

Electrical Properties of Sol-gel Derived Ferroelectric $\text{Bi}_{3.35}\text{Sm}_{0.65}\text{Ti}_3\text{O}_{12}$ Thin Films by Rapid Thermal Annealing

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Ferroelectric $\text{Bi}_{3.35}\text{Sm}_{0.65}\text{Ti}_3\text{O}_{12}$ (BSmT) thin films were synthesized using a sol-gel process. $\text{Bi}(\text{TMHD})_3$, $\text{Sm}_5(\text{O}^i\text{Pr})_{13}$, $\text{Ti}(\text{O}^i\text{Pr})_4$ were used as the precursors, which were dissolved in 2-methoxyethanol. The BSmT thin films were deposited on $\text{Pt}/\text{TiO}_x/\text{SiO}_2/\text{Si}$ substrates by spin-coating. The electrical properties of the thin films were enhanced using rapid thermal annealing process (RTA) at 600 °C for 1 min in O_2 . Thereafter, the thin films were annealed from 600 to 720 °C in oxygen ambient for 1 hr, which was followed by post-annealed for 1 hr after depositing a Pt electrode to enhance the electrical properties. X-ray diffraction (XRD) and scanning electron microscopy (SEM) were used to analyze the crystallinity and surface morphology of layered perovskite phase, respectively. The remanent polarization value of the BSmT thin films annealed at 720 °C after the RTA treatment was $35.31 \mu\text{C}/\text{cm}^2$ at an applied voltage of 5 V.

Keywords : BSmT, BTO, FRAM, Sol-gel, Spin-coating

1. INTRODUCTION

Ferroelectric random access memory (FRAM) has considerable potential for new memory applications owing to its properties for ideal memory such as high-density integration, fast read and write operation, long endurance, excellent retention and non-volatility with unlimited use in practice. Among the materials used as FRAM capacitors, bismuth layer-structured ferroelectrics have attracted considerable attention as alternative materials to conventional Pb-based ferroelectrics owing to its good fatigue property[1,2]. Essentially, $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ (BTO) is known to show high crystallinity at lower temperatures compared with $\text{SrBi}_2\text{Ta}_2\text{O}_9$ (SBT) and its related materials[3,4]. However, BTO contains unstable Bi ions in its structure, which are easily evaporated during the heating process. The volatility of Bi ions effects the ferroelectric and fatigue characteristics of the thin films[5]. Bi^{3+} in the BTO structure can be substituted with trivalent rare-earth ions, such as La^{3+} , Nd^{3+} , and Sm^{3+} , which can improve the properties of such layer-structures[6,7]. Among them, $\text{Bi}_{4-x}\text{Sm}_x\text{Ti}_3\text{O}_{12}$ (BSmT) has been received a great deal of attention owing to its larger remanent polarization than that of $\text{Bi}_{4-x}\text{La}_x\text{Ti}_3\text{O}_{12}$ (BLT)[8].

Thin films of this material are prepared by RF

sputtering, MOCVD, PLD, MOD and the sol-gel process. Among the various techniques, sol-gel processing was employed in this study because it offers excellent uniformity over large areas, easy composition control, short fabrication time, as well as it being a low temperature process at a comparatively low cost. However, the chemical stability of the solution is very important in the sol-gel process. In this experiment, a chelating agent was used to improve the chemical stability of the solution, and the thin films were prepared by spin-coating on the substrates. In order to examine the effect of RTA process, the thin films with non-RTA and the thin films with RTA were prepared. The ferroelectric properties and microstructures of the BSmT thin films according to the synthetic process and furnace annealing temperature were investigated.

