Ferroelectric Properties of SBT Capacitor with Annealing Times

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The $Sr_{0.7}Bi_{2.3}Ta_2O_9$(SBT)thin films are deposited on Pt-coated electrode ($Pt/TiO_2/SiO_2/Si$) using a RF magnetron sputtering method. The ferroelectric properties of SBT capacitors with annealing times were studied. As a result of conducting the X-ray diffraction analysis and the electron microscopy analysis, the perovskite phase began to grow from 10 minutes after annealing the specimen, and excellent crystallization was accomplished at 60 minutes after annealing the specimen. The remanet polarization ($2P_r$) value and the coercive electric field (E_c) of the SBT thin film specimen showed the most excellent characteristics at 60 minutes after annealing the specimen, which were approximately 12.40 C/cm^2 and 30 kV/cm, respectively. The leakage current density of the SBT thin film specimen as annealed for 60 minutes was approximately 2.81×10^{-9} A/cm^2.

Keywords : RF magnetron sputtering method, Annealing times, Ferroelectric properties

1. INTRODUCTION

As demands for micronization, high integration and high speed of electronic circuits and components are increased with rapid advancement of the technology for manufacturing semiconductor elements, research activities for development of a thin film element having superior electric and structural characteristics as an electronic component are actively in progress[1,2] .

A ferroelectric thin film material for FRAM on which studies have been most widely conducted is the PZT-family material. Since the PZT thin film has a high permittivity, a small coercive force and a great amount of residual polarization, it has characteristics appropriate for a non-volatile material, while it has weak points that its leakage current is great, and that its breakdown voltage is low, and that the aging and fatigue phenomenon that the residual polarization gets to be reduced depending upon the time of leaving it and the number of switching times takes place[3,4].

However, it has been reported that the bithmuth-family SBT thin film, which has improved greatly the fatigue phenomenon, the greatest problem taking place when the PZT thin film is used, is much better than the PZT thin film in such characteristics as imprint, retention and leakage current as well as in the fatigue phenomenon[5,6]. Also, it has been reported that the SBT ferroelectric thin film (SBT is a compound oxide) is much superior to the PZT ferroelectric thin film in the fatigue characteristic and the leakage current, showing that its fatigue characteristic is of 10^9 cycles and its leakage current is of 10^{-8} A/cm^2[7,8] .

Thus, SBT capacitors will be applicable to not only information telecommunication instruments but also accumulation of analog signals and embodiment of a neural net element.

In this study, SBT thin films were manufactured by using the RF magnetron sputtering method which was relatively excellent in the stability and the reproducibility, and ferroelectric characteristics of the SBT capacitor depending upon a change in the annealing time were observed and investigated. Such study results are reported.

2. EXPERIMENT

In this work, SBT target was processed by mixing $SrCo_3$, Bi_2O_3, and Ta_2O_5 powders, calcining the mixed powders at 1000 ℃ during 2 hours, and then pressing the calcined powders in a 2in. The pressed target was sintered for 1h at 1100℃ in ambient air. The composition of the ceramic target was $Sr_{0.7}Bi_{2.3}Ta_2O_9$. All substrates were thoroughly cleaned in a series of organic solvents and distilled water prior to film deposition. The detailed sputtering conditions of SBT thin films are summarized in Table 1.

Using this wafer $Pt/TiO_2/SiO_2/Si$ as a substrate, we formed a SBT thin film of 300nm thickness and a Pt top electrode of 0.1mm diameter by sputtering using a metal mask. The typical film thickness was about 300 nm, measured by α -step.

Table 1. Sputtering condition of SBT thin films .

sputtering condition	values
target	SBT(2 inch)
substrate	p-type $Pt/TiO_2/SiO_2/Si(100)$
base pressure	5×10^{-6}[Torr]
working pressure	2×10^{-2}[Torr]
RF power	100[W]
annealing temperature	750℃
Ar : O_2	1 : 1

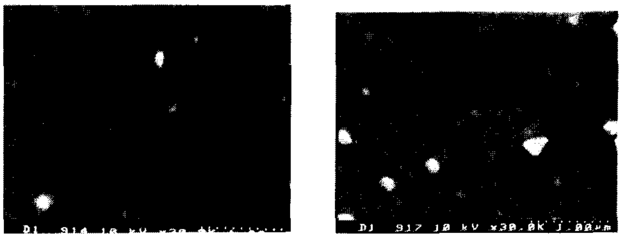
The best properties were obtained for about 750 ℃ annealing temperatures. so, this paper focuses on the structrual , ferroelectric properties of the thin films with 750 ℃ annealing temperature.

