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The Microstructure and Ferroelectric Properties of Ce-Doped $Bi_4Ti_3O_{12}$ Thin Films Fabricated by Liquid Delivery MOCVD

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ABSTRACT

Ferroelectric Ce-doped $Bi_4Ti_3O_{12}$ (BCT) thin films were deposited by liquid delivery metal organic chemical vapor deposition (MOCVD) onto a Pt(111)/Ti/SiO_2/Si(100) substrate. X-ray diffraction (XRD) and scanning electron microscopy (SEM) were used to identify the crystal structure, the surface, and the cross-section morphology of the deposited ferroelectric films. After annealing above 640°C, the BCT films exhibited a polycrystalline structure with preferred (00*l*) and (117) orientations. The BCT film capacitor with a top Pt electrode showed a large remnant polarization ($2P_r$) of 44.56 μC/cm^2 at an applied voltage of 5 V and exhibited fatigue-free behavior up to 1.0×10^{11} switching cycles at a frequency of 1 MHz. This study clearly reveals that BCT thin film has potential for application in non-volatile ferroelectric random access memories and dynamic random access memories.

Key words *: Ce-doped* $Bi_4Ti_3O_{12}$*, Polycrystalline, Randomly oriented, Fatigue-free*

1. Introduction

Ferroelectric thin films have attracted considerable attention for their potential applications in non-volatile ferroelectric random access memories (NvFeRAMs).[1] $Pb(Zr_xTi_{1-x})O_3$ (PZT) thin films with various compositions have been extensively studied as promising FeRAM candidate materials. Despite having advantages such as low processing temperatures and large remnant polarizations (P_r), PZT films with metal electrodes have been found to exhibit ferroelectric fatigue. Although the application of conductive oxide electrodes greatly improves the fatigue resistance of PZT, it also increases the process complexity and causes a larger leakage current. Also, due to the toxicity of lead, lead-free materials are preferred for use in memory applications from the viewpoint of environmental protection.[2-3] A constant search for lead-free materials with essentially fatigue-free behavior has led to the advent of a new generation of ferroelectric thin films with a bismuth oxide-layered structure. Recently, lead-free $SrBi_2Ta_2O_9$ (SBT) films are of great interest for ferroelectric memory applications partly due to their high fatigue endurance. However, SBT films suffer from some disadvantages, such as very low switchable remnant polarization values and high processing temperatures.[4-5] Recent studies have revealed that the Bi^{3+} ions in the $Bi_4Ti_3O_{12}$ (BTO) structure could be substituted by trivalent rare-earth ions, such as Ce^{3+}, Pr^{3+}, Nd^{3+}, Sm^{3+}, Eu^{3+}, Gd^{3+}, or Dy^{3+} to improve the electrical properties.[6-12] The rare-earth ions are attractive lead-free materials for memory applications because they have a large $2P_r$ and a high fatigue resistance in common Pt electrodes, which make them applicable to direct commercialization. Among these ions, Ce-doped $Bi_4Ti_3O_{12}$ (BCT) has been receiving more attention because it has a larger $2P_r$ than that of the La-doped $Bi_4Ti_3O_{12}$ (BLT) which is the most widely studied currently. BCT thin films have excellent $2P_r$ values that are comparable with those of conventional Pb-based ferroelectric films such as PZT.[13-14] In this study, we report the fabrication of the BCT thin films on Pt/Ti/SiO_2/Si(100) substrates using a liquid delivery MOCVD and their ferroelectric and electric properties including $2P_r$ and leakage current.

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2. Experimental procedure

Ferroelectric BCT thin films of approximately 200 nm in thickness were deposited on a Pt(111)/Ti/SiO_2/Si(100) substrate using a 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) cerium [$Ce(TMHD)_4$, 99%, Strem Chemicals], and di (isopropoxide) bis (2,2,6,6-tetramethyl-3,5-heptanedionato) titanium [$Ti(O^iPr)_2(TMHD)_2$, 98%, Strem Chemicals], were used as precursors for the components of Bi, Ce 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, called the cocktail source, of $Bi(ph)_3$, $Ce(TMHD)_4$, and $Ti(O^iPr)_2(TMHD)_2$ pre-