2. EXPERIMENTAL PROCEDURE

$\text{Bi}_{3.35}\text{Sm}_{0.65}\text{Ti}_3\text{O}_9$ stock solutions were synthesized using the sol-gel process. Tris(2,2,6,6-tetramethyl-3,5-heptanedionato) bismuth (III) [$\text{Bi}(\text{TMHD})_3$], Samarium (III) i-propoxide [$\text{Sm}_5\text{O}(\text{OC}_3\text{H}_7)_{13}$] and Titanium (IV) i-propoxide [$\text{Ti}[\text{OCH}(\text{CH}_3)_2]_4$] were used as precursors. In addition, 2-methoxyethanol was used as the solvent and

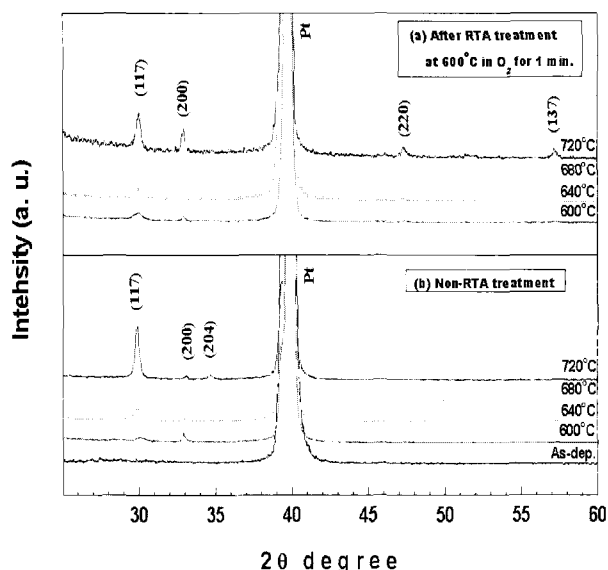


Fig. 4. XRD patterns of the BSmT thin films furnace-annealed at various temperatures for 1 hr in O_2 (a) BSmT thin films treated RTA and (b) BSmT thin films treated non-RTA.

treated BSmT thin films became larger with the increasing furnace-annealing temperatures, as shown in Figs. 4(b). However, in the case of the RTA treated BSmT thin films, the intensities of the (200) and (117) diffraction peaks increased with the increasing annealing temperature, as shown in Figs. 4(a). Generally, bismuth-layered structural materials show good ferroelectric properties in the a,b-axis orientation than c-axis orientation[9]. From these results, it is believed that the treated RTA BSmT thin films have better ferroelectric properties than the non-RTA treated BSmT thin films.

3.3 Micro-structures of BSmT thin films

Figures 5 and 6 show SEM micrographs of the BSmT thin films with various annealing temperatures. From Fig. 5, there were 30-50 nm size grains in the matrix in case of the BSmT thin films annealed at 600 °C. With increasing annealing temperature to 680 °C, approximately 200-300 nm size grains such as rod appeared in the matrix. The grains of the BSmT thin films annealed at 720 °C had a rod-like and plate-like appearance. However, the treated RTA BSmT thin films grew spherical shape grains with increasing annealing temperature. In the case of the BSmT thin films annealed 720 °C after the RTA treatment, approximately 100 nm size grains existed in the matrix. It is believed that the generation of a seed-layer by the RTA process resulted in the type of grain growth observed. Figure 7 shows a cross-section image of the BSmT thin films annealed at 640 °C. The thickness of the BSmT thin films was 240 nm.

