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Role of the Bi_2O_3 in $SrBi_2TaNbO_9/Bi_2O_3/SrBi_2TaNbO_9$ Heterostructure and Low Temperature Annealing Property

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Ferroelectric properties of $SrBi_2TaNbO_9$ (SBTN) thin films were changed by the amount of Bi content in SBTN. We suggested that the addition of excess Bi into the films could be accomplished by heat-treating SBTN/Bi_2O_3/SBTN heterostructure fabricated by r.f. magnetron sputtering method. Excess Bi composition was controlled by the thickness of the sandwiched Bi_2O_3 from 0 to 400 Å. When the SBTN thin films were inserted by 400 Å Bi_2O_3 layer, Bi_2Pt phase was formed as a second phase in SBTN films, resulting in poor ferroelectric properties. The onset temperature for hysteresis loop can be reduced by heat treating SBTN/Bi_2O_3/SBTN heterostructure. The films with SBTN/Bi_2O_3(100 Å)/SBTN hetero-structure followed by annealing at 650°C for 30 min show 2Pr and Ec of 5.66 $\mu C/cm^2$ and 54 kV/cm, respectively.

Key words: Ferroelectric, SBTN ($SrBi_2TaNbO_9$), Bismuth(Bi), Heterostructure, Annealing

I. Introduction

There has been considerable interest in ferroelectric materials for non-volatile random access memory application. Whereas, the ferroelectric fatigue, in which the remanent polarization (Pr) decreased with an increase of switching cycles, is the predominant problem for the microelectronics device application.

A candidate ferroelectric materials to control the fatigue problem in ferroelectric capacitor are $SrBi_2Ta_2O_9$ (SBT). It has been demonstrated that Pt/SBT/Pt capacitors were found to exhibit no fatigue up to 10^{12} switching cycles, very good retention properties, and low leakage current densities on Pt electrodes.[1-3]

However, there are few reports about sputter deposition of SBT thin films due to the difficulty in controlling the film composition and the high volatility of the bismuth oxide constituent.[4,5] Generally, the compensation of Bi loss was accomplished by using $SrBi_{2+x}TaNbO_9$ target. Co-sputtering technique[6] using two different sintered targets of $Sr_{0.8}Bi_{2.2}$-$Ta_{1.2}Nb_{0.8}O_9$ and Bi_2O_3, and Crystalline Buffer Layer (CBL) aided sputtering technique were also suggested.[7] SBT thin films with good ferroelectric properties were not formed by these methods because Bi content of the SBT films was not controlled exactly. Therefore, the amount of Bi content which form the perovskite structure is a key factor to improve ferroelectric properties.

In this article, we fabricated SBTN/Bi_2O_3/SBTN heterostructure on Pt/Ti/SiO_2/Si substrates by r.f. magnetron sputtering method and then investigated the effect of Bi composition control on the ferroelectric properties of SBTN thin films and the effect of low temperature annealing. We reported the relationship between the ferroelectric properties and the interfacial conditions in the SBTN/Bi_2O_3/SBTN heterostructure by analysis of the surface state and crystallography.

II. Experiment

The $SrBi_2Ta_{2-x}Nb_xO_9$ and Bi_2O_3 thin films were deposited on Pt (150 nm)/Ti (50 nm)/SiO_2(1000 nm)/Si substrates using r.f.(13.56 MHz) magnetron sputtering. The substrate temperature was fixed at 25°C during deposition. Ar and O_2 gases were used in the sputtering processes. Platinum top electrodes were deposited by dc sputtering at room temperature and patterned using lift-off method. After the top electrodes were fabricated, the capacitors were annealed at various temperatures for 30 min in O_2 flow and then the films were cooled to room temperature at a rate of 20°C/min.

The structures of the films were analyzed by x-ray diffractometer (Philips). The surface microstructure and thickness of the films were observed using field emission scanning electron microscopy (Hitachi). The ferroelectric properties of the capacitors were performed using a RT66A ferroelectric tester (Radiant Technologies).

