Growth and characterization of Eu-doped bismuth titanate (BET) thin films deposited by sol-gel method

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Abstract

Lead-free bismuth-layered perovskite ferroelectric europium-substituted $Bi_4Ti_3O_{12}$(BTO) thin films have been successfully deposited on $Pt/Ti/SiO_2/Si$ substrate by a sol-gel spin-coating process. $Bi(TMHD)_3$, $Eu(TMHD)_3$, $Ti(OiPr)_4$ were used as the precursors, which were dissolved in 2-methoxyethanol The thin films were annealed at various temperatures from 600 ° to 720 ℃ in oxygen ambient for 1 hr which was followed by post-annealed for 1 hr after depositing a Pt electrode to enhance the electrical properties. X-ray diffraction (XRD) and scanning electron microscopy (SEM) were used to analyze the crystallinity and surface morphology of layered perovskite phase, respectively. The remanent polarization value of the BET thin films annealed at 720 ℃ was 25.95 $\mu C/cm^2$ at an applied voltage of 5 V.

1. Introduction

Ferroelectric random access memories (FeRAMs) has been considered as one of future memory devices due to its ideal memory properties such as non-volatility, low power consumption, high speed, and almost unlimited endurance.[1]

As candidate materials of FeRAMs, $PbZr_xTi_{1-x}O_3$ [PZT] and $SrBi_2Ta_2O_9$ [SBT] thin films are the most intensively studied as memory media. PZT has advantages such as large remanent polarization values and low processing temperature. However, the Pr values of PZT thin films sandwiched between metal electrodes decrease dramatically with repetitive polarization switching. This phenomenon, the so-called fatigue, together with environmental issues caused by Pb evaporation, hinders the potential application of PZT. SBT was introduced to replace PZT due to its superior fatigue resistance. However, the high processing temperature of SBT above 750 ℃ is an obstacle in integration with silicon devices.[2-3]

Among others, lanthanoid (La, Pr, Nd, Sm, Eu, Gd) element-substituted bismuth titanate thin films are attractive bismuth layer-structured ferroelectrics (BLSFs) materials that have a somewhat lower deposition temperature than other BLSFs ($SrBiTa_2O_9$ [SBT]), large remanent polarization and small coercive field.[4]

Thin films of this material are prepared by RF sputtering, MOCVD, PLD, MOD and the sol-gel process. Among the various techniques, sol-gel processing was employed in this study because it offers excellent uniformity over large areas, easy composition control, short fabrication time, as well as it being a low temperature process at a comparatively low cost. However, the chemical stability of the solution is very important in the sol-gel process. In this experiment, a chelating agent was used to improve the chemical stability of the solution, and the thin films were prepared by spin-coating on the substrates. The ferroelectric properties and microstructures of the BET thin films according to the synthetic process and furnace annealing temperature were investigated.[5]

2. Experiment

$Bi_{3.3}Eu_{0.7}Ti_3O_9$ 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-heptanedionato) europium [$Eu(TMHD)_3$] 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 ℃ 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 ℃) in oxygen ambient for 1 hr and post-annealed after depositing a Pt top electrode to enhance the electrical properties.

EPMA (JEOL, JZA-8900A) was used to observe the composition of the BET thin films. The baking temperature was determined from TG-DSC (Setaram TGA 92 16-18). The crystallinity and microstructure of the films were analyzed by XRD (Rigaku, DMAX2500) and SEM (Hitachi, S-4200), respectively. The ferroelectric properties were measured with a standardized ferroelectric tester (Radiant Technologies Inc, RT-66A).

3. Results and Discussion

3.1. Thermal behavior of BET gel powder

The TG-DSC curves were measured determine the baking temperature for decomposing the organic material from the gel powder of the BET stock solution. The weight loss of the BET gel powder was observed at approximately 200 ℃ and terminated at approximately 450 ℃. These weight loss and exothermic peak show decomposition and phase transformation, respectively. From the results shown in Fig. 1, the BET thin films were baked at 450 ℃

and furnace-annealed at 600~720 ℃ to allow for crystallization in the perovskite structure.

