화학 용액 증착법으로 얻어진 $Bi_{4-x}Pr_{0.7}Ti_3O_{12}$ 박막의 강유전성과 미세구조에 관한 연구

강동균
고려대학교

Ferroelectric Properties and Microstructure of Pr-Substituted Bismuth Titanate Prepared by Chemical Solution Deposition

Dong-Kyun Kang
Department of Materials Science and Engineering, Korea Univ.

Abstract : The effect of praseodymium substitution on the ferroelectric properties of $Bi_4Ti_3O_{12}$ thin films have been investigated. Ferroelectric Pr-substituted $Bi_4Ti_3O_{12}$ thin films were fabricated by chemical solution deposition onto Pt/Ti/SiO_2/Si substrates. The structure and morphology of the films were analyzed using Xray diffraction, and scanning electron microscopy, respectively. About 200-nm-thick BPT films grown at 720 °C exhibited a polycrystalline structure and showed excellent ferroelectric properties with a remanent polarization ($2P_r$) of 28.21 μC/cm^2 at an applied voltage of 5 V. The films also demonstrate fatigue-free behavior up to 10^{11} read/write switching cycles with 1 MHz bipolar pulses at an electric field of ±5 V.

Key Words : Pr-substituted, Chemical solution deposition, Microstructure, Ferroelectric

1. Introduction

Ferroelectric thin films have received considerable attention in recent decades for the potential applications in nonvolatile random access memories [1].

Among related materials of interest, lead zirconate titanate ($PbZr_xTi_{1-x}O_3$, PZT) is probably the most extensively studied. PZT films have favourable characteristics, including high polarization, a low processing temperature, and remaining apparently fatigue-free when used as conducting oxide electrodes. Nevertheless, environmental safety issues concerning the Pb-containing formula may ultimately prevent it from being used in many applications. Layer structured perovskite like strontium bismuth tantalate ($SrBi_2Ta_2O_9$, SBT) has also been studied. Although SBT is a fatigue-free material, the practical application of SBT is limited, primarily due to its small polarization ($2P_r$ = 4~16 μC/cm^2) and high processing temperature of over 750 °C. Recently, polycrystalline lanthanide-substituted bismuth titanate ($Bi_4Ti_3O_{12}$, BIT) films have attracted attention because of their possible application to ferroelectric random access memories due to their high fatigue endurance as well as low deposition temperature. Compared with another well-known fatigue-free ferroelectric material $SrBi_2Ta_2O_9$ (SBT) which is also a Bi-layered perovskite oxide, lanthanide-substituted BIT has many attractive properties, such as low processing temperature and large values of remnant polarization [2].

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 [3].

In this study, praseodymium-substituted bismuth titanate, $Bi_{3.3}Pr_{0.7}Ti_3O_{12}$ (BPT), thin films were grown on Pt(111)/Ti/SiO_2/Si(100) substrates by a chemical solution deposition. In order to understand the annealing temperature effect on the thin film structures and the ferroelectric properties, the BPT thin films were systematically annealed at 600–720 °C for 1 hr in oxygen atmosphere. The effect of substitution Pr^{3+} for Bi^{3+} in BIT structure on the ferroelectric properties, such as remanent polarizations, capacitor–voltage characteristics, current–voltage properties, and fatigue endurances, have been reported.

2. Experimental procedure

$Bi_{3.3}Pr_{0.7}Ti_3O_9$ stock solutions were synthesized using the sol-gel process. Tris(2,2,6,6-tetramethyl-3,5-heptanedionato) bismuth [$Bi(TMHD)_3$], Tris(2,2,6,6-tetramethyl-3,5-heptanedio nato) praseodymium [$Pr(TMHD)_3$] and Titanium (IV) i-propoxide [$Ti[OCH(CH_3)_2]_4$] were used as precursors. In addition, 2-methoxyethanol was used as the solvent and ethylacetoacetate [EAcAc], which is a type of β-diketonate ligand was used as the chelating agent to improve the solution stability. Mixed solutions were hydrolyzed and condensed. Thereafter, these solutions were spin-coated onto the $Pt/Ti/SiO_2/Si$ substrates at 3000 rpm for 30 sec, and the resulting coated substrates were baked at approximately 450 °C for 5 minutes. These steps were repeated four times to prepare the 200 nm thin films. These films were furnace-annealed at various temperatures (600-720 °C) in oxygen ambient for 1 hr and post-annealed after depositing a Pt top electrode to enhance the electrical properties.