III. Results and Discussion

Ferroelectric hysteresis measurements were conducted on $SrBi_2Ta_{2-x}Nb_xO_9$ films inserted by Bi_2O_3 with various thickness, followed by annealing at 700°C for 30 min. The 2Pr as

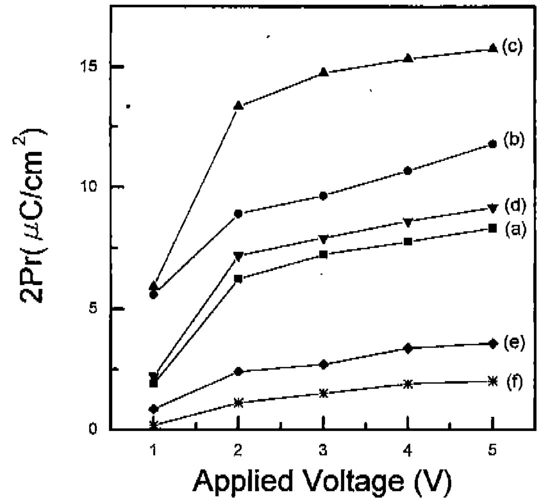

Fig. 1. Voltage dependence of 2Pr for SBTN thin films inserted by Bi_2O_3 with various thickness, followed by annealing at 700°C for 30 min. (a) 0 Å, (b) 50 Å, (c) 100 Å, (d) 150 Å, (e) 200 Å and (f) 400 Å.

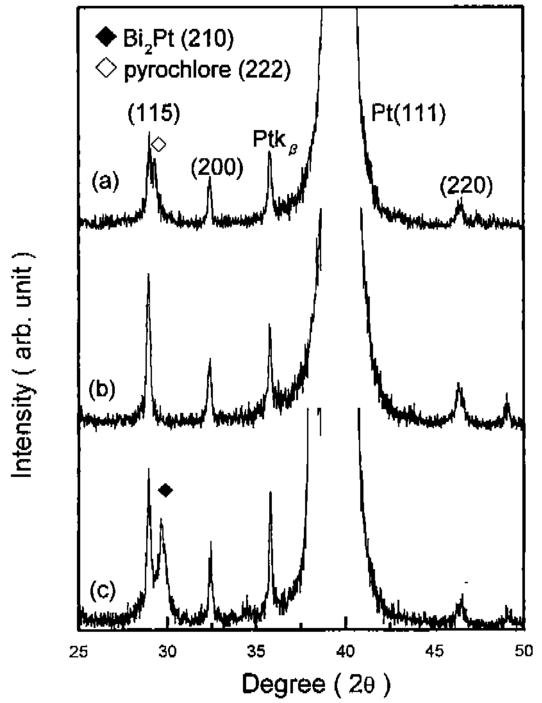

Fig. 2. X-ray diffraction patterns of SBTN thin films inserted by Bi_2O_3 with various thickness followed by annealing at 700°C for 30 min. (a) 0 Å, (b) 100 Å and (c) 400 Å.

a function of the applied voltage are shown in Fig. 1. The remanent polarization of all films was found to increase with the increase of the applied voltage. Especially, for the inserted Bi_2O_3 films of 100 Å, as shown in Fig. 1 (c), the 2Pr value initially increased rapidly with applied voltage up to 2 V. On the other hand, the 2Pr value increased rather linearly with applied voltage above 2 V.

The XRD patterns for SBTN thin films inserted by Bi_2O_3

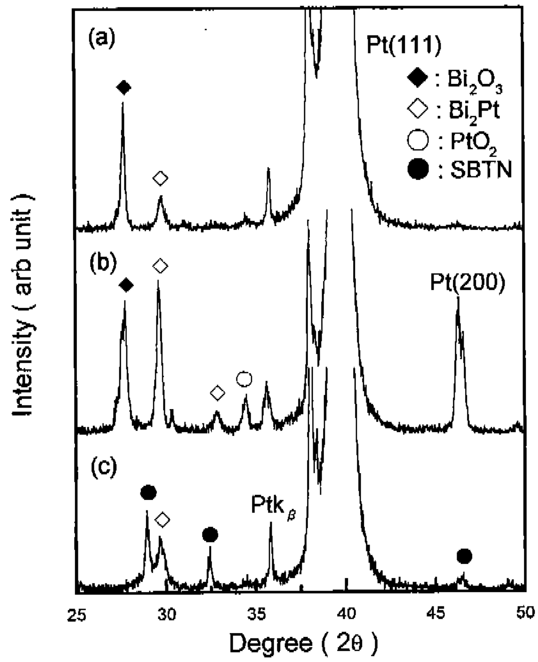

Fig. 3. X-ray diffraction patterns of (a) Bi_2O_3, (b) Pt/Bi_2O_3 and (c) $SBTN/Bi_2O_3$ (400 Å) SBTN thin films deposited on Pt/Ti/SiO_2/Si at room temperature followed by annealing at 700 Å for 30 min.

