BCeT 박막의 구조 및 강유전 특성

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Structure and Ferroelectric properties of BCeT Thin Films

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Abstract

Randomly oriented ferroelectric cerium-substituted $Bi_4Ti_3O_{12}$ thin films have been prepared by using metal-organic decomposition method. The layered perovskite structure was investigated using annealing for 1 h in the temperature range from 550 ~ 750 ℃. The structure and morphology of the films were characterized using X-ray diffraction and scanning electron microscopy. The $Bi_{3.4}Ce_{0.6}Ti_3O_{12}$ (BCeT) thin films showed a perovskite phase and dense microstructure. The grain size of the BCeT films increasedwith increasing annealing temperature. The hysteresis loops of the films were well defined at temperatures above 600 ℃. The 200-nm-thick BCeT thin films annealed at 650 ℃ showed a large remanent polarization ($2Pr$) of 59.3 μC/cm^2 at an applied voltage of 10 V. The BCeT thin films showed good fatigue endurance up to 5 × 10^9 bipolar cycling at 5 V and 100 kHz.

Key Words : Ferroelectric properties Dielectric properties; metalorganic decomposition (MOD),

1. 서 론

Ferroelectric thin films have been widely investigated due to their potential applications in ferroelectric random access memory (FRAM), pyroelectric detectors, and nonlinear optical thin films [1-4]. Lead zirconium titanate (PZT) thin films have been the most intensively investigated. The reasons are that PZT has advantages such as low processing temperature and large remanent polarization values. However, PZT films on Pt/Ti electrode have a fatigue problem during electric filed cycling, which afford only limited number of switching cycles to the FRAM [5].

The SBT thin films have received considerable attention, which were good electric and ferroelectric properties for use in FRAM, such as low leakage currents and low coercive fields. Moreover, they have fatigue-free properties with simple Pt electrode during repeated polarization reversals with electric field cycles. However, for high-density integration of FeRAMs, the SBT films have some serious disadvantages, such as high processing temperature (i.e., above 800 ℃) and low remanent polarization ($2Pr$: 20 μC/cm2). Park et al. reported on new $Bi_{3.25}La_{0.75}Ti_3O_{12}$ (BLT) thin films fabricated by a pulsed laser deposition method at 650 ℃ [6]. The ferroelectric properties, the crystal structure, and the microstructure of BIT thin films are influenced by the substitution of different sizes of ions in these bismuth layer-structured compounds. Shimakawa *et al.* reported that TiO^6 octahedra in the pseudo-perovskite blocks show the shift of the octahedron along the a-axis, which is largely enhanced due to the substitution of lanthanides (e.g. La, Pr, Nd, Sm, Eu, etc.) for Bi in the pseudo-perovskite blocks [7]. Uong *et al.* reported the fatigue-free and large remanent polarization of Sm-substitution $Bi_4Ti_3O_{12}$ (BIT) (2*Pr* of BSmT = 49 μC/cm^2) [8].

In this paper, we report high remanent polarization of cerium-substitution in BIT thin films by using metal-organic decomposition (MOD) method. We investigated the structural and the ferroelectric properties of the BCeT thin films at various annealing temperatures..

2. 실 험

The precursor solutions for $Bi_{3.4}Ce_{0.6}Ti_3O_{12}$ were prepared by MOD method using bismuth acetate, ceriumacetate, and titanium iso-propoxide as the starting materials. The solid-state bismuth acetate and cerium acetate were initially dissolved in acetic acid and then mixed together to obtain Bi and Ce stock solution. Titanium iso-propoxide was dissolved in 2-methoxyethanol under N2 atmosphere. Finally, both starting solutions were mixed together to prepare the stoichometric, clear, transparent and stable BCeT precursor. An 10% excess amount of bismuth acetate was used to compensate for the Bi loss that occurs during annealing process.