The crystallography of the films was analyzed X-ray diffraction. Surface morphology were examined by Field-Emission Scanning Electron Microscope(FE-SEM). The ferroelectric characterization of the capacitors was measured by using a RT66A ferroelectric tester(Radiant Technologies). The electrical measurements were perfor med using HP 4192A impedance analyzer and HP4155A semiconductor parameter analyzer.

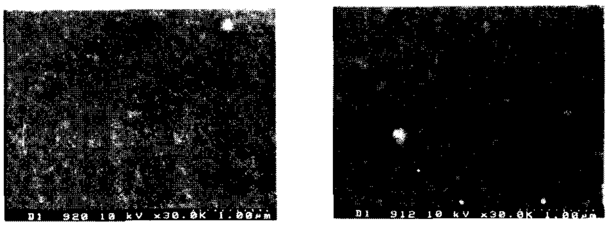
3. RESULTS AND DISCUSSION

3.1 Structural characteristics of a SBT thin film

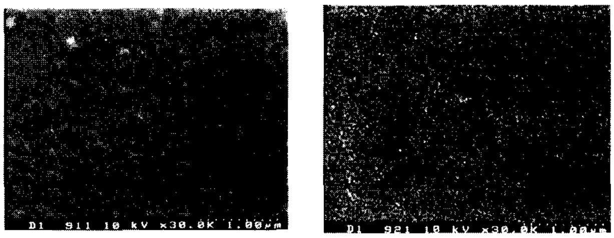
Figure 1 shows the results of observing the micro structure of the SBT thin film specimen after it was as-deposited at 400 ℃ and the annealing time was changed in the range of 1 minute to 60 minutes at 750 ℃ for observation of the structure and the surface condition of the crystal grain depending upon the annealing time. Fig. 1(a) is a SEM photo of the SBT thin film specimen as taken after as-deposition, and when comparing it with the specimen as annealed for 1 minute at 750 ℃, it could be observed that fine grains grew by annealing it.



(a) as-deposited (b) 1 min



(c) 3 min (d) 10 min



(e) 30 min (f) 60 min

Fig. 1. SEM photographs of SBT thin films with annealing times.

As the annealing time was increased, the size of the grain was gradually enlarged. Particularly, it could be observed that grains began to appear in the specimen as annealed for 10 minutes, and the size of the grain got to be very distinct and the average grain size got to be enlarged more uniformly in the specimen as annealed for 30 minutes or more.

Also, the as-deposited specimen (as-deposition temperature: 400 ℃ as shown in Fig. 1(a) was of a completely amorphous phase, and it could be observed that beginning with the specimen as annealed for 3 minutes at 750 ℃, as shown in Fig. 1(a), fine crystal grains began to grow. This was well consistent with the result of the study conducted by Nobuyuki Soyama, et al.[9] This result could be also identified in the 'XRD' as shown in Fig. 3. In the case of the specimen as shown in Fig. 1(d) and annealed for 10 minutes, its phase was transformed from the fluorite-like phase into the complete layer-structured perovskite phase, and it has been reported that this phase is of the SBT structure[10]. The SBT thin film specimen as shown in Fig. 1(e) and annealed for 30 minutes was much better crystallized than the specimen as annealed for 10 minutes. This represents the study result that SBT peaks grew much better also in the 'XRD'as shown in Fig. 3. And, it was identified that the specimen as annealed for 60 minutes had the most excellent ferroelectric characteristics. Further, it was identified from this result that the specimen as annealed for 10 minutes had the SBT ferroelectric characteristics.

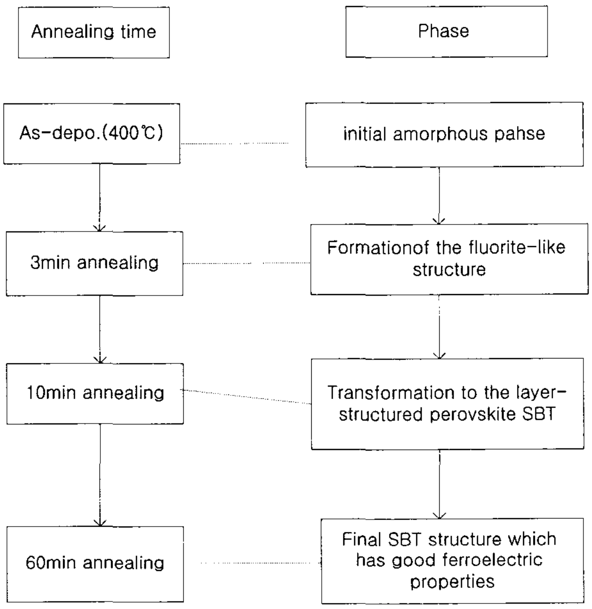


Fig. 2. The multistage crystallization process of SBT thin films with annealing times.

