Fabrication and Characterization of Ferroelectric $(Bi,Sm)_4Ti_3O_{12}$ Thin Films Prepared by Chemical Solution Deposition

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ABSTRACT

Ferroelectric $Bi_{3.35}Sm_{0.65}Ti_3O_{12}$(BST) thin films were deposited on $Pt(111)/Ti/SiO_2/Si(100)$ substrates by a sol-gel spin-coating process. In this experiments, $Bi(TMHD)_3$, $Sm_5(O^iPr)_{13}$, $Ti(O^iPr)_4$ were used as precursors, which were dissolved in 2-methoxyethanol. Thereafter, the thin films with the thickness of 240nm were annealed from 600 to 720°C in oxygen atmosphere for 1 hr, and post-annealed in oxygen atmosphere for 1 hr after deposition of Pt electrode to enhance the electrical properties. The remanent polarization and coercive voltage of the BST thin films annealed at 720°C were 19.48 $\mu C/cm^2$ and 3.40 V, respectively, and a fatigue-free characteristic. As a result, Sm-substituted bismuth titanate films with good ferroelectric properties and excellent fatigue resistance are useful candidates for ferroelectric memory applications.

1. Introduction

Bismuth titanate ($Bi_4Ti_3O_{12}$, BIT) thin film has been studied intensively in the past decade due to its large remanent polarization, low crystallization temperature, and high Curie temperature. Substitution of various trivalent rare-earth cations (such as La^{3+}, Nd^{3+}, Sm^{3+}, and Pr^{3+}) in the BIT structure is known to improve its ferroelectric properties, such as remanent polarization and fatigue characteristics [1-2]. Among them, Sm-doped BIT ($(Bi,Sm)_4Ti_3O_{12}$, BST) has been receiving much attention due to its larger ferroelectricity than that of La-doped BIT (BLT) [3-8].

Some fabrication methods, such as RF magnetron sputtering, pulsed laser deposition, metal-organic chemical vapor deposition (MOCVD), and chemical solution deposition (CSD), have been successfully developed to prepare BIT or rare-earth cation doped BIT films. Among these various techniques, CSD is the one most commonly used due to its simplicity and ability for the exact stoichiometry control and large-area coating. The CSD method is generally composed of spin-coating, baking, pre-annealing, and finally furnace post-annealing. The film is pre-annealed to remove the organic ligands, and then becomes amorphous. The subsequent furnace post-annealing is needed to crystallize the amorphous film, which plays an important role in the film quality.

In this study, a chelating agent was used for chemical stability of the solution, and the thin films prepared by the spin-coating on the substrates. Ferroelectric properties and microstructures of the BST thin films according to the synthetic process and post-annealing temperature were investigated.

2. Experimental

$Bi_{3.35}Sm_{0.65}Ti_3O_9$ stock solutions were synthesized by sol-gel process. Tris(2,2,6,6-tetramethyl-3,5-heptanedionato) bismuth (III) $[Bi((CH_3)_3CCOCHCOC(CH_3)_3)_3]$, Samarium (III) i-propoxide $[Sm_5O(OC_3H_7)_{13}]$ and Titanium (IV) i-propoxide $[Ti[OCH(CH_3)_2]_4]$ were used as precursors. Also, 2-methoxyethanol was used as solvent and ethylacetoacetate [EAcAc], a kind of β-diketonate ligands was used as a chelating agent to improve the solution stability. Thereafter, the mixed solutions were hydrolyzed and condensed. These solutions were spin-coated on the $Pt/Ti/SiO_2/Si$ substrates at 3000 rpm for 30 sec and were baked at about 450°C for 5 min. To prepare the thin films with the thickness of 240 nm, these steps were repeated four times. The films were post-annealed at the various temperatures (600-720°C) in oxygen atmosphere for 1 hr and post-annealed after deposition of Pt top electrode to enhance the electrical properties.

In order to observe composition of the BST thin films, EPMA (JEOL, JZA-8900A) was investigated. The baking temperature was determined from TG-DSC (Setaram TGA 92 16-18). The crystalline phases after the heat treatment at the various temperatures were identified by XRD (RIGAKU, DXAM 200 X-ray Diffractometer). The surface microstructure was analyzed by FESEM (Hitachi S-4300) and AFM (PSIA, Au toprobe cp). The electrical properties for polarization-electrical field (P-E), leakage currents density (I-V) characteristics and reliability property were performed by the RT66A (Radient Technologies, Inc).

3. Results and discussion

3.1. Thermal behavior of the BST gel powder

In order to decide the baking temperature for decomposing organic material from the BST powder, TG-DSC curves were measured. The weight loss of the BST gel powder was started at around 200°C and terminated at around 450°C. These weight loss and exothermic peak show decomposition and phase transformation of materials. From the results of Fig. 1, the BST thin films were baked at 450°C and post-annealed at 600~720°C for crystallization with perovskite structure.

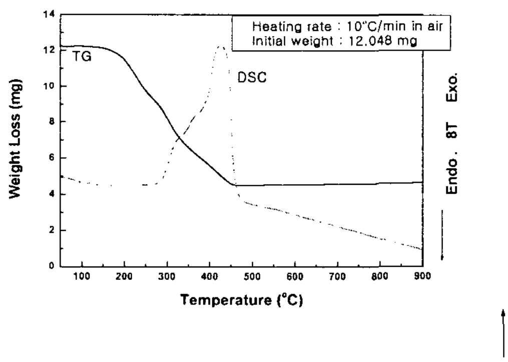

Fig. 1. TG-DSC curves of the BST gel powder.