Table 1. MOCVD Process Conditions Used to Deposit the BCT thin Films

Deposition Parameter	Range Investigated
Substrate temperature	540 - 600°C
Total reactor pressure	3 - 6 Torr
Deposition time	50 min
Ar flow rate	200 sccm
O_2 flow rate	200 sccm
Precursor solution concentration [Bi:Ce:Ti]	0.05:0.01:0.05 (M)
Flow rate of precursor solution	0.1 ml/min
Vaporizer temperature	200 - 220°C

cursors was prepared to be used in the liquid delivery MOCVD. The BCT thin films were deposited on a Pt(111)/Ti/SiO_2/Si(100) substrate. Thereafter, the films were annealed at various temperatures in ambient oxygen for 1 h for full crystallization. To measure the electric properties, platinum was coated by sputtering on the surface of the films with a diameter of 200 μm using a shadow mask and then post-annealed in ambient oxygen for 30 min. The constituent phase and crystal orientation of the films were identified by X-ray diffraction (XRD) using a Rigaku DMAX2500 diffractometer with CuK_α radiation at 30 kV. The surface morphology of the layered perovskite phase and the thickness of the thin films were analyzed using a scanning electron microscopy (SEM) (Hitachi S-4300). The electrical properties, ferroelectric 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

Fig. 1 shows the XRD patterns of BCT thin films annealed under various temperatures ranging from 600 to 720°C at intervals of 40°C. The diffraction peaks were identified and indexed using the standard XRD data of BCT. It was found that all of the films consisted of a single phase of a bismuth-layered structure showing the preferred (00*l*) and (117) orientation without any second phases within the detection limits of the XRD. It is evident that the Ce^{3+} substitution does not affect the bismuth-layered structure of $Bi_4Ti_3O_{12}$, but the Ce^{3+} concentration greatly affects the preferred orientation of the crystal. With the increasing annealing temperatures, it can be seen in Fig. 1 that the (00*l*) and (117) diffraction peaks become stronger and sharper. This shows that the film already has good crystallinity when the annealing temperatures were above 640°C. Compared with those of films annealed at other temperatures, the film annealed at 720°C had sharper (00*l*) and (117) peaks, and the latter peak was the strongest one. Since $Bi_4Ti_3O_{12}$-based ferroelectrics possess two polar axes along the a- and c-axes, [15] the physical properties will be sensitively influenced by the degree of the preferred orientations.

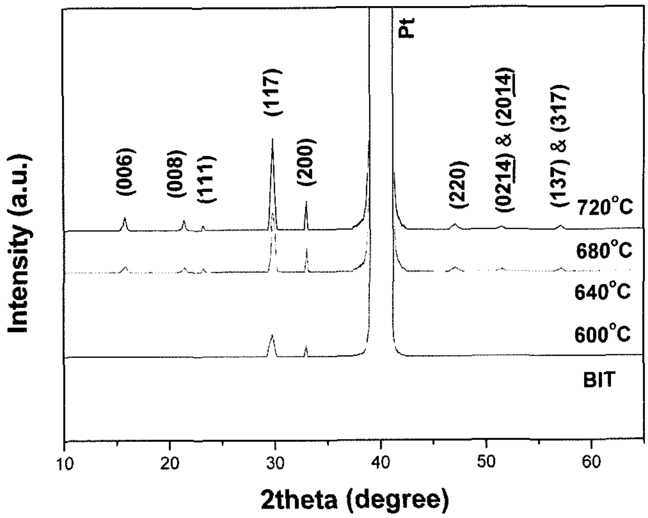

Fig. 1. XRD patterns of BCT thin films annealed at various temperatures.

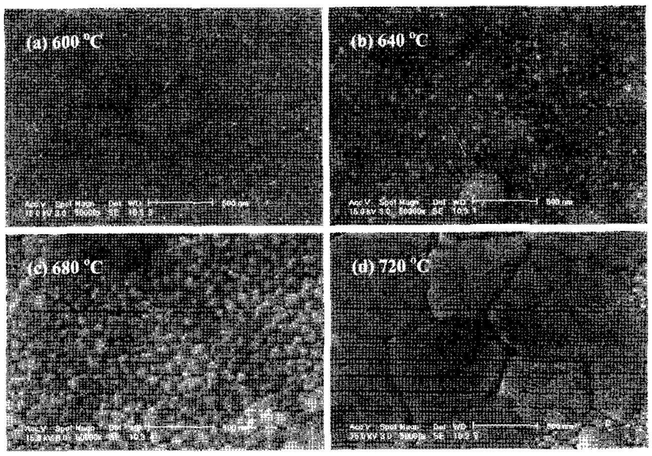

Fig. 2. SEM micrographs of BCT thin films annealed at various temperatures.