For the fabrication of BCeT thin films, the BCeT precursor solution was syringed through a 0.2 m syringe filter on the Pt(120 nm)/Ti(30 nm)/SiO_2/Si substrateThe films were deposited by the spin-coating technique at 4000 rpm for 30 s. To remove the organic contaminations, after the spin-coating procedure the films were kept on hot plate at 400℃ for 10 min. The pre-baked film was annealed at various temperaturesin the range 550~700 ℃ for 1 h under an oxygen atmosphere for crystallization. The final thickness of the BCeT film was 200 nm. Top electrodes with 200 m in diameter were fabricated by depositing a 150-nm-thick Pt film at room temperature using dc magnetron sputtering.

The X-ray diffraction (XRD) profiles were obtained using CuK radiation source at 30 kV and 60 mA (Rigaku-D/MAX) to determine the crystallinity of the BCeT thin films. The surface morphology of the films was examined using a JOEL JSM-6300 field-emission scanning electron microscope (FE-SEM). The dielectric constant and loss measured using HP 4192 impedance analyzer. The ferroelectric properties were examined using a precision workstation ferroelectric tester (Radiant Technologies, USA) equipped with a micrometer probe station.

3. 결과 및 고찰

Figure 2 shows the XRD patterns of the BCeTthin films annealed for 1 h in an oxygen atmosphere at temperatures ranging from 550 to 700 ℃. As the annealing temperature increases to 550 ℃, the BCeT thin film begins to crystallize. It is observed that all the films have a Bi-layered structure showing the preferred (010) and (171) orientation, and no pyrochlore phase. The correlation of the diffraction peaks of the BCeT thin films with those of BIT implies that Ce-substitution does not affect the layered-perovskite structure of BIT. This fact indicates that the Ce^{3+} ions in the BCeT films do not form pyrochlorephase, but dissolve into the pseudo-perovskite structure. Therefore, it seems that Ce^{3+} ions can readily substitute for Bi^{3+} ions in pseudo-perovskite structure, and partial substitution of Ce^{3+} ions for Bi^{3+} ions in BIT influenced on the structural of Bi layer. The peak intensities increased, and the full width at half maximum (FWHM) of the peaks decreased with increasing annealing temperature. These can be assumed that the grain size was increasing with annealing temperature.

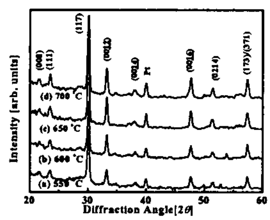

Fig. 1. X-ray diffraction patterns of BCeT thin films annealed at different temperature.

Figure 2 shows the surface-FE-SEM micrographs of BCeTthin films as functions of annealing temperatures. The surface morphology is very sensitive to the annealing temperature. The BCeT thin film annealed at 550 ℃ [Fig. 3(a)] exhibited coarse grains and considerable amounts of secondary structures among the grains. The grain size of the BCeT films increased with increasing annealing temperature. These facts can be assumed that the crystal growth is proceeded and the ferroelectric properties of the BCeT films can be improved by increasing the annealing temperature. The BCeT films at annealed 700 ℃ have round-plate-like grains of 300 nm.

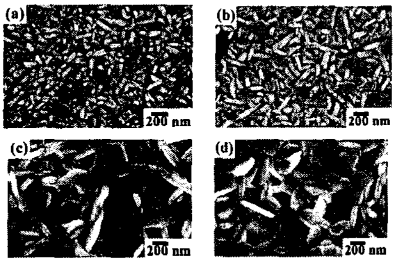

Fig. 2. Surface morphology of BCeT thin films annealed at (a) 550℃,(b) 600℃,(c) 650℃, and (d) 700℃.

