Electrical Properties of $(Bi,Y)_4Ti_3O_{12}$ Thin Films Grown by RF Sputtering Method

Sung-Pill Nam*, Sung-Gap Lee, Seon-Gi Bae*** and Young-Hie Lee†**

Abstract - Yttrium(Y)-substituted bismuth titanate $(Bi_{4-x}Y_x)Ti_3O_{12}$ [x=0, 0.25, 0.5, 0.75, 1] (BYT) thin films were deposited using an RF sputtering method on the $Pt/TiO_2/SiO_2/Si$ substrates. The structural properties and electrical properties of yttrium-substituted $(Bi_4\text{-}xYx)Ti_3O_{12}$ thin films were analyzed. The remanent polarization of $(Bi_4\text{-}xYx)Ti_3O_{12}$ films increased with increasing Y-content. The $(Bi_{3.25}Y_{0.75})Ti_3O_{12}$ films fabricated using a top Au electrode showed saturated polarization-electric field (*P-E*) switching curves with a remanent polarization (*Pr*) of 8 $\mu C/cm^2$ and coercive field (*Ec*) of 53 kV/cm at an applied voltage of 7 V. The $(Bi_{3.25}Y_{0.75})Ti_3O_{12}$ films exhibited fatigue-free behavior up to 4.5×10^{11} read/write switching cycles at a frequency of 1MHz.

Keywords: BYT, Fatigue property, RF sputtering, Thin film

1. Introduction

The concern for ferroelectric materials for nonvolatile random access memory (FRAM) applications has intensified, creating significant attention and demand due to their low-power requirements, fast access speed and low cost. Among various ferroelectric materials, lead zirconate titanate (PZT) offers the advantages of various electrical properties and a large remanant polarization [1-2]. Although the PZT thin films have the advantage of low processing temperature and large polarization, PZT films on Pt electrodes for ferroelectric random access memories still exhibit several degradation problems such as severe polarization fatigue after long bipolar switching pulses. Recently, Bismuth layered perovskite-like structure ferroelectric thin films such as $SrBi_2Ta_2O_9$ and $(Bi_{3.25}La_{0.75})Ti_3O_{12}$ (BLT) have been found to exhibit no significant polarization fatigue and a low coercive field with Pt bottom electrodes [3-6]. Substituting a lanthanoid element for Bi with a smaller ionic radius than La in the pseudoperovskite layer improves the ferroelectric properties. The effects of substituting Nd, Sm and Eu for Bi with a smaller ionic radius than La in the pseudoperovskite layer on ferroelectric properties were reported [7-9]. However, the effects of bismuth substitution by yttrium in the perovskite layer have not been reported so far.

In this study, $(Bi_{4-x}Y_x)Ti_3O_{12}$ thin films with various Y-content were grown on $Pt/TiO_2/SiO_2/Si$ substrates using the RF sputtering method. The effect of substituting yttrium for bismuth in structure on the ferroelectric properties, such as the remanent polarization and fatigue has been investigated systematically.

2. Experiments

The BYT ceramics target of the RF sputtering system was prepared by the conventional mixed oxide method. The starting materials were Bi_2O_3, Y_2O_3, and TiO_2. Those materials were weighed according to the composition of $(Bi_{4-x}Y_x)Ti_3O_{12}$ [x=0, 0.25, 0.5, 0.75, 1], the weight ratio of zirconia ball to powder in the mill was 1:1 and ethyl alcohol was used as a process control agent. The slurry was dried at 100℃ for 24 hr. The dried powder was calcinated at 750℃ for 2hr in air. Calcined powders were screened by mesh (#200) and the screened powders were then pressed to cylindrical pellets in steel die (φ=2 inch) and sintered at 1050℃ for 3 hr. The sintered ceramic target was lapped and silver paste was fired on the sample faces at 600℃. The BYT thin films were grown on $Pt/TiO_2/SiO_2/Si$ substrates by RF sputtering method. The initial vacuum was about 3×10^{-6} [Torr] and the sputtering atmosphere was controlled by the Ar/O_2 ratio at a total pressure of 3×10^{-3} [Torr]. The RF power for the BYT targets was 100W and the target-substrate distance was about 7[mm]. The total of the BYT thin films was deposited in our experiment. The thickness of the films was measured using a field emission electron microscope and α