However, at this stage, the structure of the specimen grew non-uniformly so that it was not appropriate for application. However, it could be observed that the crystal and the texture of the specimen as annealed for 30 minutes or more grew very uniformly and evenly.

Figure 2 is a block diagram showing the mechanism for crystallization of the SBT thin film specimen. The specimen as vapor-deposited at the substrate temperature of 400 ℃ was of the amorphous phase. Its structure was transformed into the fluorite-like structure after it was annealed at 750 ℃ for 3 minutes, and the crystal phase of the specimen as annealed for 10 minutes was transformed into the layer-structured perovskite phase. At this stage, it could be observed that growth of grains was not uniform. However, as it was annealed for 60 minute, the crystal of the SBT thin film specimen grew well, and the texture and the crystallinity of the specimen were very excellent.

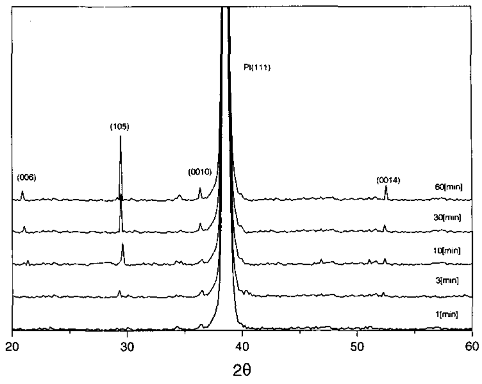
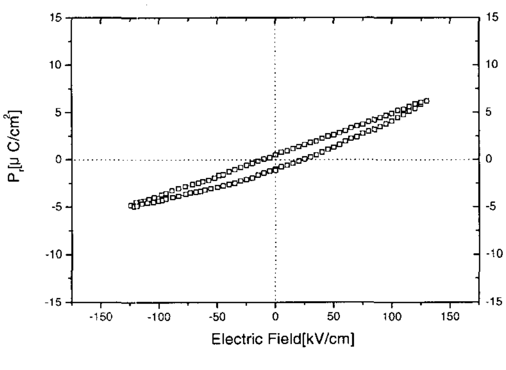


Fig. 3. X-ray patterns of SBT thin films with annealing times.

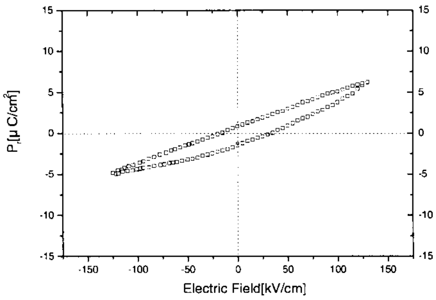
In order to observe the crystal structure and the orientation of the SBT thin film specimen depending upon a change in the annealing time in the oxygen atmosphere, the 'XRD' pattern was illustrated in Fig. 3. It can be identified from Fig. 3 that as the annealing time was increased, the orientation of the 'XRD' peak depending upon a change in the annealing time at 750 ℃ was improved in the same direction.

It is thought that this result came out because as the annealing time was more increased, deposited atoms got to have the activation energy enough to move to a stable position so that crystallization of the specimen was increased. Also, in all specimens, (105) preferred orientation and weak (0010) (006) (0014) peaks were observed irrespective of the annealing temperature, and it could be known that (105) beginning with the specimen as annealed for 10 minutes, the peak was relatively greatly increased.

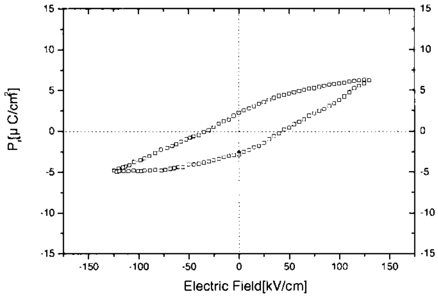
3.2 Ferroelectric characteristics of SBT capacitors



