강유전체 $(Bi,Nd)_4Ti_3O_{12}$ 박막의 결정 구조와 분극 특성

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Crystal Structure and Polarization Properties of Ferroelectric Nd-Substituted $Bi_4Ti_3O_{12}$ Thin Films Prepared by MOCVD

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Abstract

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. Among them, neodymuim-substituted bismuth titanate, ($(Bi,Nd)_4Ti_3O_{12}$, BNT) has been receiving much attention due to its larger ferroelectricity. In this study, Ferroelectric $Bi_{3.3}Nd_{0.7}Ti_3O_{12}$ thin films were successfully fabricated by liquid delivery MOCVD process onto Pt(111)/Ti/SiO_2/Si(100) substrates. Fabricated polycrystalline BNT thin films were found to be random orientations,which were confirmed by X-ray diffraction and scanning electron microscope analyses. The remanent polarization of these films increased with increase in annealing temperature. And the film also demonstrated fatigue-free behavior up to 10^{11} read/write switching cycles. These results indicate that the randomly oriented BNT thin film is a promising candidate among ferroelectric materials useful for lead-free nonvolatile ferroelectric random access memory applications.

Key Words : Ferroelectric; Polycrystalline; Randomly-oriented; Fatigue-free

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) [1].

A number of different methods have been developed for the fabrication of Bi-layered perovskite thin films, such as sputtering, PLD, MOD, Sol-Gel and MOCVD [3-4]. Among these methods metal organic chemical vapor deposition (MOCVD) has the advantage of offering conformable step coverage and good uniformity of thickness and composition.

Many researchers have studied possible candidates for ferroelectric materials that can be used in non-volatile random access memories (NVRAMs) [5]. In recent years, some Bi-layered oxide perovskites, such as $SrBi_2Ta_2O_9$ (SBT) and $Bi_{3.75}La_{0.25}Ti_3O_{12}$ (BLT) have been intensively studied, in order to evaluate their possible use in NVRAMs. However, the use of SBT and BLT thin films for high density integration in NVRAMs is disadvantaged by the fact that these films have a low remanent polarization ($2P_r$ for SBT = 20 μC/㎠, and for BLT = 27 μC/㎠) [6]. Recently, U. Chon et al. reported the fatigue free and large remanent polarization of Nd-substituted $Bi_4Ti_3O_{12}$ (BTO) ($2P_r$ of BNT =100 μC/㎠) [7].

In this paper, the properties of epitaxial BNT films grown by the metal organic chemical vapor deposition (MOCVD) method on a Pt/Ti/SiO_2/Si substratewere studied. The crystallinity, microstructure, electrical and ferroelectric properties of the BNT thin films were investigated and discussed in detail.

2. Experimental

BNT films with a thickness of 150nm were deposited at 600°C by the LDS-MOCVD method. Triphenyl bismuth [$Bi(ph)_3$], tri(2,2,6,6-tetramethyl-3,5-heptanedionate) Neodymium [$Nd(TMHD)_3$] and di(i-propoxide) bis(2,2,6,6-tetramethyl-3,5-hep tanedionate) titanium [$Ti(O^iPr)_2(TMHD)_2$] were used as the precursors for Bi, Nd and Ti, respectively. These precursors were dissolved n-butyl acetate to form a single stock solution. In this study, the structural, electrical and ferroelectric properties of the deposited films were investigated.

3. Results and Discussion

Fig. 1. shows the polarization-electric field (P-E) hysteresis loops of the BNT thin films annealed in the temperature of 720°C. Well-saturated P-E hysteresis curves were obtained for the BNT thin films annealed at 720°C, which showed $2P_r$ value of 31.91μC/cm^2 and $2V_c$ value of 3.58 V, respectively. The substitution of Nd for bismuth titanate in the $Bi_4Ti_3O_{12}$ (BTO) thin films was found to be effective for improving the ferroelectric properties of the thin films. Therefore, the poor ferroelectric and fatigue characteristics if the BTO thin films can be attributed to the volatility of the Bi ions. The Bi^{3+} ions in the BTO structure can be substituted by Nd^{3+} in order to improve the properties of such layer-structures.

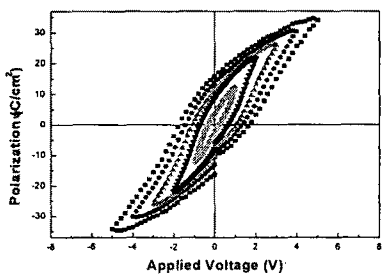

Fig. 1. Hysteresis loops of BNT thin films.

The leakage current of the Pt/BNT/Pt thin films was measured by applying a staircase DC voltage to the top and bottom electrodes. Fig. 2 shows a plot of the leakage current density of the BNT thin films versus the applied DC electric voltage. The leakage current density is typically less than 10^{-6} A/cm^{2}under an applied voltage of up to about 2.5 V, which demonstrates the relatively good insulating properties of the thin films. The breakdown voltage of the 150nm BNT thin films was about 2.6 V.

The switched polarization was determined as a function of the number of switching cycles using bipolar pulses of ±5 V at 1 MHz, and the results are plotted in Fig. 2. The degradation of the switching charge after 1.0×10^{11} switching cycles was within 10%. As seen in this figure, the hysteresis loops obtained during the fatigue periods indicate that the BNT thin film has a strong resistance against fatigue.

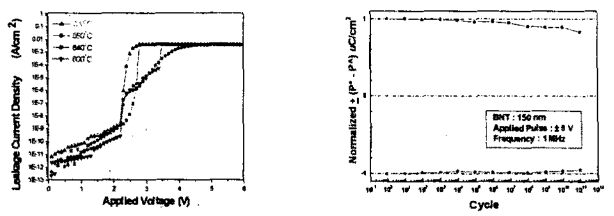

Fig. 2. Leakage current density-voltage characteristics fatigue test of BNT thin films.

4. Conclusions

Ferroelectric BNT thin films were successfully fabricated on $Pt(111)/Ti/SiO_2/Si$ substrates by LDS-MOCVD techniques. The BNT thin films showed good ferroelectric properties and a low annealing temperature that should satisfy the requirements for high-density and non-volatile memory device applications. All of the deposited BNT thin films were fully crystallized to almost randomly oriented polycrystalline structures at annealing temperatures of over 640 °C. As a result, well-saturated hysteresis loops are obtained for the BNT films at a maximum applied voltage of 5V. The saturated $2P_r$ and $2V_c$ values are 31.91μC/cm^2 and 3.58V, respectively. The leakage current density is typically less than 10^{-7}A/cm^2 at an applied voltage of up to about 3V. The degradation of the switching charge after 1×10^{11} switching cycles was within 10%. Thus, it is anticipated that ferroelectric BNT could be used to fabricate high-density FeRAMs.

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