Properties of $Sr_{0.8}Bi_{2.3}(Ta_{1-x}Nb_x)_2O_{9+\alpha}$ Thin Films

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Polycrystalline SBTN layered ferroelectric thin films with various Nb mole ratios were prepared by sol-gel method on $Pt/SiO_2/Si$ (100) substrates. The films were annealed at different temperatures and characterized in terms of phase and microstructure. The films were crystallized with a high (105) diffraction intensity and had rodlike structure. SBTN films fired at 800°C revealed standard hysteresis loops with no fatigue for up to 10^{10} cycles. At an applied voltage of 5V, the dielectric constant (ε_r), dissipation factor (tanδ), remanent polarization (2Pr) and coercive field (Ec) of typical $Sr_{0.8}Bi_{2.3}(Ta_{1-x}Nb_x)_2O_{9+\alpha}$ thin film(x=0.1) prepared on $Pt/SiO_2/Si(100)$ were about 277.7, 0.042, 3.74μC/cm², and 24.8kv/cm respectively.

Keywords : ferroelectrics, Sol-gel method, dielectric constant, fatigue property, C-V characteristics

I. INTRODUCTION

The nonvolatile memory devices using ferroelectric thin film are proposed as the next generation memory. A conventionally used ferroelectric material is lead zirconate titanate (PZT). However, the use of PZT films in these memory devices has been limited since they undergo severe polarization fatigue with metal electrodes. Fatigue can be defined as a decrease in the amount of switched charge for each polarization reversal applied until there is no distinction between the polarized states. On the other hand, Bi-layered perovskite thin films such as $SrBi_2Ta_2O_9$ (SBT), $SrBi_2Nb_2O_9$ (SBN) or $SrBi_2TaNbO_9$ (SBTN) have been widely investigated for FRAM (ferroelectric random access memory) applications[1-5] because of their excellent ferroelectric properties, especially no fatigue up to about 10^{12} switching cycles.[6, 7] The structure of SBTN is the same as that of SBT with Nb simply substuting for Ta to form the solid solution of SBT and SBN. Both elements reside in the same periodic series. They also have the same ionic number and similar ionic radii.

In this work, SBTN thin films with nonstoichiometric compositions were fabricated on $Pt/SiO_2/Si$ (100) substrates by the sol-gel method and then we have studied the effects of process parameters on the phase formation, microstructure and ferroelectric properties of the films.

II. EXPERIMENT

SBTN thin films were prepared on $Pt/SiO_2/Si(100)$ by the sol-gel method. Figure 1 shows a flow diagram for preparation of the SBTN thin films by the sol-gel method.

All compounds were handled with rigorous exclusion of air and water using an anaerobic chamber (like glove box). Strontium isopropoxide, tantalum ethoxide, Nb ethoxide, and bismuth acetate were used as the starting materials with pyridine [C_5H_5N] and acetic acid [CH_3COOH] as the main solvent. Two separate mixtures were combined to generate the precursor solution. Initially, tantalum ethoxide, Nb ethoxide, and strontium isopropoxide were dissolved in acetic acid to form the first solution. The second solution was synthesized by dissolving bismuth acetate in pyridine and acetic acid with stirring at about 70°C. Both mixtures were stirred for 20min(or until dissolution occurs) and then combined. The solutions were typically prepared to a concentration of 0.1mol/l. SBTN precursor solutions were spin coated onto $Pt/SiO_2/Si$ (100) substrates at approximately 2,500rpm for 30 seconds in air. The coated films were dried on hot plate at 150°C for 10 minutes to remove all the excess solvents. The spin-dry cycle was repeated several times to obtain the desired thickness of the final films. The measured film thickness on Pt/SiO_2/Si substrate was about 300nm. After several spin-dry cycles,

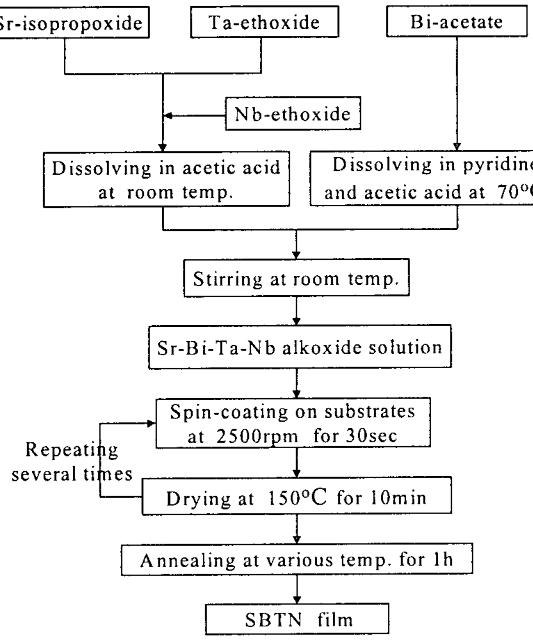

Fig. 1. Flow diagram for preparation of the SBTN thin films by the sol-gel method.