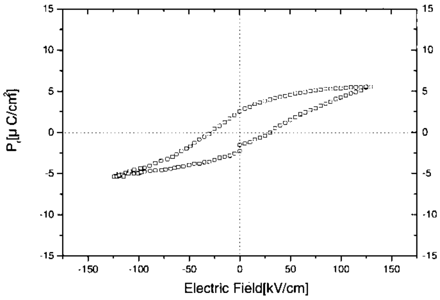
(a) 1 min



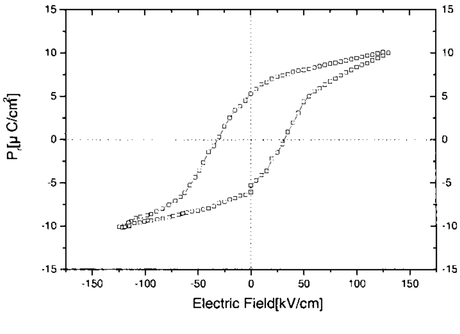
(b) 3 min



(c) 10 min



(d) 30 min



(e) 60 min

Fig. 4. P-E hysteresis loops of SBT capacitors with annealing times.

Figure 4 shows the polarization hysteresis curve depending upon a change in the annealing time at 750 ℃. In Fig. 4(a) where hysteresis characteristics were measured after annealing the specimen for 1 minute following as-deposition, hysteresis characteristics appeared a little.

Also, in the specimen as annealed for 3 minutes, polarization hysteresis characteristics did not appear greatly as shown in Fig. 4(b).

However, in the case of the specimen as annealed for 10 minutes and shown in Fig. 4(c), saturation began to take place. It is thought that this is because in the case of the specimen as annealed for 10 minutes, as shown in Fig. 2, its structure was transformed into the perovskite structure so that hysteresis characteristics appeared[11].

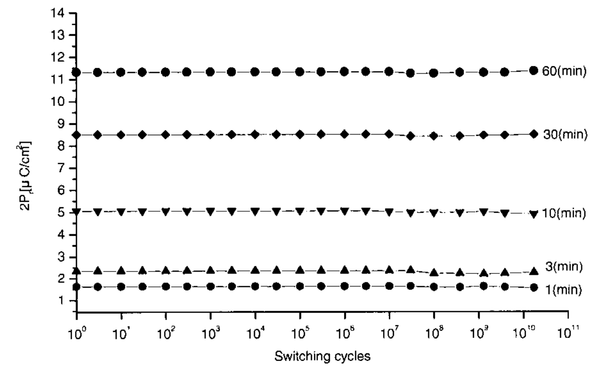


Fig. 5. Fatigue properties of SBT capacitors with annealing times.

Also, in the case of the specimen as annealed for 30 minutes and shown in Fig. 4(d), saturation was well done, and in the case of the specimen as annealed for 60 minutes and shown in Fig. 4(e), saturation was best done, and the residual polarization ($2P_r$) value and the coercive electric field (E_c) were approximately 12.40 C/cm^2 and 30 kV/cm, respectively.

Figure 5 shows the result of observing a change in non-volatile polarization when 5 V was applied to the specimen depending upon a change in the annealing time at 750 ℃. Wherein, a good fatigue characteristic that non-volatile polarization was not reduced even though the annealing time was changed upto 10^{10} cycles was observed.

Figure 6 shows the result of measuring the leakage current density of the SBT capacitor depending upon a change in the annealing time. It can be known from Fig. 6 that in case the annealing time is 1~3 minutes, the leakage current density is very high. This is consistent with the fact that the hysteresis curve is not saturate, as shown in Fig. 4(a) and (b). As the annealing time is increased, the leakage current density gets to be lowered. This is well consistent with the study result that the hysteresis curve is saturated, as shown in Fig. 4(e) and (f). In the case of the specimen as annealed for 60 minutes, it showed the best leakage current characteristic, which was approximately 2.81×10^{-9} A/cm^2 at 5 V.

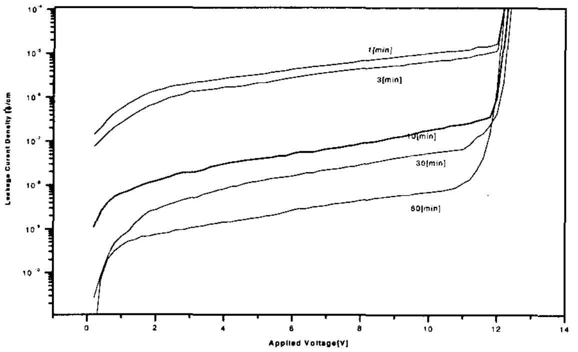


Fig. 6. Leakage current densities of SBT capacitors with annealing times.