layer with various thickness are shown in Fig. 2. In the case of crystal structure of the SBTN thin films without inserted Bi_2O_3 layer, as shown in Fig. 2 (a), the pyrochlore and polycrystalline phases existed together. When the thickness of Bi_2O_3 was increased to 100 Å, as shown in Fig. 2 (b), pyrochlore phase disappeared and (115) peak intensity of SBTN diffraction pattern was increased. However, for the case of SBTN thin films inserted by 400 Å Bi_2O_3 layer, as shown in Fig. 2 (c), Bi_2Pt phase with the SBTN phase appears as a second phase.

Fig. 3 shows x-ray diffraction patterns of Bi_2O_3 and Pt/Bi_2O_3 films deposited on Pt/Ti/SiO_2/Si at room temperature followed by annealing at 700°C for 30 min in O_2 flow. For the case of Bi_2O_3 films deposited on platinized Si wafer, as shown in Fig. 3 (a), the Bi_2O_3 phase and Bi_2Pt phase existed together. On the other hand, for the case of Pt/Bi_2O_3 films deposited on platinized Si wafer, as shown in Fig. 3 (b), (210) peak intensity of Bi_2Pt diffraction pattern was increas-ed. This indicates that a Bi_2Pt phase was formed by the reaction between Pt layer and Bi_2O_3 layer. Most Bi_xPt_y phase were formed by the reaction between Bi and Pt at 660-760°C.[8]

The microstructures of the $SBTN/Bi_2O_3/SBTN$ heterostructure annealed at 700°C for 30 min in O_2 flow, as shown in Fig. 4. The SBTN films without inserted Bi_2O_3 layer, as shown in Fig. 4 (a), large bismuth layered structure grains and fine pyrochlore structure grains were shown. This bimodal distribution appeared because Bi atoms are heterogeneously present in crystallization.[9] For the SBTN thin films inserted by 100 Å Bi_2O_3 layers, as shown in Fig. 4 (b), fine pyrochlore grains changed to uniform rod-like grains

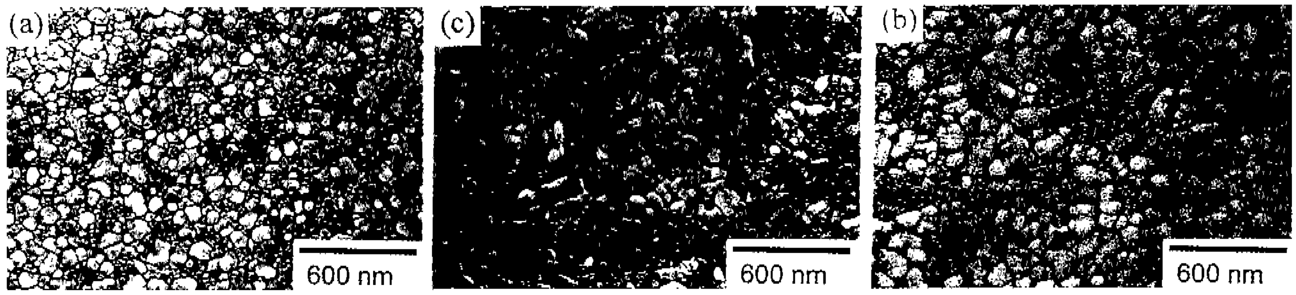

Fig. 4. SEM surface micrographs of SBTN thin films inserted by Bi_2O_3 with various thickness followed by annealing at 700Å for 30 min. (a) 0 Å, (b) 100 Å and (c) 400 Å.