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step. The crystalline structures of the BYT thin films were analyzed by X-ray diffraction (XRD). A Digital Instrument NanoScope Ⅲa atom force microscope (AFM) was used to investigate the surface morphology of the films. The surface and cross-sectional microstructures of the films were examined by a field emission scanning electron microscope (FESEM). The compositional depth profile and interdiffusion between the films and substrate were investigated by Auger electron spectroscopy (AES). For electrical measurements, an Au thin film was deposited by an evaporator at room temperature as the top electrode with a diameter of 0.1 mm. The dielectric constant and dielectric loss measurements were carried out by using an impedance/gain phase analyzer (HP4192A). The ferroelectric properties of the BYT thin films were measured by RT66A tester (Radiant Technologies).

3. Results and discussion

The X-ray diffraction (XRD) patterns of $(Bi_{4-x}Y_x)Ti_3O_{12}$ thin films are presented in Fig. 1 (x=0, 0.25, 0.5, 0.75, 1), after being annealed at 650℃. XRD results indicated that the films consisted of a Bi-layered perovskite structure. The *c*-axis orientation is obtained by comparing the series of peaks to the (117) peak, which is normally the dominant peak in $Bi_4Ti_3O_{12}$ with random orientation.

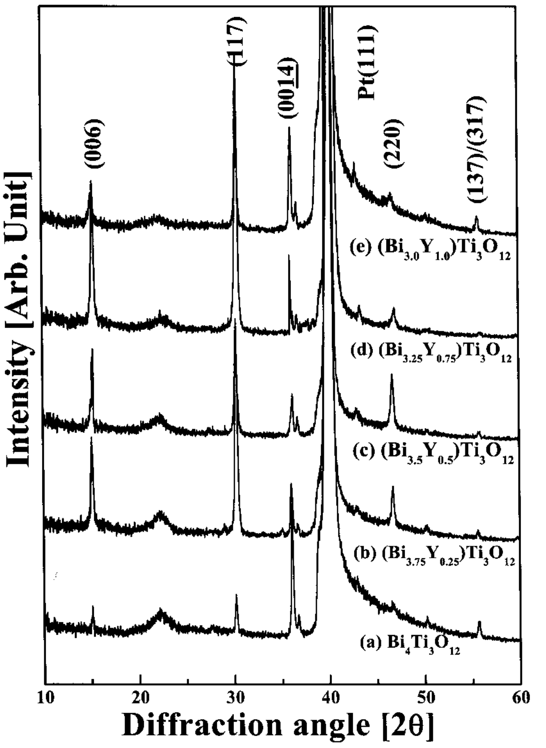

Fig. 1. XRD patterns of $(Bi_{4-x}Y_x)Ti_4O_{12}$ films with various Y compositions

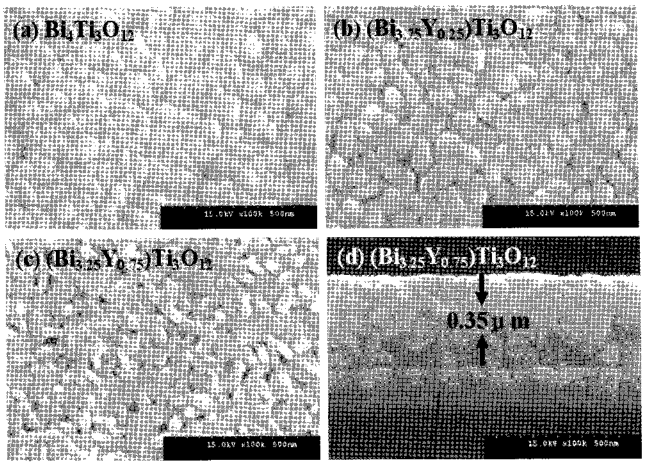

Fig. 2. (a), (b), (c) Surface morphology and (d) cross-sectional micrograph of $Bi_4Ti_3O_{12}$, $(Bi_{3.75}Y_{0.25})Ti_3O_{12}$ and $(Bi_{3.25}Y_{0.75})Ti_3O_{12}$ thin films deposited on Pt/Ti/SiO$_2$/Si substrate

The $Bi_4Ti_3O_{12}$ films had the preferred orientation of (117) peak. As the content of Y in $(Bi_{4-x}Y_x)Ti_3O_{12}$ films increased, the (006) peak gradually increased. However, the $(Bi_{4-x}Y_x)Ti_3O_{12}$ film with x=1.0 showed low intensities of (006), (117). These results indicate that the substitution of Y for Bi in $Bi_4Ti_3O_{12}$ crystals substantially increases the peak.

