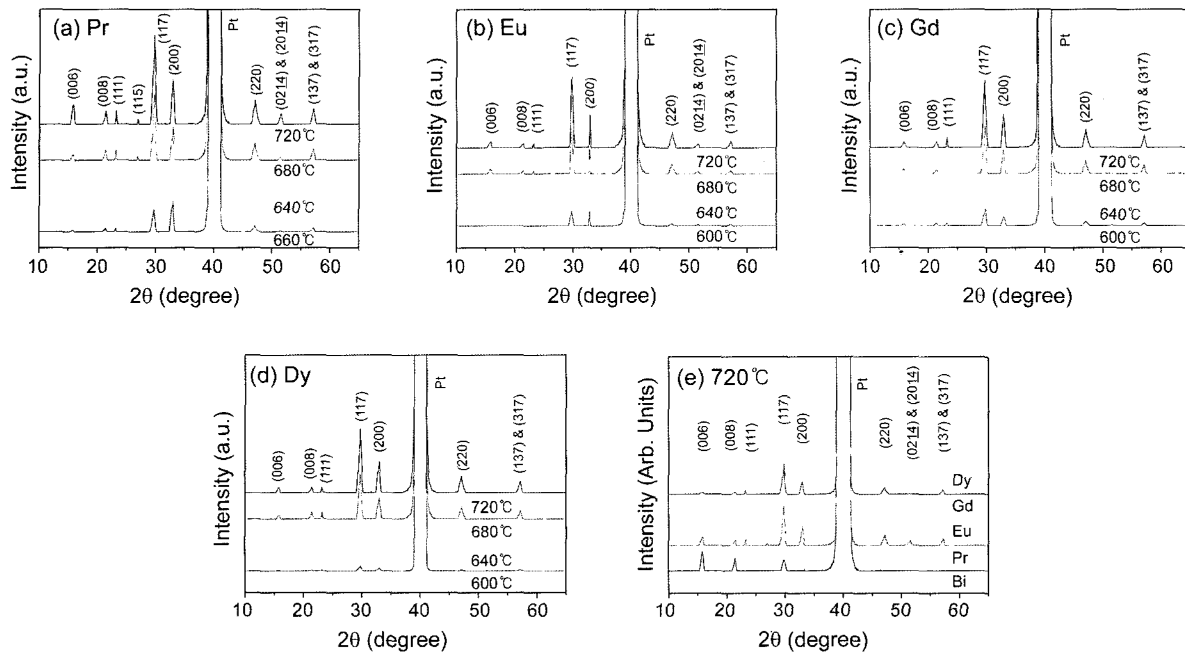

Fig. 1. XRD patterns of various BLnT thin films annealed at temperatures ranging from 640°C to 720°C.

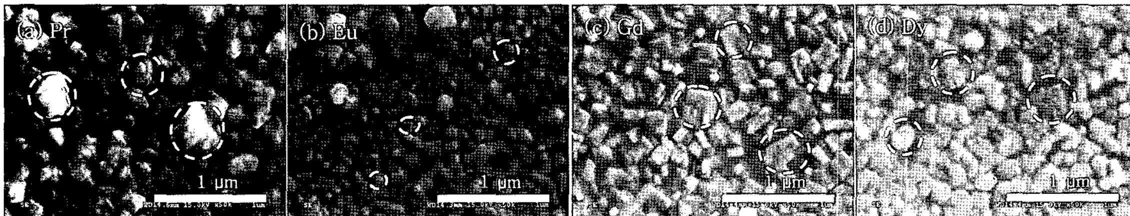

Fig. 2. SEM micrographs of various BLnT thin films annealed at 720°C.

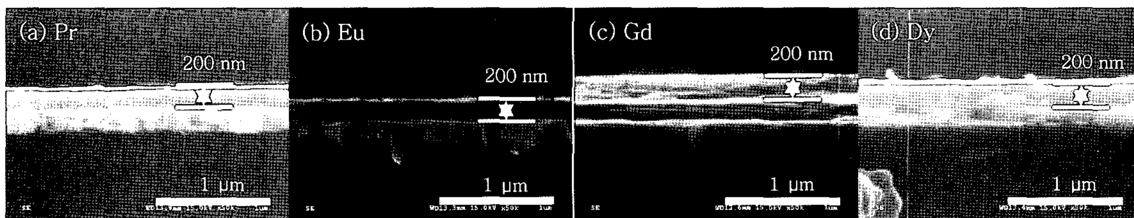

Fig. 3. Cross-sectional SEM images of various as-deposited BLnT thin films.