The surface morphologies of the samples corresponding to Fig. 1 were also examined with SEM, as shown in Fig. 2. All films showed smooth and dense microstructures. The thin film prepared at 640°C consisted of small grains of approximately 30 - 50 nm, which grew to larger grains of 300 - 500 nm as the crystalline temperature increased to 720°C. The average grain size of the films increased with the annealing temperatures. Furthermore, the BCT thin films were crystallized into the layered perovskite phase after annealing, and thus the ferroelectric properties of the films could be improved by increasing the annealing temperature. Fig. 3 shows a typical cross-section SEM micrograph of the final BCT thin films deposited on the Pt(111)/Ti/SiO_2/Si(100) substrate at 720°C, in which the interface between the BCT layer and substrate can be seen clearly. The thickness of the deposited BCT thin films was approximately 200 nm.

The ferroelectric hysteresis loops of the BCT thin film

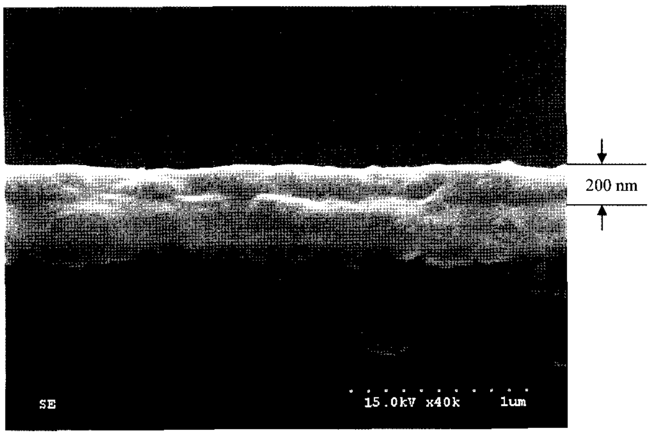

Fig. 3. Cross-sectional SEM image of BCT thin film.

capacitor annealed in the temperature range from 600 to 720°C are shown in Fig. 4. The BCT thin films were measured at various applied voltages ranging between 1 V and 5 V. By increasing the annealing temperature of the films, the degree of squareness of the hysteresis loops of the films was clearly improved. Under a maximum applied voltage of 5 V, the $2P_r$ values of the prepared films annealed at 600, 640, 680 and 720°C were 14.34, 21.33, 33.99 and 44.56 μC/cm^2, respectively. These results mean that the Ce-doped $Bi_4Ti_3O_{12}$ thin films have a high ferroelectric performance. In previous studies, to improve the relatively low remnant polarization and fatigue properties, some trivalent elements, such as La^{3+} and Nd^{3+}, were used to substitute Bi^{3+} at the A-site. $Bi_{3.25}La_{0.75}Ti_3O_{12}$ (BLT) thin film annealed at 650°C exhibited a large remnant polarization (P_r=12 μC/cm^2) and good fatigue characteristics even after 3×10^{10} switching cycles.[6] Nd doping of BTO films led to a high P_r value of 25 μC/cm^2.[16] These imply that lanthanides-substituted bismuth titanate is a more competitive candidate for FeRAM applications compared with the well known BTO. The reason for this result can be explained by a shift of TiO_6 octahedra in the layered structure due to the substitution of Ce^{3+} for Bi^{3+} since Ce^{3+} (1.03 Å) has a larger ionic radius than Bi^{3+} (0.96 Å). Hence, substituting for Bi in the layer structure enhances the ferroelectric properties.[17]

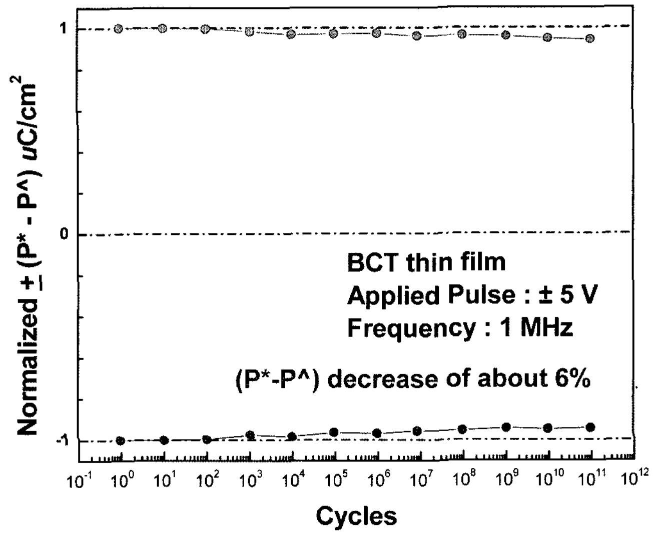

Fig. 5. Ferroelectric fatigue in BCT thin films.

