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PREFERRED ORIENTATION AND MICROSTRUCTURE OF MOD DERIVED $SrBi_{2x}Ta_2O_9$ THIN FILMS WITH Bi CONTENT x

Dae Joong Yeon, Joo Dong Park, and Tae Sung Oh

Department of Metallurgy and Materials Science, Hong Ik University, Seoul 121-791, Korea

ABSTRACT

$SrBi_{2x}Ta_2O_9$ ferroelectric thin films were prepared on platinized silicon substrates using MOD proces, and crystallization behavior of the films was investigated with variation of the annealing temperature and Bi content x. Crystalline phase of bismuth layered perovskite structure was formed even by baking the films at 800℃ for 5 minutes in air, and was not changed by annealing at temperatures raning from 700℃ to 900℃ for 1 hour in oxygen ambient. When $SrBi_{2x}Ta_2O_9$ thin films ($0.8 \leq x \leq 1.6$) were annealed at 800℃, Preferred orientation of the films along c-axis was observed with $x \geq 1.2$. With increasing Bi content x, surface morphology of the films was changed from equiaxed grains to elongated grains.

INTRODUCTION

Ferroelectric thin films for use in non-volatile random access memories have drawn much attention in recent years, since they exhibit an electrically switchable remanant polarization[1-3]. Lead zirconate titanate (PZT) thin films have been extensively investigated to apply for ferroelectric memory devices[1,4,5]. However, reliability of Pt/PZT/Pt capacitors, such as polarization fatigue and imprint, limits the realization of the commercial ferroelectric memories[6,7].

To suppress the polarization fatigue in PZT based capacitors, many investigations have been performed to replace Pt electrode with conducting oxide electrodes such as RuO_2 and IrO_2[8-10]. In this configuration, oxide electrodes help to control the oxygen vacancy concentration at the electrode/ferroelectric interface, which is known to be responsible for the fatigue phenomena[8-10]. Oxide electrodes have been proven suitable for controlling polarization fatigue. However, their electrical conductivities are not as high as those of Pt electrode, resulting in undesirable characteristics of the device such as high RC time constant and high leakage currents[11]. In addition, non-ferroelectric secondary phases may be formed by reactions between PZT film and oxide electrode[12].

To overcome the polarization fatigue in ferroelectric capacitors without such detrimental side-effects caused by oxide electrodes, $SrBi_2Ta_2O_9$ ferroelectric thin films of bismuth layered perovskite structure has been developed recently[1,2,13,14]. $SrBi_2Ta_2O_9$ may be written as $(Bi_2O_2)^{2+}(SrTa_2O_7)^{2-}$ consisted of two perovskite-like $(SrTa_2O_7)^{2-}$ layers, alternating with a layer of $(Bi_2O_2)^{2+}$, along the c-axis[7,13].

$SrBi_2Ta_2O_9$ thin film capacitors with Pt electrode can be fatigue-free due to the fact that the oxygen vacancy concentration at the electrode/ferroelectric interface is reduced by entrapping of oxygen vacancies in $(Bi_2O_2)^{2+}$ layers[7].

Electrical properties of $SrBi_2Ta_2O_9$ thin films are largely dependent on the stoichiometry and preferred orientation of the films[7, 15]. As bismuth volatility during annealing process of sol-gel or MCD derived $SrBi_2Ta_2O_9$ thin films usually occurs, addition of excess bismuth oxide precursor into a coating solution is required to prevent the bismuth deficiency of the films. In this study, $SrBi_{2x}Ta_2O_9$ thin films ($0.8 \leq x \leq 1.6$) are fabricated by MOD process on the platinized silicon substrates, and preferred orientation and microstructural behavior of the films have been investigated with Bi content x.

EXPERIMENTAL PROCEDURE

$SrBi_{2x}Ta_2O_9$ (SBT) thin films were prepared on Pt(100nm)/Ti(5nm)/SiO_2(100nm)/Si substrates by MOD method. Sr-2-ethylhexanate [$Sr(CH_3(CH_2)_3CH(C_2H_5)COO)_2$], Bi-2-ethylhexanate and Ta-2-ethylhex-anate were used as starting materials, and the concentration of each precursor solutions was 0.5 M. In order to prepare spin-coating solution, 2-ethylhexanate metal precursors were mixed with Sr:Bi:Ta mole ratio of 1:2x:2 ($0.8 \leq x \leq 1.6$), and stirred for several hours using magnetic stirrer. Mixed precursor solutions were then diluted with n-butyl acetate [$CH_3CO_2(CH_2)_3CH_3$] to make the concentration of stock solution 0.25 M. To modify hydrolysis and condensation rates of sol, 1 M NH_4OH or pure H_2O was added into the stock solution. Without depending on pH of the hydrolysis solution, no gelation or precipitation occurred for H_2O/SBT mole ratio up to unity. However, white precipitates were formed when H_2O/SBT more than unity. Formation of precipitates were accelerated water (H_2O/SBT mole ratio=1) abd used to fabricate SBT films.