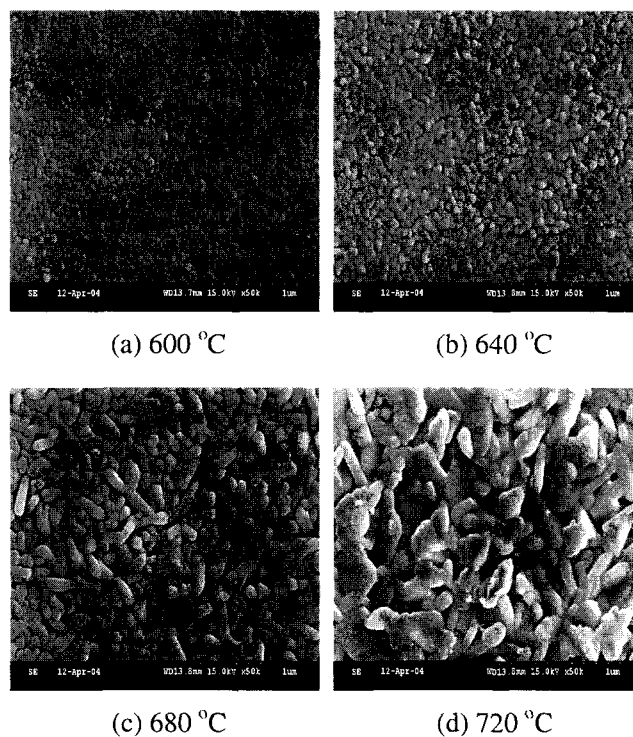


Fig. 5. SEM surface images of the BSmT thin films furnace-annealed at various temperatures for 1 hr in O_2 (a) 600 °C, (b) 640 °C, (c) 680 °C, and (d) 720 °C.

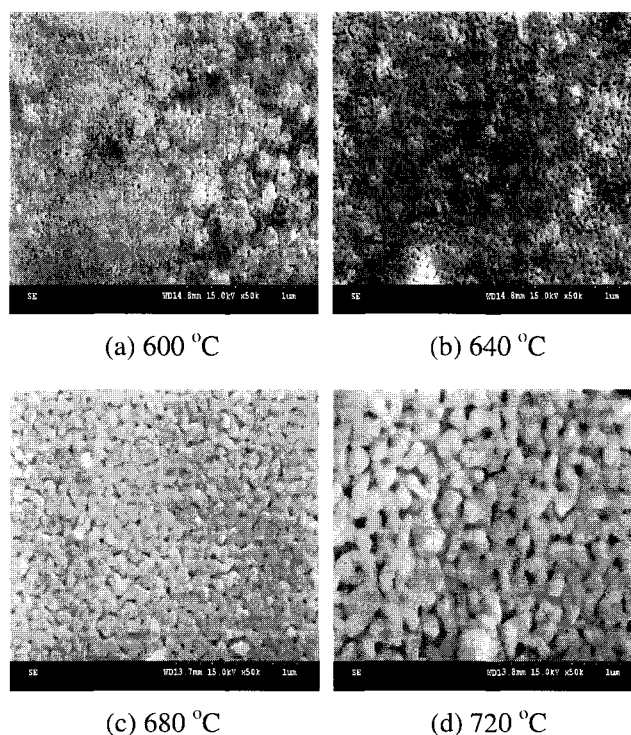


Fig. 6. SEM surface images of the BSmT thin films furnace-annealed at various temperatures for 1 hr in O_2 after the RTA treatment for 1 min in O_2 (a) 600 °C, (b) 640 °C, (c) 680 °C, and (d) 720 °C.

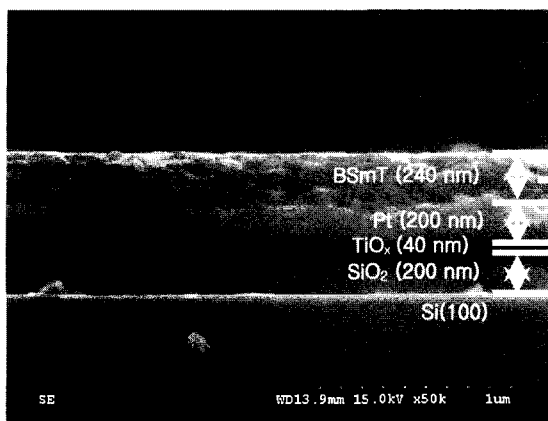


Fig. 7. The cross-section image of the BSmT thin films furnace-annealed at 640 °C for 1 hr in O₂.

3.4 Ferroelectric property of BSmT thin films

Figures 8 and 9 show the P-V hysteresis loops of the BSmT thin films at various post annealing temperatures. From Fig. 8, the BSmT thin films annealed at the relative low temperatures (600, 640 °C) exhibited paraelectric properties. However, according to the increase in the annealing temperatures to 680 °C and 720 °C, the BSmT thin films exhibited ferroelectric properties. With increasing annealing temperature from 600 to 720 °C, the remanent polarization (2Pr) values of the BSmT thin films were 5.64, 7.74, 12.85, and 19.48 $\mu\text{C}/\text{cm}^2$ at an applied voltage of 5 V, respectively. However, in the case of the treated RTA BSmT thin films, better ferroelectric properties than the non-RTA treated BSmT thin films were observed. With increasing annealing temperature, the remanent polarization values are 6.44, 13.33, 21.89, and 35.31 $\mu\text{C}/\text{cm}^2$ at an applied voltage of 5 V, respectively. This indicates that the RTA treatment improves the ferroelectric properties of the BSmT thin films.