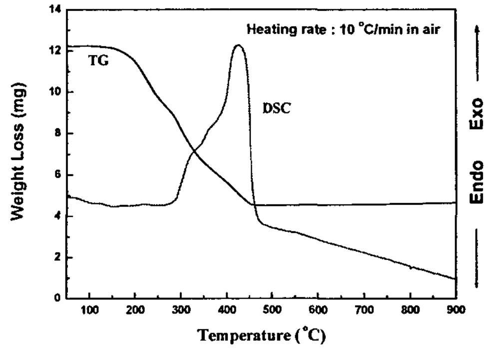

Fig. 3. TG-DSC curves of BET gel powder.

3.2. Micro-structures of BET thin films

Fig. 2 show SEM micrographs of the BET thin films with various annealing temperatures. From Fig. 2, there were 20-30 nm size grains in the matrix in case of the BET thin films annealed at 600 ℃. With increasing annealing temperature to 680 ℃, approximately 200-300 nm size grains such as rod appeared in the matrix. The grains of the BET thin films annealed at 720 ℃ had a rod-like and plate-like appearance.

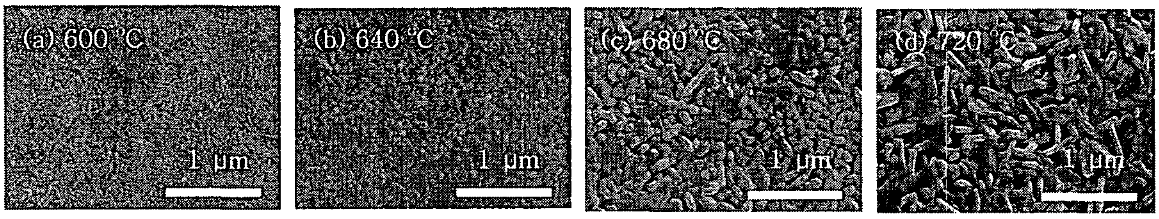

Fig. 2. SEM images of the BET thin films with various annealing temperatures

3.3. Electrical Properties of the BET thin films

Figs. 3 show the P-V hysteresis loops of the BET thin films at various post annealing temperatures. From Fig. 3, the BET thin films annealed at the relative low temperatures (600 ℃) exhibited paraelectric properties. However, according to the increase in the annealing temperatures to 680 ℃ and 720 ℃, the BET thin films exhibited ferroelectric properties. The remanent polarization value ($2P_r$) of the BET thin film annealed at 720 ℃ at an applied voltage of 5 V was 25.95 $\mu C/cm^2$.

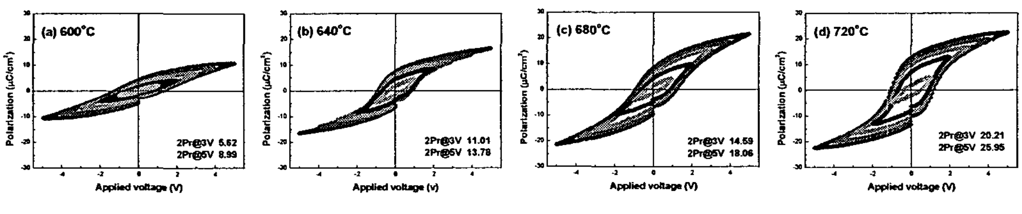

Fig. 3. Hysteresis loops of BET thin films annealed at various temperatures.

4. Conclusions

Ferroelectric BET thin films were prepared by a spin-coating method using a sol-gel solution. The electric properties of the BET thin films were investigated. The results can be summarized as follows :

1. With increasing annealing temperature, the BET thin films had a rod-like and plate-like appearance.
2. The BET thin films showed good ferroelectric properties, and the remanent polarization value ($2P_r$) of the BET thin film annealed at 720 ℃ at an applied voltage of 5 V was 25.95 $\mu C/cm^2$.

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