annealed at 640°C contained pseudo-spherical particles, exhibited intermediate grain growth of the layered perovskite phase, and had a somewhat rough surface morphology. Some of the grains became larger in case of the BLnT thin films annealed at 680°C, and their surfaces consisted of relatively large grains. The grain size of the BLnT thin film annealed at 720°C ranges from 0.1 to 0.3 μm. The grain size of the films increased with annealing temperature. It is assumed that crystal growth was enhanced, and thus that the ferroelectric properties of the films can be improved by increasing the temperature. Fig. 3 shows cross-sectional SEM micrographs of various as-deposited BLnT thin films on a platinized Si substrate. The thickness of various BLnT thin films was approximately 200 nm. The cross-sectional SEM images revealed a dense microstructure with a uniform thickness.

3.3. Electrical Properties of the BLnT Thin Films

The ferroelectric hysteresis loops of various BLnT thin film capacitors annealed at 720°C are shown in Fig. 4. The BLnT thin films were measured at various applied voltages ranging from 1 to 5 V. As presented in Fig. 4, the BLnT thin film capacitors are characterized by well-saturated polarization-electric field (P-E) curves. Among them, the $2P_r$ value of the BDT thin film was the largest. The $2P_r$ and $2E_c$ values of the BDT thin film annealed at 720°C were 43.25 $\mu C/cm^2$ and

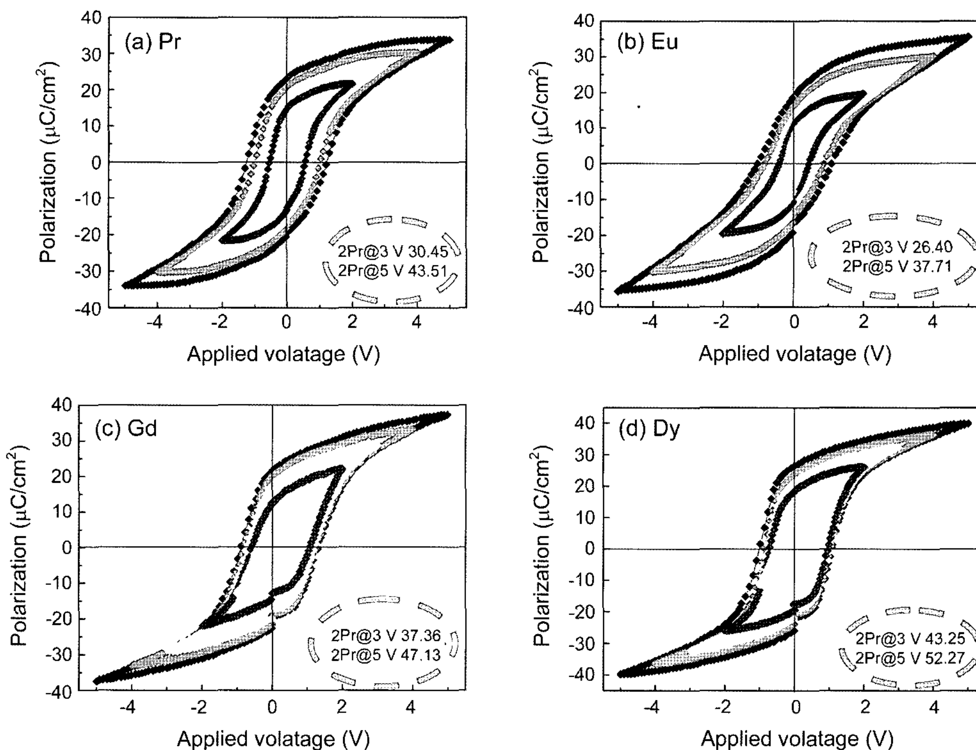

Fig. 4. Hysteresis loops of various BLnT thin films annealed at 720°C.