3. Results and discussion

Fig. 1 shows surface morphologies of BPT thin films annealed at various temperatures. With increasing annealing temperature to 680 °C, approximately 0.2-0.3 μm size grains such as rod appeared in the matrix. For the BPT thin films annealed at 720 °C, the rod-like and plate-like grains were randomly distributed on the substrate.

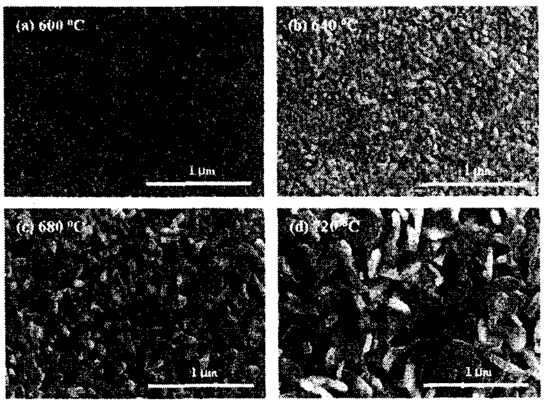

Fig. 1. SEM micrographs images of BPT thin films annealed at various temperatures.

Figs. 2 show the P-V hysteresis loops of the BPT thin films post-annealed at various temperatures. The BPT thin films showed good ferroelectric properties, and the remanent polarization value (2Pr) of the BPT thin films annealed at 720 °C was 28.21 $\mu C/cm^2$ at an applied voltage of 5 V.

The fatigue-free behavior of the BPT thin film is shown in Fig. 3, with little change in the switching polarization (P*) and the non-switching polarization (P^) up to 1×10^{11} read/write switching cycles 1 MHz bipolar pulses at a voltage of ±5 V. The degradation of the switching charge after 1×10^{11} switching cycles was within 10 %.

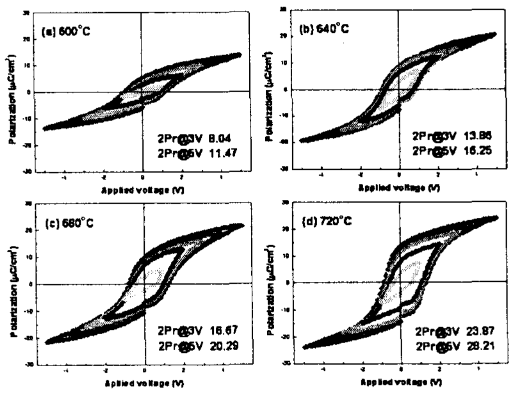

Fig. 2. Ferroelectric hysteresis loops of BPT thin films annealed at various temperatures.

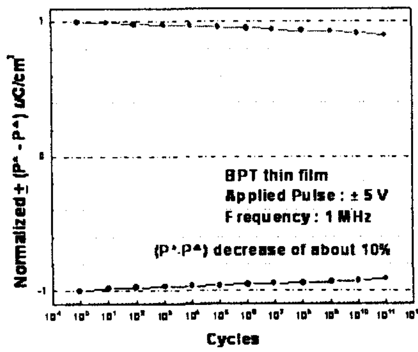

Fig. 3. Fatigue characteristics of BPT thin film capacitor

4. Conclusions

Ferroelectric $Bi_{3.3}Pr_{0.7}Ti_3O_{12}$ thin films were fabricated by chemical solution deposition onto $Pt/Ti/SiO_2/Si$ substrates. For the CSD derived BPT films, the grain size and the ferroelectricity (or the remanent polarization) increases monotonously as the crystallization temperature increases from 600 to 720 ° with an interval of 40 °. As the results, Pr-substituted bismuth titanate films with good ferroelectric properties and excellent fatigue resistance are useful candidates for ferroelectric memory applications.

References

[1] C. A. Araujo, et al, Nature, Vol. 347, p. 627, 1995
[2] B. H. park, et al, Nature, Vol. 401, p. 682, 1999
[3] F. Hou, et al, Mater. Sci. Eng. B, Vol. 122, p. 164, 2005