The ferroelectric and fatigue properties in Gd-modified bismuth titanate (BGT) thin films deposited by liquid delivery MOCVD

Dong-kyun Kang, Won-Tae Park, Byong-Ho Kim

Department of Materials Science and Engineering, Korea University, Seoul 136-713, Korea

Abstract

Gadolinium-substituted bismuth titanate, $Bi_{3.3}Gd_{0.7}Ti_3O_{12}$, thin films were successfully fabricated on $Pt(111)/Ti/SiO_2/Si(100)$ substrates by a MOCVD process. Fabricated BGT thin films were found to be random orientations, which were confirmed by X-ray diffraction and scanning electron microscope analysis. The remanent polarization value ($2P_r$) of the BGT thin film annealed at 720 ℃ was 45.13 $\mu C/cm^2$, at an applied voltage of 5 V. The BGT thin film exhibits a good fatigue resistance up to 1×10^{11} switching cycles at a frequency of 1 MHz with applied voltage of 5 V. These results indicate that the randomly oriented BGT thin film is a promising candidate among ferroelectric materials useful in lead-free nonvolatile ferroelectric random access memory applications.

1. Introduction

Ferroelectric thin films have recently attracted much attention due to their rapid response of polarization switching, low power consumption and long lifetime of 10^{12} read/write cycles. These strengths have led to the application of FeRAMs in small devices, such as smart cards, personal digital assistants and future personal computers.[1]

As candidate materials of FeRAMs, $PbZr_xTi_{1-x}O_3$ (PZT) thin films have been extensively investigated, since PZT exhibits several advantages such as a large remanent polarization and a relatively low processing temperature. However, PZT exhibits serious disadvantages in switching endurance with common Pt electrodes. Although fatigue resistance of PZT has been improved with oxide electrode, usage of oxide electrode increases complexity of fabrication process and cost. Furthermore, PZT contains an environmentally hazardous element, Pb. Therefore, environmentally safe alternative ferroelectric materials, i.e., lead-free, have been investigated for memory applications.[2]

$SrBi_2Ta_2O_9$ (SBT) and $Bi_4Ti_3O_{12}$ (BIT), among lead-free ferroelectric, are promising materials for these purposes and have been extensively studied. SBT thin films show superior fatigue endurances against polarization switching over 10^{12} cycles, but in has a few disadvantages, such as high process temperature of 750-850 °C and relatively small remanent polarizations ($2P_r$) of 4-8 $\mu C/cm^2$, which make it difficult to use BIT for real device applications. Recent studies revealed that Bi3+ ions in BIT structure could be substituted by trivalent lanthanide ions, and their ferroelectric properties were in the reasonable ranges for memory applications. Lanthanide-substituted BIT thin films are attractive lead-free materials for memory applications because of their relatively large remanent polarization and fatigue-free characteristics.[3]

A wide array of deposition techniques have been used for the fabrication of lanthanoid element-substituted bismuth titanate thin films, including metal organic chemical vapor deposition (MOCVD), sputter deposition, Laser ablation deposition, sol-gel deposition, metalorganic deposition (MOD) and pulse laser deposition (PLD). Among these processes, MOCVD has attracted a great deal of attention, due to its providing conformable step coverage and good uniformity of thickness and composition. In this study, we prepared Gd-modified $Bi_4Ti_3O_{12}$ thin films by means of the liquid delivery MOCVD system. 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.[4-5]

2. Experiment

A single mixture solution of $Bi(ph)_3$, $Gd(TMHD)_3$ 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. BGT 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 BGT precursors was confirmed by TG analysis. The composition of the films was measured by EPMA (JEOL, JXA-8900R). 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.

3. Results and Discussion

3.1. Surface morphology of BGT thin films

The surface morphology of the BGT thin films was recorded by SEM. As shown in Fig. 1, the grain size of the BGT thin films annealed at 720 °C ranged from 0.2 to 0.3 μm. The grain size of the films increases with increased annealing temperatures. It is assumed that crystal growth was enhanced, and thus that the ferroelectric properties of the films can be improved by increasing the annealing temperature.

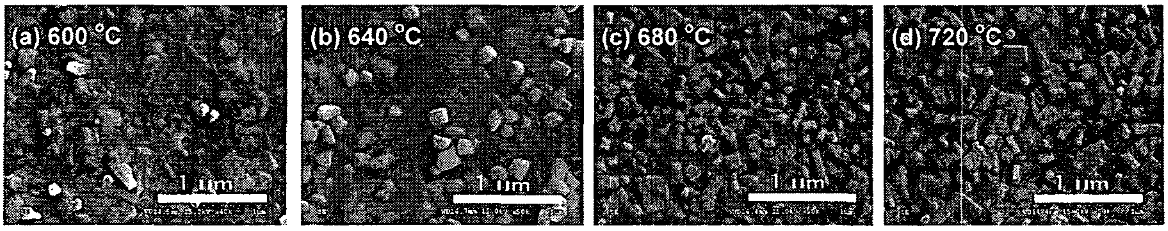

Fig. 1. SEM micrographs of the BGT thin films with various annealing temperatures.