The surface morphologies and cross-sectional micrograph of $Bi_4Ti_3O_{12}$, $(Bi_{3.75}Y_{0.25})Ti_3O_{12}$ and $(Bi_{3.25}Y_{0.75})Ti_3O_{12}$ thin films on Pt(111)/Ti/SiO$_2$/Si substrates investigated by FESEM are shown in Fig. 2(a), (b), (c) and (c), respectively. The $Bi_4Ti_3O_{12}$ thin film exhibits more dense surface texture and grain size compared with $(Bi_{3.25}Y_{0.75})Ti_3O_{12}$ thin film. The plate-like grains were randomly distributed on the substrates. The planar grains may correspond to the preferred orientation of XRD. These results are consistent with the results observed using XRD analysis. Also, the average grain size of BYT films decreases with increasing Y-content. Fig. 2(c) shows the cross-sectional micrograph of $(Bi_{3.25}Y_{0.75})Ti_3O_{12}$ thin films. The images exhibit a clear and sharp boundary between the films and Pt bottom electrodes. The thickness of $(Bi_{3.25}Y_{0.75})Ti_3O_{12}$ thin films was approximately 350nm.

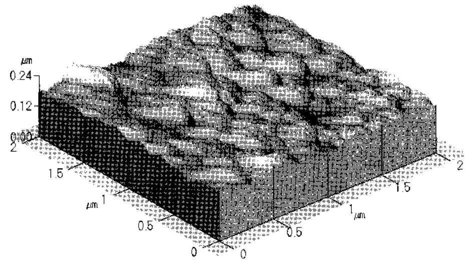

Fig. 3. AFM image of $(Bi_{3.25}Y_{0.75})Ti_3O_{12}$ thin films surface taken over the scanning area of 2×2 μm^2

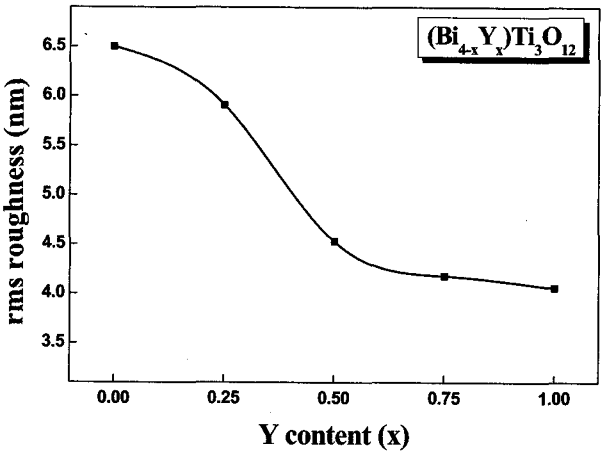

Fig. 4. Root mean square roughness of $(Bi_{4-x}Y_x)Ti_3O_{12}$ thin films with various Y compositions

Fig. 3 shows the AFM image of the $(Bi_{3.25}Y_{0.75})Ti_3O_{12}$ film surface with roughness of about 5.91nm. The surfaces of $(Bi_{3.25}Y_{0.75})Ti_3O_{12}$ thin films are uniform and crack free. The coarse grains seem to be a weakly crystalline bismuth layered perovskite phase. The variation of root mean square (rms) roughness of $(Bi_{4-x}Y_x)Ti_3O_{12}$ thin films with various yttrium compositions is shown in Fig. 4. The rms value of the BYT films was approximately 3.3-6.5nm, indicating a relatively smooth surface.

Fig. 5 depicts the polarization-electric field (*P-E*) hysteresis curves of the $(Bi_{3.25}Y_{0.75})T_3O_{12}$ and $Bi_4Ti_3O_{12}$ thin films measured at an applied voltage of 7V. The remanent polarization (P_r) of $(Bi_{3.25}Y_{0.75})T_3O_{12}$ and $Bi_4Ti_3O_{12}$ thin films are 8μC/cm^2 and 4.9μC/cm^2, respectively. The ferroelectric properties are related to content stoichiometry, grain size and crystallization.