Figure 10 shows the leakage current densities of the BSmT thin films annealed at various temperatures as a function of the applied field. Generally, a leakage current density under 10^{-6} A/cm² is required in the application of FRAM capacitors. The non-treated BSmT thin films exhibit a resistivity in the range of 10^{-11} - 10^{-12} A/cm² at a DC bias of 0-2.8 V applied to the capacitor. In constant, the RTA treated BSmT thin films exhibited a resistivity $\leq 10^{-9}$ A/cm² when a DC bias of 0-2.3 V was applied to the capacitor. Beyond this range, the leakage current of the thin films increased markedly. As the annealing temperature of the BSmT thin films was increased from 600 to 720 °C, the breakdown voltage was decreased. It is assumed that the higher leakage current may be caused by the larger grain sizes of the BSmT thin films, and the RTA process affects the leakage current densities of the BSmT thin films.

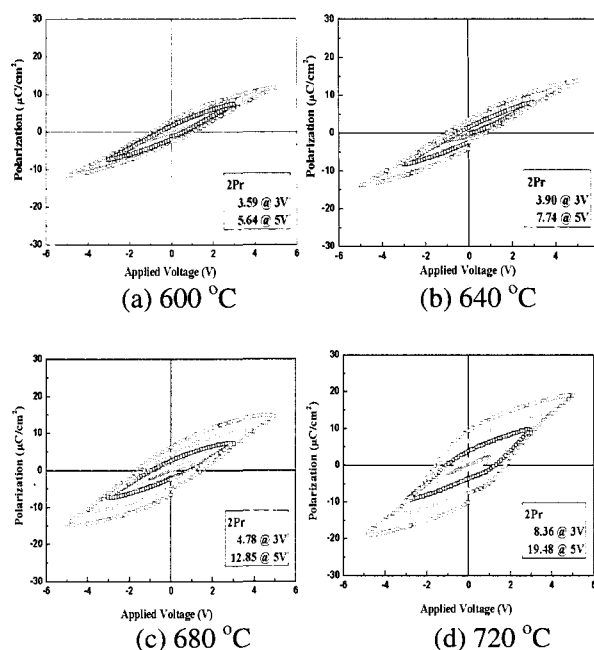


Fig. 8. Hysteresis loops of the BSmT thin films furnace-annealed at various temperatures for 1 hr in O₂ (a) 600 °C, (b) 640 °C, (c) 680 °C, and (d) 720 °C.

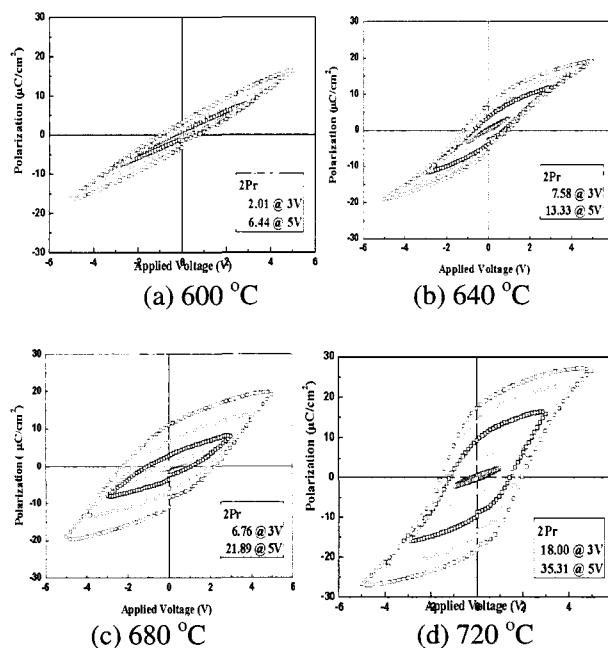


Fig. 9. Hysteresis loops of the BSmT thin films furnace-annealed at various temperatures for 1 hr in O₂ after the RTA treatment (a) 600 °C, (b) 640 °C, (c) 680 °C, and (d) 720 °C.