the pre-baked films were annealed in an O_2 flow at 600-800°C for 1h. The crystalline phases of thin films were identified by an X-ray diffraction (XRD). The microstructure and film thickness were observed by a scanning electron microscopy (SEM). Values of the dielectric constant (ε_r) were calculated from capacitance values obtained using an impedance analyzer (HP 4194A) at 100kHz. P-E hysteresis loops were measured using a RT-66A tester (Radiant Technologies, Inc.) operated in the virtual-ground mode.

III. RESULTS

Figure 2 shows XRD patterns of $Sr_{0.8}Bi_{2.3}(Ta_{1-x}Nb_x)_2O_{9+\alpha}$ thin films with various Nb compositions(x=0, 0.1, 0.2, 0.3, 1) deposited on Pt-coated Si substrates at 800°C for 1h.

As shown in Fig. 2, peak patterns are very similar to each other except for some variations in the relative intensity of prominent reflections such as (105) plane at 28.97±0.03 degrees (2∝). Even though XRD patterns at 800°C are quite similar, crystallization of SBTN thin films starts at different temperatures in terms of Nb composition ratios. XRD patterns indicated that the

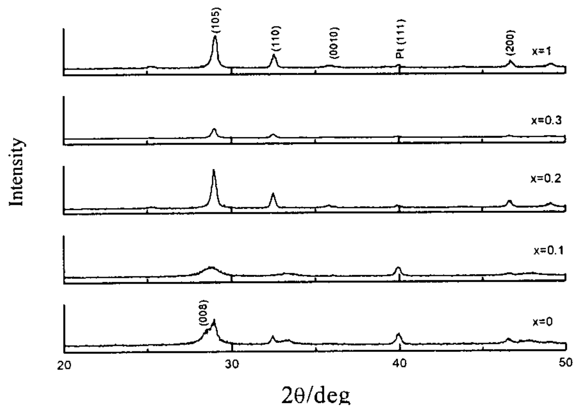

Fig. 2. XRD patterns of $Sr_{0.8}Bi_{2.3}(Ta_{1-x}Nb_x)_2O_{9+\alpha}$ thin films with various Nb compositions (x=0, 0.1, 0.2, 0.3, 1) deposited on Pt/SiO_2/Si(100) substrates at 800°C for 1h.

SBTN films consisted of a polycrystalline phases and little second phase was observed, whereas it usually appeared in the films reported by others.[8] The formation of a secondary phase (pyrochlore phase) may be induced due to a composition off-stoichiometry, the selected precursor, compounds solvents, and the preparation conditions. In general, the secondary phase may be considered harmful to the formation of the SBTN phase.

Figure 3 shows SEM images of $Sr_{0.8}Bi_{2.3}(Ta_{1-x}Nb_x)_2O_{9+\alpha}$ thin films prepared on Pt/SiO_2/Si(100) as a function of Nb composition ratios. The microstructures of the films annealed at 800°C for 1h were found to be rod-like structure and the grains with the layered-perovskite phase were oriented randomly at the surface of the film.

The dielectric properties of SBTN thin films were also analyzed in terms of dielectric constant (ε_r) and dissipation factor (tanδ). Figure 4 shows capacitance-voltage curves as a function of different Nb compositions for the $Sr_{0.8}Bi_{2.3}(Ta_{1-x}Nb_x)_2O_{9+\alpha}$ thin films on Pt/SiO_2/Si (100) substrates. Preliminary result suggests that the capacitance values of SBTN thin films were systematically decreased when Nb was added to strontium bismuth tantalate (SBT). Dissipation factors (tanδ) of $Sr_{0.8}Bi_{2.3}(Ta_{1-x}Nb_x)_2O_{9+\alpha}$ thin films measured as a function of Nb compositions at 100Hz-10MHz were shown in Fig. 5. The values of dissipation factor were below 0.042 without depending on Nb mole ratios. The dielectric constant (ε_r, 277.7) and dissipation factor (tanδ, 0.042) were measured at 100kHz.