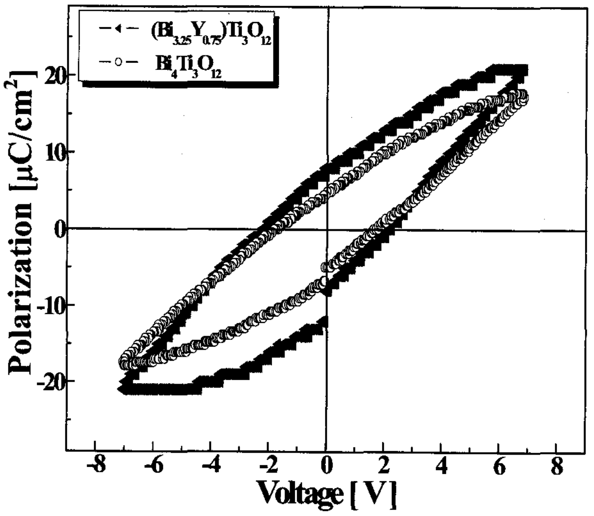

Fig. 5. P-E hysteresis curves of the $Bi_4Ti_3O_{12}$ and $(Bi_{3.25}Y_{0.75})Ti_3O_{12}$

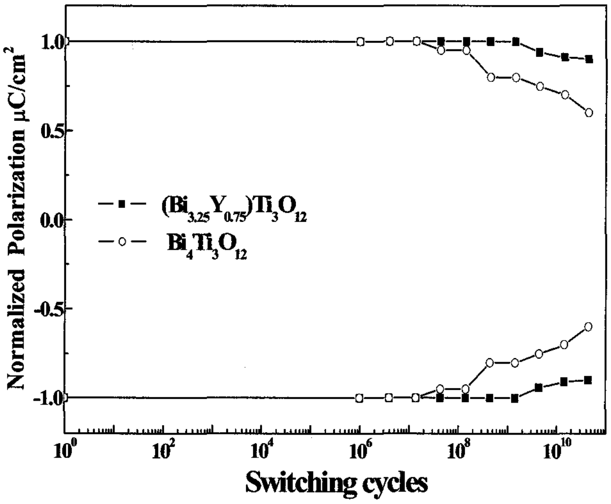

Fig. 6. Fatigue properties of $Bi_4Ti_3O_{12}$ and $(Bi_{3.25}Y0_{.75})Ti_3O_{12}$ thin films measured at 5V and 1MHz

As shown in Fig. 6, fatigue properties of $(Bi_{3.25}Y_{0.75})T_3O_{12}$ and $Bi_4Ti_3O_{12}$ films were measured using a bipolar square wave of 5V in the 1MHz. The $(Bi_{3.25}Y_{0.75})T_3O_{12}$ films showed practically no polarization fatigue after the sample was switched up to 1.0 × 10^{11} cycles. The fatigue characteristic of the $(Bi_{3.25}Y_{0.75})T_3O_{12}$ thin films are similar to the BLT thin films. These effects indicated that the substitution of Y for Bi in $Bi_4Ti_3O_{12}$ crystals significantly enhances the resistance against the polarization fatigue.

4. Conclusion

The $(Bi_{4-x}Y_x)T_3O_{12}$ thin films with Y-contents between x=0 and 1.0 have been grown on Pt/TiO_2/SiO_2/Si substrates by RF sputtering method. Y-doped $(Bi_{3.25}Y_{0.75})Ti_3O_{12}$ films exhibited large remanent polarization and a low coercive field. The 2P_r indicates maximum value of 20μm/cm^2 at x=0.75 of $(Bi_{4-x}Y_x)T_3O_{12}$ films. The $(Bi_{3.25}Y_{0.75})Ti_3O_{12}$ films demonstrated practically no polarization fatigue after the film was switched up to 4.5 × 10^{11} cycles. From these results, $(Bi_{3.25}Y_{0.75})Ti_3O_{12}$ films having a good ferroelectric property are useful candidates for ferroelectric random access memory applications.

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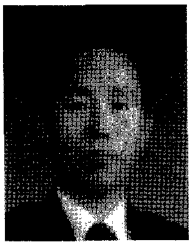

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