Figure 11 summarizes the fatigue-free characteristics of the BSmT capacitor films. Regardless of the RTA process, the capacitors showed little change in both the

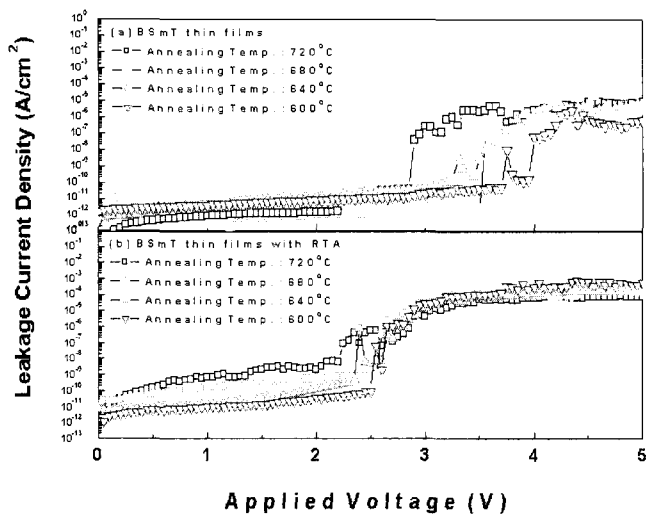


Fig. 10. Leakage current density of the BSMT thin films at various temperatures for 1 hr in O_2 (a) non-RTA treated BSMT thin films and (b) RTA treated BSMT thin films.

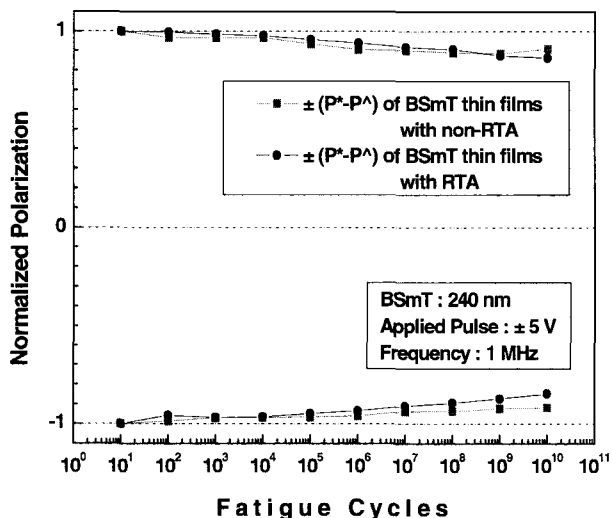


Fig. 11. Results of the fatigue test of the BSMT thin film at 1 MHz bipolar square pulse wave.

(P^*-P^A) and $(-P^*-(-P^A))$ values at a switching voltage of ± 5 V. The degradations of the switching charge after 1×10^{10} switching cycles were within 10 % and 15 %, respectively. The improved fatigue characteristics of the lanthanide-doped films may be attributed to the lower concentration of oxygen vacancies in the perovskite layers than in the BTO thin films[10].

4. CONCLUSION

Ferroelectric BSMT thin films were prepared by a

spin-coating method using a sol-gel solution. The electric properties of the BSMT thin films were investigated. The results can be summarized as follows :

1. The treated RTA BSMT thin films treated RTA showed good ferroelectric properties, and the remanent polarization value ($2P_r$) of the BSMT thin films annealed at 720°C at an applied voltage of 5 V was $35.31 \mu\text{C}/\text{cm}^2$ at an applied voltage of 5 V.
2. The sol-gel derived BSMT thin films showed good fatigue properties. The degradation of the switching charge after 1×10^{10} switching cycles was within 15 %.

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