3.2. Electrical Properties of the BGT thin films

Ferroelectric hysteresis loops of BGT thin film capacitor annealed at the temperature range from 600 to 720 ℃ are shown in Fig. 2. As presented in Fig. 2, the BGT thin film capacitor is characterized by well-saturated polarization-electric field (P-E) curves. The remanent polarization ($2P_r$) values of BGT thin film annealed at 720 ℃, which are 37.36 and 45.13 μC/cm^2 at applied voltages of 3 V and 5 V, respectively, indicate high performance of ferroelectricity.

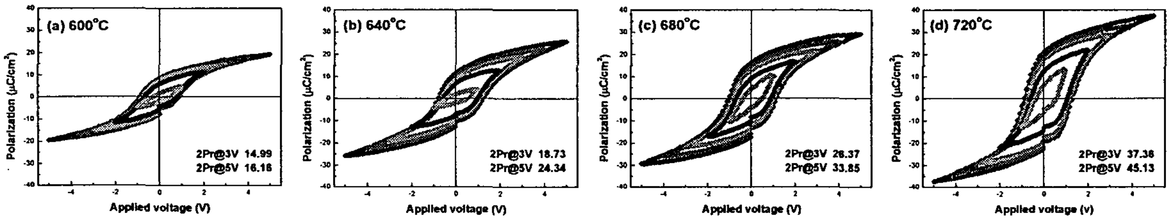

Fig. 2. Hysteresis loops of BGT thin films annealed at various temperatures.

3.3. Reliability of the BGT thin films

Leakage current of Pt/BGT/Pt thin film capacitors was measured by applying a staircase DC voltage on the top and bottom electrodes. Fig. 3 exhibits leakage current density of BGT thin films versus applied DC electric voltage. The leakage current density is typically less than 10^{-6} A/cm^2 under the applied voltage up to about 4.3 V, which demonstrates that relatively good insulating properties were obtained for BGT thin films. The switched polarization as a function of the number of switching cycles, as determined using 1 MHz bipolar pulses at 5 V, is plotted in Fig. 3. The degradation of switching charge after 1×10^{11} switching cycles was within 5 %. It was experimentally shown that there was almost no data loss at least up to 1×10^{11} switching cycles.

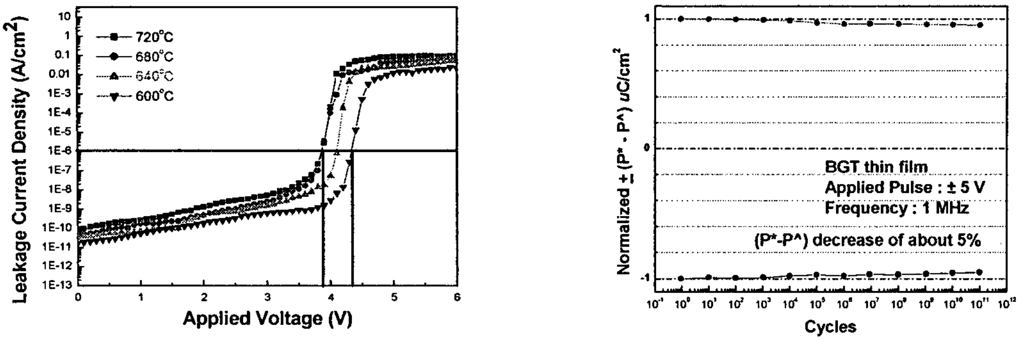

Fig. 3. I-V and fatigue characteristics of the BGT thin film capacitor.

4. Conclusions

Ferroelectric BGT thin films were reproducibly fabricated on Pt(111)/Ti/SiO_2/Si(100) substrates by liquid delivery MOCVD system. The BGT thin films showed good ferroelectric properties and low annealing temperature that could satisfy the requirements for high-density complementary metal oxide semiconductor (CMOS) devices. As the results, the BGT thin films are potentially important candidates for non-volatile ferroelectric memories applications.

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

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

References

[1] Bondurant D, et al, IEEE Spectrum, (1989), P. 30~33
[2] C. A. Paz de Araujo, et al, Nature, Vol. 374 , (1995), P.627
[3] S. E. Cummins, et al, J. Appl. Phy., Vol. 39, (1968), P. 2268
[4] T. Watanabe, et al, J. Appl. Phys., Vol. 90 , (2001), P. 6533
[5] D. K. Kang, et al, Thin Solid Films, Vol. 492, (2005), P.140-145