0.97 V at an applied voltage of 3 V and 52.27 μC/cm^2 and 1.05 V at an applied voltage of 5 V, respectively, indicating high ferroelectric performance. As BLnT thin films were used in place of lanthanides element (Pr, Eu, Gd, Dy) with a smaller ionic radius, the remnant polarization ($2P_r$) values had a tendency to increase. This result can be explained by the shift of the TiO_6 octahedra in the layered structure due to the substitution of Ln^{3+} ions for Bi^{3+} ions since Ln^{3+} has a smaller ionic radius than Bi^{3+}. The origin of ferroelectric polarization in the Aurivillius phase was due to the large distortion of TiO_6 octahedra and the displacement of the Bi_2O_2 layers with respect to the perovskite structure. Considering that the substitution with a smaller cation could cause considerably larger distortion and more internal stress, which might result in a larger remnant polarization. Hence, the substitution for Bi in the layer structure enhances the ferroelectric properties.[17] However, the remnant polarization ($2P_r$) value made an exception in the Eu-substituted case because BEuT thin films had smaller grain sizes than the others. It is well known that grain size is closely related to ferroelectric properties in both simple ABO_3 type materials and bismuth layered perovskite materials. Generally, better properties can be expected for films composed of larger grains.[18]

3.4. Reliability of the BLnT Thin Films

Fig. 5 shows the fatigue characteristics of various BLnT thin films annealed at 720°C. The fatigue test was conducted using 5 V bipolar pulses at 1 MHz produced by a function generator. The BLnT thin films exhibited a fatigue-free characteristic with no polarization reduction up to 1×10^{11} switching cycles. Ferroelectric properties are affected by defects, such as oxygen and metal ion vacancies within the structure of materials. In case of BIT, oxygen vacancies must be generated along with bismuth vacancies, which were associated with the Bi_2O_3 volatilization that occurred

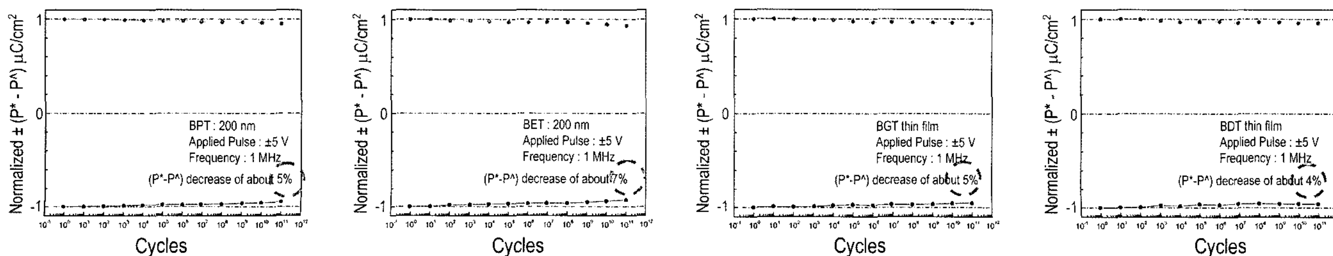

Fig. 5. Ferroelectric fatigue in various BLnT thin films.

during an annealing processing at elevated temperatures. The reasons for the improvement of electric properties in the BIT films might result from the use of 20% excess Bi_2O_3 to compensate for Bi loss, and/or the processing methods employed to reduce the generation of Bi and O vacancies. On the other hand, when lanthanide elements are incorporated into the BIT system, lanthanide elements seem to be placed more favorably in some of the Bi sites due to the ionic size and valence of lanthanide elements. In the BLnT thin films, lanthanide elements were also known to occupy some Bi sites. Therefore, we believe that the fatigue-free behavior of the lanthanide-doped BIT film is due to the chemical and structural stabilization of perovskite layers by the inclusion of lanthanide ions, as well as a possible charge-compensating role in the Bi_2O_2-layers.[19] The Pt/BLnT/Pt capacitors exhibited almost no polarization fatigue after electric field cycling for up to 1×10^{11} switching cycles at an applied voltage of 5 V.

4. Conclusions

In this paper, we report the preparation and electrical properties of $Bi_{4-x}Ln_xTi_3O_{12}$ (Ln : Pr, Eu, Gd, Dy) thin films for applications in FeRAMs. It was found in this study that the presence of lanthanide elements in the $Bi_4Ti_3O_{12}$ lattice affects its ferroelectric characteristics. Ln-substituted BIT thin films with 200 nm thickness were deposited onto a Pt(111)/Ti/SiO_2/Si(100) substrate by a liquid delivery MOCVD process. By using X-ray diffraction and a scanning electron microscope to analyze the structure and morphology of the films, it was found that the lanthanide elements substitution of Bi at the A-site induces changes in film orientation and the lattice distortion that are probably responsible for the improved ferroelectric properties. The BLnT thin films showed good ferroelectric properties and excellent fatigue-free characteristics that can satisfy the requirements for high-density Complementary Metal Oxide Semiconductor (CMOS) devices. From these results, we can confirm that the BLnT thin films are potentially important candidates for non-volatile ferroelectric memories applications.

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