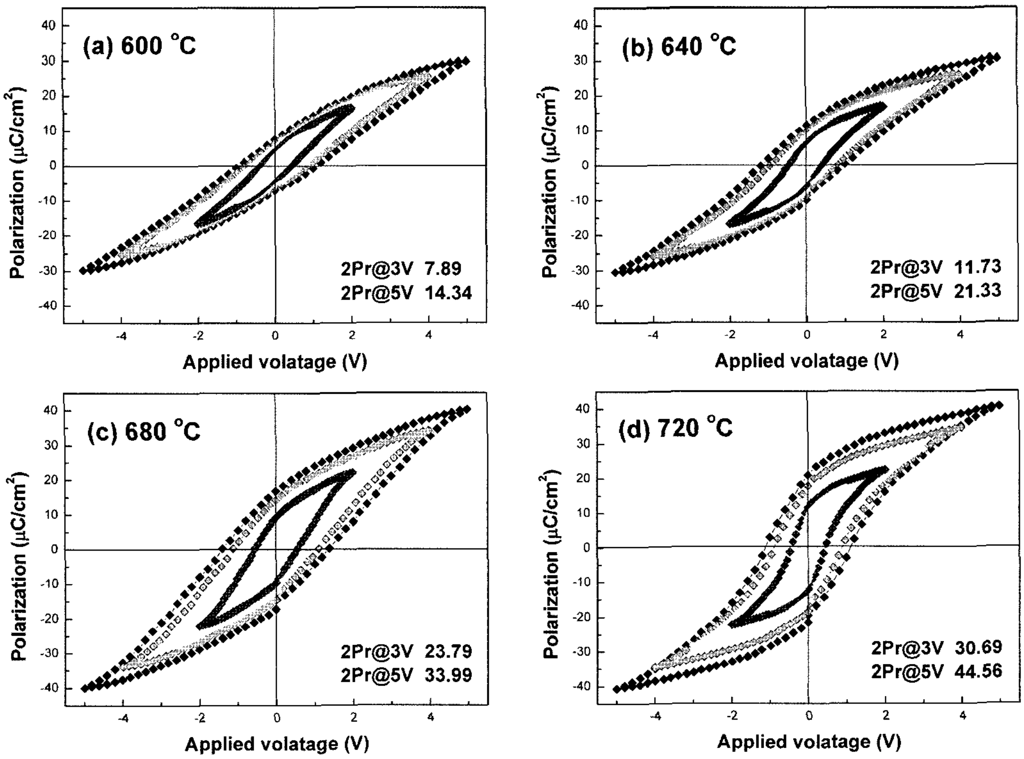

Fig. 4. Hysteresis loops of BCT thin films annealed at various temperatures.

The fatigue-resistant characteristics of the BCT films crystallized at 720°C are presented in Fig. 5, where the normalized difference between the switched and non-switched polarization (P_{sw}-P_{ns}) is plotted as a function of switching cycles. The BCT films capacitors showed little change in remnant polarization up to 1.0×10^{11} switching cycles using a frequency of 1 MHz with fatigue voltage of ±5 V. There were no significant changes in the shape of the P–E curves, suggesting that ferroelectric BCT thin films have good fatigue-free properties.

4. Conclusions

Polycrystalline ferroelectric BCT thin films were reproducibly fabricated on Pt(111)/Ti/SiO_2/Si(100) substrates using a liquid delivery MOCVD system. When the annealing temperatures were above 640°C, the BCT thin films were crystallized and exhibited a polycrystalline structure. The BCT thin film annealed at 720°C showed typical ferroelectric hysteresis loops, and its $2P_r$ and $2E_c$ values were 44.56 μC/cm^2 and 1.23 V, respectively, at an applied voltage of 5 V. The BCT thin films exhibited no significant degradation in the switching charge for up to at least 1.0×10^{11} switching cycles at a frequency of 1 MHz below the cycling fields of ±5 V. As seen by these results, the BCT thin films showed good ferroelectric properties and low annealing temperatures that can satisfy the requirements for high-density complementary metal oxide semiconductor (CMOS) devices. Therefore, the BCT thin film is an important candidate for non-volatile ferroelectric memory applications.

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