Ferroelectric and Structural Properties of Nd-substituted $Bi_4Ti_3O_{12}$ Thin Films Fabricated by MOCVD

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ABSTRACT

A promising capacitor, which has conformable step coverage and good uniformity of thickness and composition, is needed to manufacture high-density non-volatile FeRAM capacitors with a stacked cell structure. In this study, ferroelectric $Bi_{3.61}Nd_{0.39}Ti_3O_{12}$ (BNT) thin films were prepared on Pt(111)/Ti/SiO_2/Si substrates by the liquid delivery system MOCVD method. In these experiments, $Bi(ph)_3$, $Nd(TMHD)_3$ and $Ti(O^iPr)_2(TMHD)_2$ were used as the precursors and were dissolved in *n*-butyl acetate. The BNT thin films were deposited at a substrate temperature and reactor pressure of approximately 600 °C and 4.8 Torr, respectively. The microstructure of the layered perovskite phase was observed by XRD and SEM. The remanent polarization value (2Pr) of the BNT thin film was 31.67 μC/㎠ at an applied voltage of 5 V.

1. Introduction

Ferroelectric memory is not only an ideal form of memory with clear advantages such as non-volatility, low power consumption, high endurance and high speed writing, but is also the most suitable device for memory embedded applications [1]. A number of different methods have been developed for the fabrication of Bi-layered perovskite thin films, such as sputtering [2], PLD [3], MOD [4], Sol-Gel [5] and MOCVD [6]. 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) [7]. 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/㎠) [8]. 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/㎠) [9].

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 substrate were 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-heptanedionate) titanium [Ti(O^{i}Pr)$_2$(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. This solution was deposited onto a Pt/Ti/SiO$_2$/Si substrate for 50 min by the liquid delivery system MOCVD (LDS-MOCVD) method. The compositions of the resultant films were characterized by means of an electron probe micro analyzer (JEOL, JXA-8900R). The crystalline structures of the BNT thin films were studied by X-ray diffraction using a Rigaku DMAX 2500 X-ray diffractometer. The surface microstructure was analyzed by means of the field emission scanning electron microscope (HITACHI, S-4200). The electric and ferroelectric properties of the deposited films were measured with a standard ferroelectric test system (RADIENT, RT66A) after the formation of Pt top electrodes on the film surface by means of RF-Sputter using a shadow mask.

3. Results and discussion

3.1. Crystalline phases and preferred orientations of BNT thin films

Fig. 1 shows the X-ray diffraction patterns of the BNT thin films deposited on the Pt/Ti/SiO$_2$/Si substrate. Following their deposition, these thin films were annealed at various temperatures for 1h in an O$_2$ atmosphere. All of the films exhibited a Bi-layered perovskite structure, which could be well indexed by the JCPDS card (No.12-0213) of Bi$_4$Ti$_3$O$_{12}$. The most notable characteristics were the predominant (117)-oriented growth on the Pt bottom layers, and the fact that the (117), (200) random orientation of the films became dominant with increasing annealing temperatures and the BNT films annealed at higher temperatures exhibited stronger and sharper diffraction peaks. It can thus be assumed that the grain size increased with increasing annealing temperature. The correlation of the diffraction peaks of the BNT thin films with those of BTO implies that the Nd substitution does not affect the layered-perovskite structure of Bi$_4$Ti$_3$O$_{12}$. This implies that the Nd^{3+} ions in the BNT films do not form a pyrochlore phase, but dissolve into the pseudo-perovskite structure. Based on the XRD patterns, it is suggested that the resultant properties can be attributed to the combination of the a, b and c-axis orientation. This combination of a, b and c-axis orientation leads to an improvement in the remanent polarization.

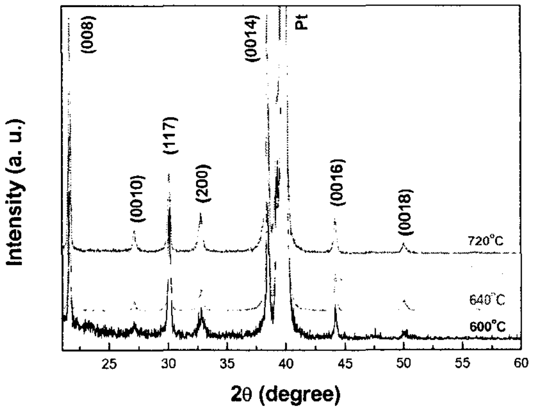

Fig. 1. XRD patterns of BNT thin films.

3.2. Eletrical properties of BNT thin films

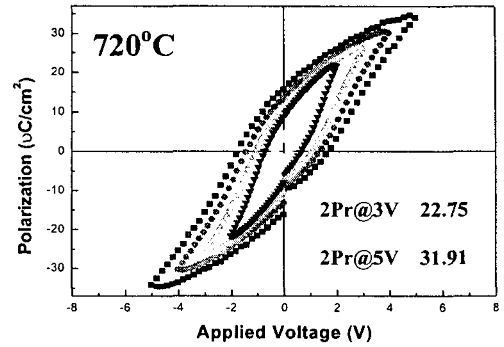

Fig. 2. Hysteresis loops of BNT thin films.

Fig. 2. shows the polarization-electric field (P-E) hysteresis loops of the BNT thin films annealed in the temperature of 720°C. It can be seen that the BNT thin films annealed at 600 and 640 °C exhibited $2P_r$ values of 12.13 and 16.97 $\mu C/cm^2$ and $2V_c$ values of 3.35 and 3.18 V, respected, even when the applied voltage was as low as 5 V. Furthermore, well-saturated P-E hysteresis curves were obtained for the BNT thin films annealed at 680 and 720°C, which showed $2P_r$ values of 21.78 and 31.91 $\mu C/cm^2$ and $2V_c$ values of 2.61 and 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.

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. 3 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/cm² 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. 4. 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.

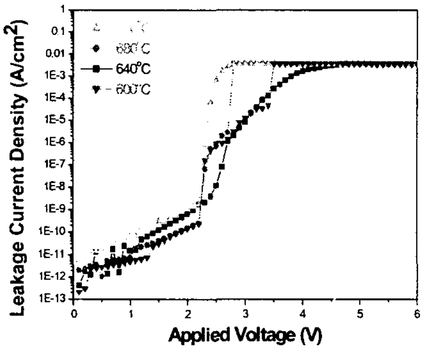

Fig. 3. Leakage current density-voltage characteristics BNT thin films.

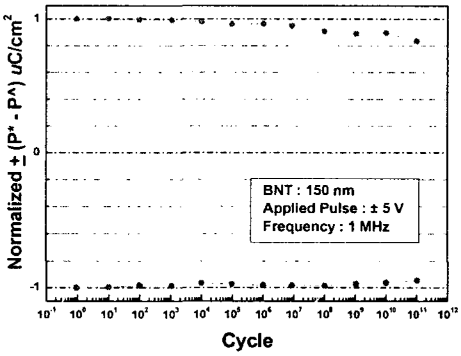

Fig. 4. Results of the fatigue test of BNT thin film.

4. Concl

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. The ferroelectric characteristic of the $Bi_{3.61}Nd_{0.39}Ti_3O_{12}$ thin films was optimized at a substrate temperature of 600 °C and a reactor pressure of 4.8Torr. 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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