Figure 3 shows the dielectric constant and the dielectric loss at 1 MHz of BCeT thin films annealed at different temperatures. The measured values of relative permittivity ata frequency of 1 MHz are 165, 312, 379 and 385 for the films annealed at 550, 600, 650 and 700 ℃, respectively. The lower value of dielectric constant of the film annealed at 550 ℃ might be due to poor crystallinity and smaller grain size. The dielectric constant increased with increasing annealing temperatures. This effect may be related to variations in the grain size, as observed in Fig. 3, and it leads to higher values of dielectric constant. The measured values of dielectric loss at 1 MHz are 0.032, 0.019, 0.021 and 0.032 for the films annealed at annealing temperatures of 550, 600, 650 and 700 ℃, respectively. It is well known that the dielectric loss in ferroelectic materials is mainly due to contributions from various sources such as domain wall pinning, space charge polarization, interfacial diffusion, and the presence of secondary phases. The higher loss (0.032) of films annealed at 550℃ may be due to finer grains with the space charge accumulation at grain boundaries. The relative dielectric constant and the dielectric loss of the BCeT thin film annealed at 650 ℃ were 379 and 0.021 at 1 MHz, respectively. These values are similar to those of BLT, BSmT, and SBT.

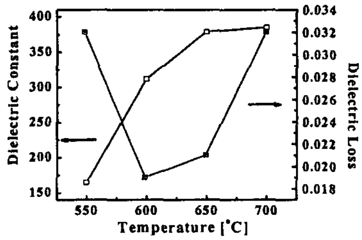

Fig. 3. Dielectric constant and dielectric loss of BCeT thin films as a function of the annealing temperature.

Figure 4 shows the polarizationelectric field (P-E) hysteresis curves of the BCeT thin film annealed temperature ranging from 550 ℃ to 700 ℃ and the P-E loops measured at 10 V. The ferroelectric properties are related to content stoichometry, grain size, and crystallinity of the film. The polarizations for the BCeT thin film annealed temperature at 550 ℃ and 600 ℃ were significantly suppressed as compared to the films annealing temperature above 650 ℃. The better ferroelectric properties were observed for the films annealed at above 650 ℃, which may be attributed to better crystallization, and larger grain size in comparison with the films at annealed below 600 ℃. The BCeT thin film annealed at 650 ℃ and 700 ℃ show the well-defined P-E loops. Theremanent (*2Pr*) and coercive field (*Ec*) values of BCeT thin films annealed at 650 ℃ and 700 ℃ were 59.3 and 62.1 μC/cm^2, and 160.5 and 167 kV/cm. The *2Pr* value of the polycrystalline BCeT thin film annealed at 700 ℃ was 62.1 μC/cm^2, which is larger than that of a highly *c*-axis oriented BSmT thin film (*2Pr* = 49 μC/cm^2), or a BLT thin film ($2P\ r$ = 27 μC/cm^2). The reason for this result may be explained by a large tilting of TiO^6 octahedra in a layered structure due to the substitution of Ce^{3+} for Bi^{3+}, and the Ce^{3+} has smaller ionic radius than the Bi^{3+}. Hence, the substitution of Ce for Bi in layer structure is able to enhance the ferroelectric properties.

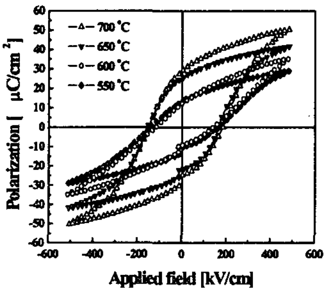

Fig. 4. P-E hysteresis curves of the BCeT thin films annealed at (a) 550 ℃, (b) 600 ℃, (c) 650℃, and (d) 700 ℃ measured at various applied voltages between 1 and 10 V.

4. 결 론

Cerium-substituted BIT thin films have been successfully prepared by MOD method. Cerium-substituted BIT thin films show a large $2Pr$ value (62.1 μC/cm^2), whichis much larger than that of Sm-modified BIT thin films ($2Pr$ of BSmT = 49 μC/cm^2) and BLT thin films ($2Pr$ = 27 μC/cm^2) at an applied voltage of 10 V. The relative dielectric constant and the dielectric loss of the BCeT thin film annealed at 650 ℃ were 379 and 0.021 at 1 MHz, respectively. The substitution of Ce for Bi in layer structure is able to enhance the ferroelectric properties. The BCeT thin films demonstrated no polarization fatigue of up to 5×10^9 switching cycles at a frequency of 100 kHz.

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