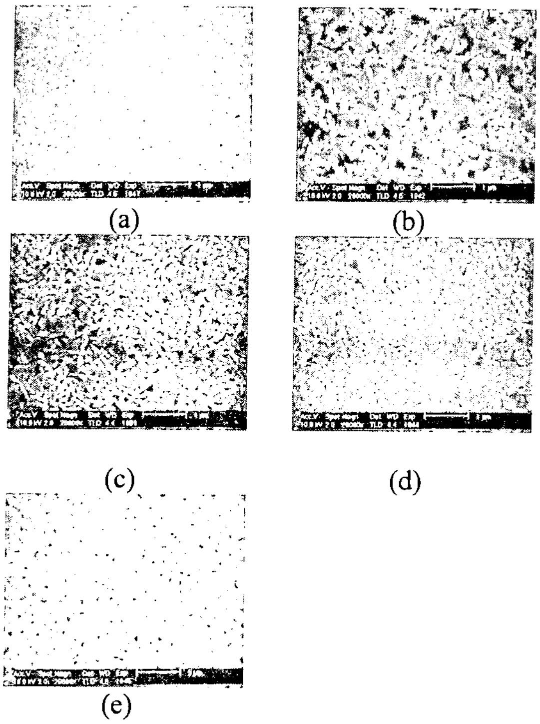

Fig. 3. SEM images of $Sr_{0.8}Bi_{2.3}(Ta_{1-x}Nb_x)_2O_{9+\alpha}$ thin films prepared on $Pt/SiO_2/Si(100)$ as a function of Nb composition ratios.: (a) x=0, (b) 0.1, (c) 0.2 , (d) 0.3, and (e) 1.0

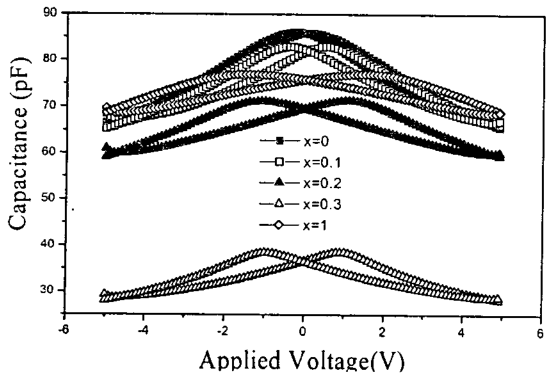

Fig. 4. Capacitance-voltage curves as a function of different Nb compositions for the $Sr_{0.8}Bi_{2.3}(Ta_{1-x}Nb_x)_2O_{9+\alpha}$ thin films on $Pt/SiO_2/Si(100)$ substrates.

Dissipation factors (tanδ) of $Sr_{0.8}Bi_{2.3}(Ta_{1-x}Nb_x)_2O_{9+\alpha}$ thin films measured as a function of Nb compositions at 100Hz-10MHz were shown in Fig. 5. The values of dissipation factor were below 0.042 without depending on Nb mole ratios. The typical dielectric constant (ε_r) and dissipation factor (tanδ) measured at 100kHz were 277.7 and 0.042 respectively.

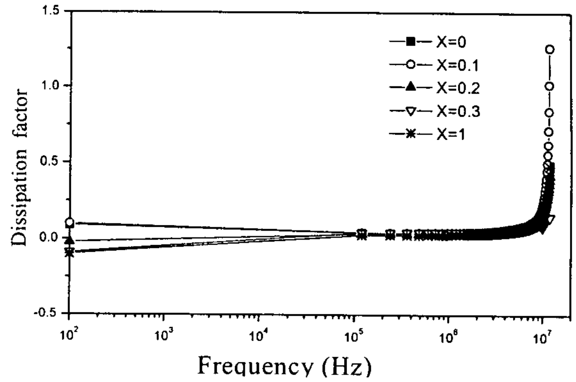

Fig. 5. Dissipation factors (tanδ) of $Sr_{0.8}Bi_{2.3}(Ta_{1-x}Nb_x)_2O_{9+\alpha}$ thin films measured as a function of Nb compositions.

Figure 6 shows the hysteresis loop of 350nm-thickness $Sr_{0.8}Bi_{2.3}(Ta_{1-x}Nb_x)_2O_{9+\alpha}$ thin film(x=0.1) at an applied voltage 5V, which is not saturated fully. The measured remanent polarization (2Pr) and the coercive field (Ec) at an applied voltage 5V were 3.74μC/cm^2 and 24.8kV/cm, respectively.

