MOCVD로 증착된 $Bi_4Ti_3O_{12}$ 박막의 미세구조와 강유전성에 Cerium 첨가가 미치는 영향

강동균, 박원태, 김병호
고려대학교

The Effect of Ce Substitution on Microstructure and Ferroelectric Properties of $Bi_4Ti_3O_{12}$ Thin Films Prepared by MOCVD

Dong-Kyun Kang, Won-Tae Park, Byong-Ho Kim
Department of Materials Science and Engineering, Korea Univ.

Abstract : Ferroelectric Cerium-substituted $Bi_4Ti_3O_{12}$ thin films with a thickness of 200 nm were deposited using the liquid delivery metal organic chemical vapor deposition process onto a $Pt(111)/Ti/SiO_2/Si(100)$ substrate. At annealing temperature above 600 °C, the BCT thin films became crystallized and exhibited a polycrystalline structure. The BCT thin film annealed at 720 °C showed a large remanent polarization ($2P_r$) of 44.56 $\mu C/cm^2$ at an applied voltage of 5V. The BCT thin film exhibits a good fatigue resistance up to 1×10^{11} switching cycles at a frequency of 1 MHz with applied electric field of ±5 V.

Key Words : Ce substitution, MOCVD, Microstructure, Ferroelectric

1. Introduction

In the past several years, a number of researches and developments into the practical utility of ferroelectric random access memories (FeRAMs) have been reported. For memory application, development of optimum ferroelectric thin film fabrication techniques which are compatible with the latest LSI manufacturing is very important, because integration of ferroelectric thin film with silicon-based LSIs is indispensable. In particular, development of low-temperature thin film deposition techniques is one of the most important key issues [1].

As candidate materials for FeRAMs, lanthanide (La, Pr, Nd, Sm, Eu, Ce and Gd) element-substituted bismuth titanate thin films are recently 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 [2-3]. Among the many ferroelectric thin film fabrication techniques, metalorganic chemical vapor deposition (MOCVD) is one of most promising techniques, because it can achieve low-temperature deposition of ferroelectric thin films, large-area deposition and conformal deposition on three-dimensional surfaces [4].

In this study, we prepared Ce-substituted $Bi_4Ti_3O_{12}$ thin films by means of the liquid delivery MOCVD system [5]. After deposition of the ferroelectric thin films, the effects of the substrate temperature and the reactor pressure on the film composition were investigated. In addition, the microstructure and the dielectric and electrical properties of the thin films were determined.

2. Experimental

A single mixture solution of $Bi(ph)_3$, $Ce(TMHD)_3$ and $Ti(O^iPr)_2(TMHD)_2$ precursors was prepared to be used in liquid delivery MOCVD. The precursors were dissolved together in n-butyl acetate. BCT thin films were deposited on a $Pt(111)/Ti/SiO_2/Si(100)$. Thereafter, the films were annealed at various temperatures in oxygen ambient for 1 h. and post-annealed in oxygen ambient for 30 min., thereafter the deposition of a Pt top electrode with a diameter of 200 μm, in order to enhance the electrical properties of the thin film. The thermal stability of the BCT precursors was confirmed by TG analysis. 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).

Typical deposition conditions are summarized in Table 1.

Table 1. MOCVD process conditions used to deposit BCT thin films.

Deposition parameters	Range Investigated
Substrate Temperature	540 - 600 °C
Total reactor pressure	3 - 6 Torr
Vaporizer Temperature	200 - 220 °C
Carrier gas flow rate	200 sccm
Oxidizing gas flow rate	200 sccm
Stock solution conc.	0.05:0.01:0.05 [Bi:Ce:Ti]

3. Recults and discussion

XRD patterns of BCT thin films annealed at different temperatures (600–720 °C) and the BIT thin film annealed at 720 °C are shown in Fig. 1. Although XRD peaks that corresponded to the bismuth-layered perovskite structure were detected for the thin films annealed at low temperatures, the peaks were generally small and broad, indicating poor crystallization of the films. Above 680 °C, sharp diffraction peaks appeared, and their intensity was found to be sensitive to the annealing temperatures. As the temperature of the BCT thin films were increased from 600 to 720 °C, the peaks in the XRD patterns became sharper. As shown in Fig. 1, the XRD results for BCT and BIT thin films deposited under the same conditions clearly show that BIT thin film favors the growth of (00*l*)-oriented grains, while BCT thin films prefer to grow along (117)-orientation. This result indicates that the BCT thin film is close to that of the randomly orientated powder.