3.2. Micro-structures of the BST thin films

SEM micrographs of the BST thin films with the various annealing temperatures were exhibited in Fig. 2. In the case of the BST thin films annealed at 600 °C, grains of 30-50 nm size existed in matrix. With the increase in the annealing temperature to 680 °C, grains of 200-300 nm size such as rod appeared in matrix. Grains of the BST thin films annealed at 720 °C turned into rod-like and plate-like ones. The grain sizes of the BST thin films were increased significantly as the crystallization temperature increased from 600 to 720 °C

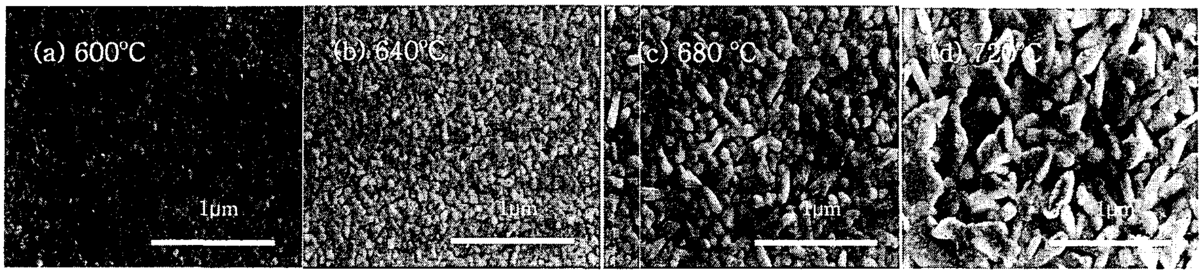

Fig. 2. SEM surface images of the BST thin films post-annealed at the various temperatures for 1 hr in oxygen atmosphere (a) BST thin film annealed at 600 °C, (b) BST thin film annealed at 640 °C, (c) BST thin film annealed at 680 °C, (d) BST thin film annealed at 720 °C.

3. 3. Ferroelectric property of the BST thin films

Fig. 3 shows the P-V hysteresis loops of the BST thin films with the various post-annealing temperatures. The BST thin films annealed at the relative low temperatures (600, 640 °C) exhibited poor ferroelectric properties. However, as the annealing temperature increases, the BST thin films exhibit better ferroelectric property. As the annealing temperature of the BST thin film from 600 to 720 °C increases, the remanent polarization ($2P_r$) values of the BST thin films are 5.64, 7.74, 12.85 and 19.48 $\mu C/cm^2$ at an the applied voltage of 5 V, respectively. And coercive voltage ($2V_c$) values are 2.00, 1.80, 3.20 and 3.40 V at the applied voltage of 5 V, respectively.

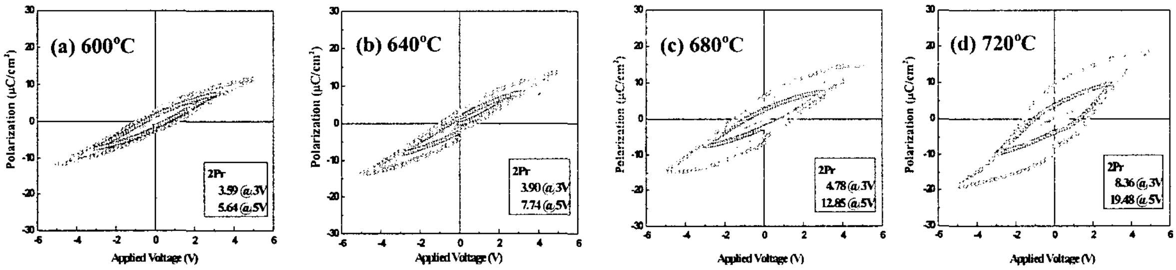

Fig. 3. Hysteresis loops of the BST thin films post-annealed at the various temperatures for 1 hr in oxygen atmosphere (a) BST thin film annealed at 600 °C, (b) BST thin film annealed at 640 °C, (c) BST thin film annealed at 680 °C, (d) BST thin film annealed at 720 °C.

3. 4. Reliability of the BST thin films

Fatigue behavior of the BST thin films annealed at 720°C in O_2 for 1hr was measured using 1 MHz bipolar pulses at ±5 V of applied electric field. Fig. 4 shows the results of the fatigue behavior test. The BST capacitors show little change both (P*-P^) and (-P*)-(-P^) value at the switching voltage of ± 5 V. The degradation of the switching charge after 1×10^{10} switching cycles was within 10 %.

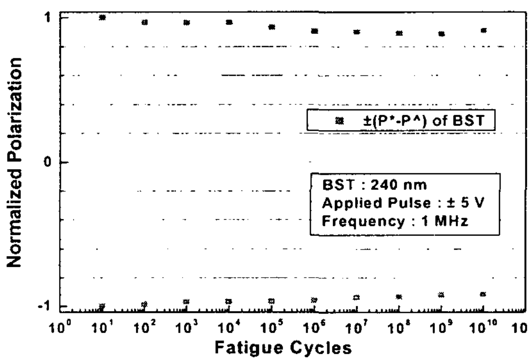

Fig. 4. Fatigue test of the BST thin film.

4. Conclusions

Polycrystalline ferroelectric BST thin films were successfully deposited on Pt(111)/Ti/SiO_2/Si(100) substrates by a sol–gel spin-coating process. The $2P_r$ and $2V_c$ values of the BST thin films annealed at 720 °C for 1 hr in an oxygen atmosphere were 19.48 $\mu C/cm^2$ and 3.40 V at an electric field of 5 V, respectively. Moreover, the BST thin film capacitors did not show significant fatigue up to 1.0×10^{10} switching cycles at a frequency of 1 MHz.

In this study, we have demonstrated that sol–gel derived BST thin films deposited on Pt(111)/Ti/SiO_2/Si(100) substrates exhibit good ferroelectric properties and fatigue-free characteristic and therefore potentially candidates for nonvolatile ferroelectric memory applications.

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