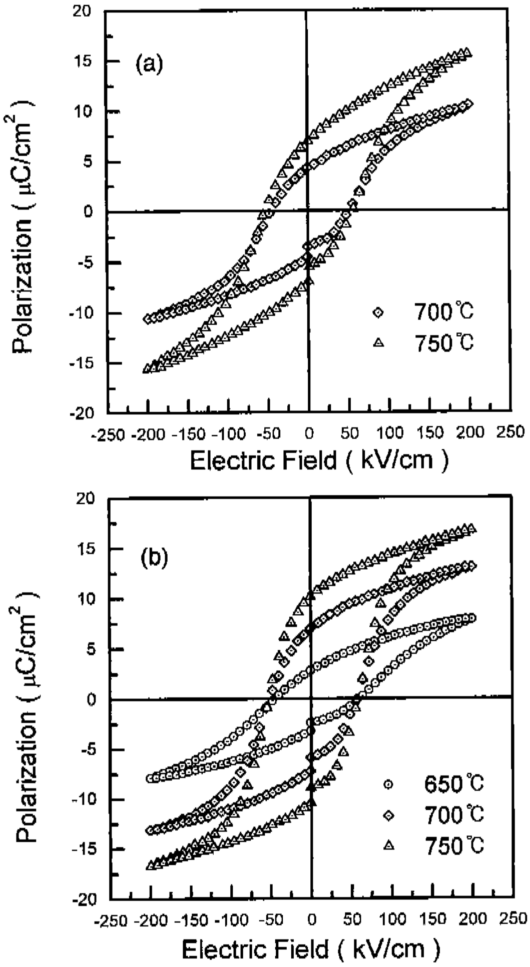

Fig. 5. P-E hysteresis loops of (a) SBTN and (b) SBTN/Bi_2O_3 (100 Å)/SBTN films as a fuction of annealing temperatures.

with constant grain size of 0.2 μm. However, for the SBTN thin films inserted by 400 Å Bi_2O_3 layers, as shown in Fig. 4 (c), grain size was decreased. Such grain size reduction is possibly associated with Bi_2Pt phase formation along with SBTN phase.

We also investigated inserting Bi_2O_3 layer effect on ferroelectric properties with low temperature process in SBTN thin film. Fig. 5 shows the P-E hysteresis curve as a function of annealing temperature for SBTN and SBTN/Bi_2O_3 (100 Å)/SBTN films annealed at temperatures of 650-750 Å for 30 min in O_2 flow. As the SBTN thin films without inserted Bi_2O_3 layer were annealed at 650°C for 30 min, as shown in Fig. 5 (a), a good hysteresis curves could not be obtained. As the annealing temperature was increased from 700°C to 750°C, the remanent polarization (2Pr) was increased from 8.8 to 13.9 μC/cm^2 at an applied electric field of 200 kV/cm, respectively. On the other hand, as the SBTN/Bi_2O_3 (100 Å)/SBTN thin films annealed at 650°C for 30 min, as shown in Fig. 5 (b), the remanent polarization (2Pr) and coercive field (Ec) exhibited 5.66 μC/cm^2 and 54 kV/cm at an applied electric field of 200 kV/cm, respectively. As the annealing temperature increased from 700°C to 750°C, the remanent polarization (2Pr) increased from 14.2 to 20.6 μC/cm^2 at an applied electric field of 200 kV/cm^2, respectively. Therefore, In order to lower the hysteresis onset temperature of SBTN thin films, excess bismuth was required.

IV. Conclusion

The $SrBi_2TaNbO_9$ thin films with an excessive Bi content were formed on Pt/Ti/SiO_2/Si by heat-treating SBTN/Bi_2O_3/SBTN heterostructure fabricated by r.f. magnetron sputtering method. As the thickness of Bi_2O_3 films increased from 0 to 100 Å, pyrochlore phase disappeared and (115) peak intensity of SBTN diffraction pattern increased. On the other hand, for the case of SBTN thin films inserted by 400 Å Bi_2O_3 layer, Bi_2Pt phase was formed as a second phase in SBTN films. A Bi_2Pt phase was formed by the reaction between bottom Pt layer and Bi_2O_3 layer. Such a formation of Bi_2Pt phase was found to depend on the annealing temperature and Bi content.

The inserted Bi_2O_3 layer between SBTN films reduced the crystallization temperature and also enhanced the grain growth at lower annealing temperature, resulting in a good ferroelectric properties of SBTN films.

Acknowledgments

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