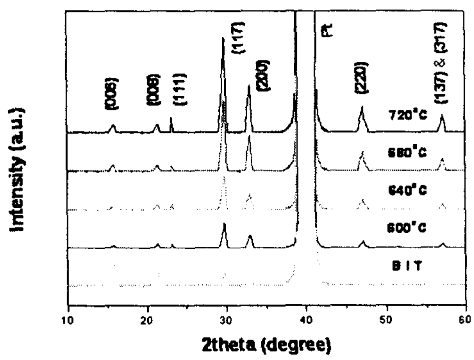

Fig. 1. XRD patterns of BIT thin film annealed at 720 °C and BCT thin films annealed at various temperatures.

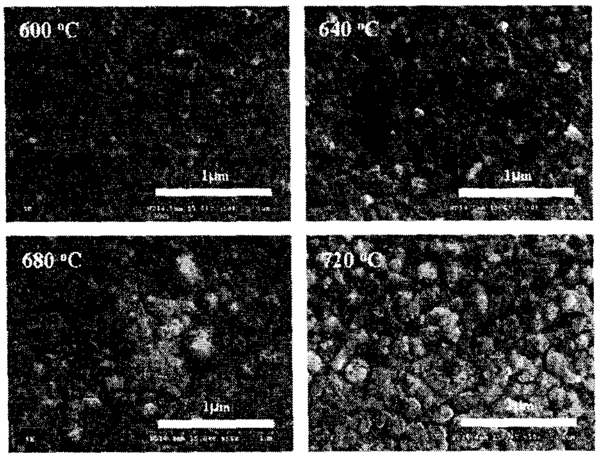

Fig. 2. SEM images of BCT thin films annealed at various temperatures.

Fig. 2 shows the surface morphology of BCT thin films annealed at various temperatures. The grain size increases with increased annealing temperatures and the grain size of the BCT thin film annealed at 720 °C ranges from 0.2 to 0.3 μm. For the BCT thin film annealed at 720 °C, the spherical grains were randomly distributed on the substrate. These characteristics agree with those of XRD analysis results.

Fig. 3 shows ferroelectric hysteresis loops of the BCT thin film capacitor annealed at various temperatures. As shown, the BCT thin film capacitor exhibited well-saturated polarization-electric field (P–E) curves. The remanent polarization value (2Pr) of the BCT thin films annealed at 720 °C was 44.56 μC/cm^2 at an applied voltage of 5 V, indicate high performance of ferroelectricity.

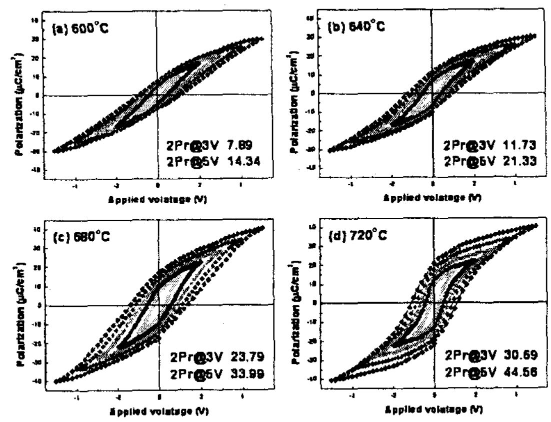

Fig. 3. Ferroelectric hysteresis curves of BCT thin films annealed at various temperatures.

4. Conclutsions

Polycrystalline bismuth-layered perovskite ferroelectric BCT thin films were fabricated by liquid delivery MOCVD process onto Pt(111)/Ti/SiO_2/Si(100) substrates. The BCT thin films showed good ferroelectric properties and low anneal temperature that could satisfy the requirements for high-density complementary metal oxide semiconductor (CMOS) devices. From the results, it indicates that the BCT thin films are new candidates for non-volatile ferroelectric random access memory for integration in CMOS structures.

참고 문헌

[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] U. Chon, et al, J. Appl. Phys., Vol. 93, p. 4769, 2003.
[4] T. Watanabe, et al, J. Cryst. Growth, Vol. 235, p. 389, 2002.
[5] D. K. Kang, et al, Thin Solid Films, Vol. 492, p. 140, 2005.