The dielectric and ferroelectric properties of the $Sr_{0.8}Bi_{2.3}(Ta_{1-x}Nb_x)_2O_{9+\alpha}$ thin films on $Pt/SiO_2/Si$ (100) substrates were summarized in Table. 1.

No fatigue was observed up to 6×10^{10} switching cycles, as shown in Fig. 7 and after 10^{10} polarization cycle at 5V, the normalized polarization reduced by a factor of only 4%.

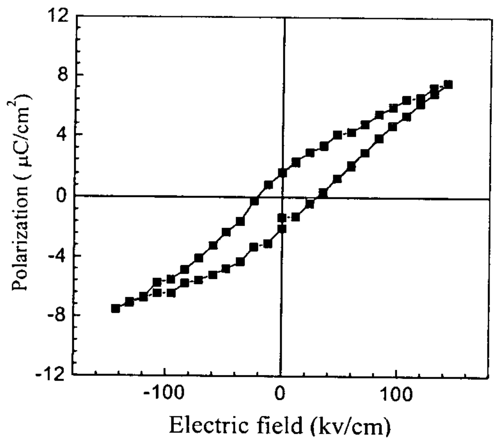

Fig. 6. The hysteresis loop of 350nm-thickness $Sr_{0.8}Bi_{2.3}(Ta_{1-x}Nb_x)_2O_{9+\alpha}$ at an applied voltage 5V (x=0.1).

Based on the above results, it can be concluded that the control of SBTN composition ratios is important parameter to decide dielectric properties.

Table. 1. The values of dielectric constant (ε_r), dissipation factor (tanδ), remanent polarization (2Pr), and coercive field (Ec) as a function of Nb compositions in SBTN thin films.

$Sr_{0.8}Bi_{2.3}(Ta_{1x}Nb_x)_2O_{9+\alpha}$	X=0	0.1	0.2	0.3	1
ε_r	234.8	277.7	236.2	278.8	258.5
tanδ	0.042	0.042	0.034	0.041	0.026
2Pr(μC/cm^2)	2.02	3.74	4.28	4.19	2.58
Ec(kv/cm)	17.76	24.8	38.8	35.77	26.8

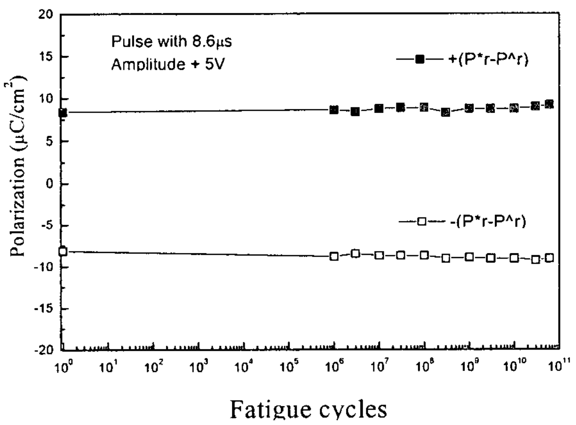

Fig. 7. Fatigue characteristics of $Sr_{0.8}Bi_{2.3}(Ta_{1-x}Nb_x)_2O_{9+\alpha}$ thin film(x=0.1) annealed at 800°C for 1h.

IV. CONCLUSIONS

We prepared $Sr_{0.8}Bi_{2.3}(Ta_{1-x}Nb_x)_2O_{9+\alpha}$ thin films on platinum coated silicon substrates by sol-gel method. The microstructure and electrical properties of the films were found to be strongly dependent on composition ratios of precursor solutions. A well-crystallized film with rod-like structure was obtained by firing the spin-on films at 800°C. There were no significant differences in crystallinity or grain structure among the SBTN thin films with different compositions at 800°C for 1h while electrical properties depended on Nb content. The hysteresis loop was obtained for the $Sr_{0.8}Bi_{2.3}Ta_{1.8}$-$Nb_{0.2}O_{9+\alpha}$ thin film prepared on Pt/SiO_2/Si(100) substrates. The thin film exhibited ε_r of 277.7(100kHz), 2Pr of about 3.74μC/cm^2 and Ec of 24.8kV/cm at an applied voltage of 5V. Based on the results of the phase formation, microstructure and ferroelectric properties, the control of the composition ratio of SBTN precursor solutions is essential for the development of high-quality films suitable for FRAM application.

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