4. CONCLUSION

As a result of conducting the study on ferroelectric characteristics of the SBT capacitor, which was manufactured by using the RF magnetron sputtering method, depending upon a change in the annealing time at 750 ℃ in the oxygen atmosphere, the following results have been obtained.

1) As a result of conducting the X-ray diffraction analysis and the electron microscopy analysis, the perovskite phase began to grow from 10 minutes after annealing the specimen, and excellent crystallization was accomplished at 60 minutes after annealing the specimen.

2) The remanent polarization ($2P_r$) value and the coercive electric field (E_c) of the SBT thin film specimen showed the most excellent characteristics at 60 minutes after annealing the specimen, which were approximately 12.40 C/cm^2 and 30 kV/cm, respectively.

3) The leakage current density of the SBT thin film specimen as annealed for 60 minutes after vapor-deposition thereof was approximately 2.81×10^{-9} A/cm^2.

REFERENCES

[1] Dong-soo Paik, "Fabrication and characteristics of PZT ferroelectric thin films by sol-gel processing and rapid thermal annealing", J. of KIEEME(in Korean), Vol. 13, No. 4, p. 369, 1994.

[2] Tsuyoshi Hioki, Masahiko Akiyama, Tomomasa Ueda, Yutaka Onozuka, Yujiro Hara, and Kouji Suuki, "Measurement of electic-field-induced displacements in (Pb,La)/TiO_3 thin films using scanning probe microscopy preparation of Pb(Zr,Ti)O_3 thin films on glass substrates", Jpn. J. Appl. Phys., Vol. 39, Pt. 1, No. 9B, p. 5408, 2000 .

[3] Ichiro Koiwa, Kanehara, Hiroyo Kato, Sachiko Ono, Akira Sakakibara Tetsuya Osaka, and Katsuhiko Asami, "Effects of H_2 shintering and Pt Upper Electrode on Metallic Bi Content in $SrBi_2Ta_2O_9$ Thin films for Ferroelectric Memories Prepared by Sol -Gel Method ", Jpn. J. Appl. Phys., Vol. 37, Pt.1, No. 9B, p. 5192, 1998.

[4] D. S. Shin, Ho Nyung Lee, Chang Woo Lee, Yong Tae Kim, and In Hoon Choi, "Effects of morphological changes of Pt/$SrBi_2Ta_2O_9$ interface on the electrical properties of ferroelectric capacitor", Jpn. J. Appl. Phys., Vol. 37. p. 5189, 1998.

[5] S. Y. Chen, "Aging behavior and recovery of polarization in $Sr_{0.8}Bi_{2.4}Ta_2O_9$ thin films", J. Appl. Phys., Vol. 87, No. 6, p. 3050, 2000.

[6] Kazumi Kato, "Low-temperature synthesis of Sr $Bi_2Ta_2O_9$ ferroelectric thin films through the complex alkoxide method:effects of functional group, hydrolysis and water vapor treatment", Jpn. J. Appl. Phys., Vol. 37, Pt.1, No. 9B, p. 5178, 1998.

[7] Kazunari Maki, Nobuyuki Soyama, Satoru Mori, and Katsumi Ogi "Evaluationof Pb(Zr,Ti)O_3 films derived from propylene-glycol-based sol-gel solutions" Jpn. J. Appl. Phys., Vol. 39, Pt. 1, No. 9B, p. 5421, 2000.

[8] Nobuyuki Soyama, Kazunari Maki, Satoru Mori, and Katsumi Ogi, "Preparation and evaluation of Pb(Zr,Ti)O_3 thin films for low voltage operation" Jpn. J. Appl. Phys., Vol. 39, Pt. 1, No. 9B, p. 5434, 2000.

[9] C. I. Cheon, Jeong-Seog Kim, D. L. Kwong, "Electrical properties of SBT ferroelectric thin films prepared by MOD", J. of KIEEME(in Korean), Vol. 12, No. 2, p.151, 1999.

[10] M. A. Rodrinues and Satoru Mori, "Phase formation and characterization of the $SrBi_2Ta_2O_9$ layered-perovskite ferroeelctric" Intergrated Ferroelectric, Vol. 14, p. 201, 1997.

[11] Norifumi, Darin T. Thomas, Stephen K. Streiffer and Angus I. Kingon, "Preferred orientation, phase formation and the electrical properties of pulsed laser deposited $SrBi_2Ta_2O_9$ thin films", Jpn. J. Appl. Phys., Vol. 37, Pt. 1, No. 9B, p. 5185, 1998.