Sol-Gel법으로 증착된 $Bi_4Ti_3O_{12}$ 박막의 형태적, 구조적 특성과 강유전성에 Gadolinium 치환이 미치는 효과

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Influence of Gd Substitution on the Morphological, Structural and Ferroelectric Properties of $Bi_4Ti_3O_{12}$ Thin Films Obtained by Sol-Gel Method

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Abstract : Gadolinium-substituted bismuth titanate, $Bi_{3.3}Gd_{0.7}Ti_3O_{12}$ (BGT), thin films were successfully fabricated on $Pt(111)/Ti/SiO_2/Si$ substrates by a sol-gel method and their structural and ferroelectric properties have been characterized. Fabricated BGT thin films were found to be random orientations, which were confirmed by X-ray diffraction experiment and scanning electron microscope analysis. The remanent polarization ($2P_r$) of BGT thin film annealed at 720 °C was 25.85 $\mu C/cm^2$ at an applied voltage of 5 V. The BGT thin films exhibited a 11 % reduction in their switching charge after no less than 10^{11} switching cycles at a frequency of 1 MHz.

Key Words : Gd-substituted, Sol-gel, Ferroelectric, Polycrystalline

1. Introduction

Ferroelectric materials deserve much attention because of their application to logic circuit and mobile application as a non-volatile memory utilizing its low electric consumption and its high write-read-out property [1].

As candidate materials for FeRAMs, 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+}, Pr^{3+}, Gd^{3+}, Eu^{3+} and Ce^{3+}) in the BIT structure is known to improve its ferroelectric properties, such as remanent polarization and fatigue characteristics. Among them, Gd-doped BIT ($(Bi,Gd)_4Ti_3O_{12}$, BGT) has been receiving much attention due to its larger ferroelectricity than that of other lanthanide-doped BIT [2-3].

Ferroelectric films have been fabricated by rf sputtering, pulsed laser deposition, electron cyclotron resonance plasma sputtering, sol-gel and metal organic chemical vapor deposition. In this work, we report the preparation of BGT thin films on platinum-coated silicon substrates by the sol-gel precursor method. Compared with other techniques, the sol-gel precursor method has the advantages of easier composition control, better homogeneity, low processing temperature (compatible with Si processing), easier fabrication of large areas and low cost. However, the chemical stability of the solution is very important in the sol-gel process [4].

In this work, a chelating agent was used to improve the chemical stability of the solution, and BGT thin films were prepared by the sol-gel precursor method. The effects of Gd substitution on the structural, morphological and electrical properties of BGT thin films were investigated. The ferroelectric properties and microstructures of the BGT thin films according to the synthetic process and furnace annealing temperature were also discussed.

2. Experimental procedure

$Bi_{3.3}Gd_{0.7}Ti_3O_9$ 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) gadolinium [$Gd(TMHD)_3$] 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.

The composition and thermal behavior of the thin films were observed by .EPMA (JEOL, JZA-8900A) and TG-DSC (Setaram TGA 92 16-18), respectively. 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

X-ray diffraction (XRD) patterns of the BGT thin films annealed at various temperatures are shown in Fig. 1. From the XRD patterns, it is clear that reflection peaks can be indexed as a bismuth-layered perovskite structure. With increased annealing temperature, the peaks in the XRD patterns became sharper, which suggest that the crystallization of the BGT was improved as the annealing temperature increases. From the intensity ratio between (00*l*) and (117) to estimate the degree of c-axis orientation, we could be known that the BGT thin film was randomly orientated.

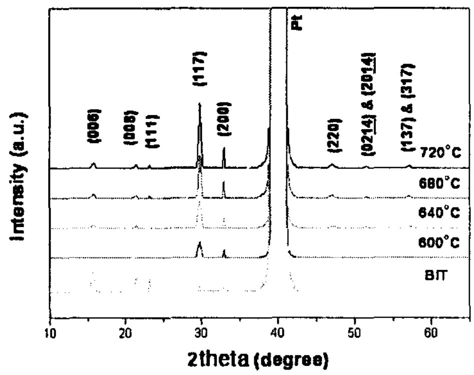

Fig. 1. XRD patterns of BGT thin films annealed at various temperatures.

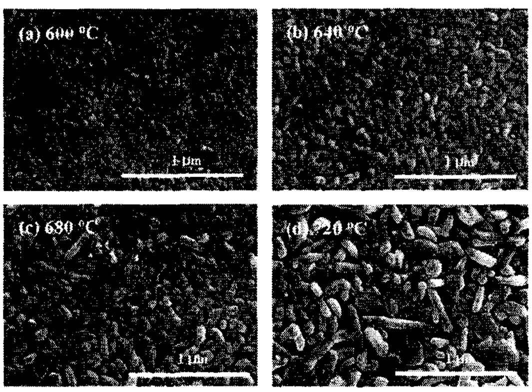

Fig. 2. SEM images of BGT thin films annealed at various temperatures.

Fig. 2 shows surface morphologies of BGT thin films annealed at various temperatures. The grain size increases with increased annealing temperatures and the grain size of the BGT thin film annealed at 720 °C ranges from 0.2 to 0.3 μm. For the BGT thin films annealed at 720 °C, the rod-like and plate-like grains were randomly distributed on the substrate.

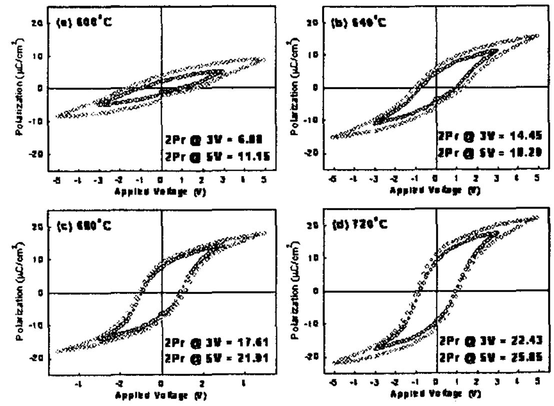

Fig. 3. Ferroelectric hysteresis curves of BGT thin films annealed at various temperatures.

Ferroelectricity in the BGT thin films .was performed with a standardized ferroelectric tester and the results are presented in Fig. 3. Well-saturated rectangular hysteresis loops were obtained. The remanent polarization increase with increasing annealing temperature. This indicates that BGT films have good ferroelectric switching properties and large enough remanent polarization for FeRAM applications.

4. Conclusions

Ferroelectric BGT thin films were prepared by a spin-coating method using a sol-gel solution. The thin films showed good ferroelectric properties, and the remanent polarization value of the thin film annealed at 720 °C at an applied voltage of 5 V was 25.85 μC/cm^2. The films also exhibited fatigue-free behavior up to 10^{11} read/write switching cycles. These results indicate that the randomly oriented BGT thin film is a promising candidate among ferroelectric materials useful in lead-free non-volatile ferroelectric random access memory applications.

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