SBT films were deposited on platinized silicon (100) substrates by spin-casting at 3000 rpm for 40 seconds. The coated gel films were dried and baked in air at 250℃ for 10 minutes and at 800℃ for 5 minutes, respectively. This procedure was repeated several times to obtain the desired film thickness of 200nm. Finally, films were annealed at 700℃ ~900℃ for 1 hour in oxygen ambient.

Thermal analysis (TG/DTA) of gel powder prepared by heating the coating solutins at 180℃ for 20 hours was carried out up to 900℃ at a heating rate of 5℃/min. Crystalline phase of MOD derived films were characterized by low-angle X-ray diffractometry with incident angle of 5°. Microstructure of the film surface was observed using scanning electron microscopy (SEM) and atomic force microscopy (AFM). Composition of the films was determined by energy dispersive spectroscopy (EDS).

RESULTS AND DISCUSSION

TG/DTA curves of the SBT gel powder are illustrated in Fig. 1. Weight loss of about 30% occurred at temperature between 250℃ and 400℃ due to the burn-out of organics, which could be confirmed by the exothermic peak at this temperature range on the DTA

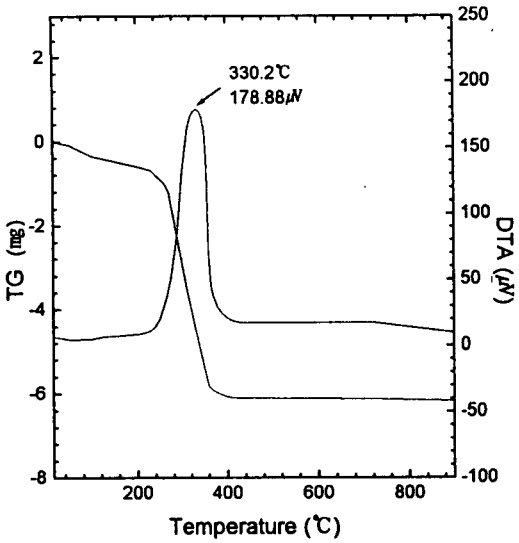

Fig. 1 TG/DTA curves of $SrBi_2Ta_2O_9$ gel powder

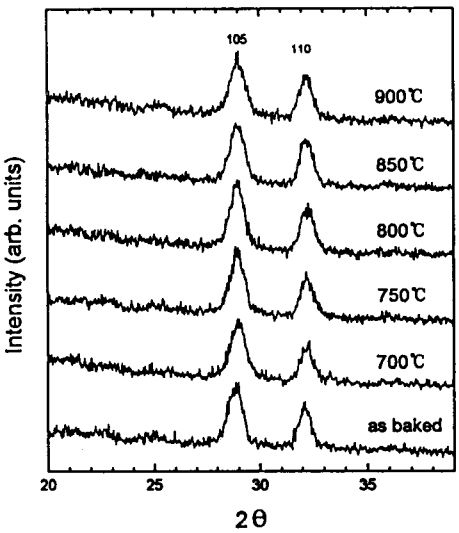

Fig. 2 XRD patterns of $SrBi_2Ta_2O_9$ thin films anealed at various temperatures.

curve. Based on this result, drying temperature for the spin-coated films was determined to be 250℃, and films with crack-free surface could be obtained after multiple coatings.

XRD patterns of SBT(x=1 in $SrBi_{2x}Ta_2O_9$) thin films, annealed at various temperatures, are shown in Fig. 2. MOD derived SBT films could be crystallized to the bismuth layered perovskite structure even by baking at 800℃ for 5 minutes in air. Crystalline phase of the SBT films was not changed by annealing at temperatures ranging from 700℃ to 900℃ for 1 hour in oxygen ambient. All SBT films, just baked at 800℃ or baked and annealed at temperatures of 700℃~900℃ in oxygen atmosphere, were observed to be non-oriented.

AFM images and root mean square (RMS) surface roughness of SBT films are shown in Fig. 3 and Fig. 4, respectively. The scan area was 1㎛×1㎛. SBT films were composed of equiaxed the ins without depending on the annealing temperature, and the grain size of the films increased from 100nm to 200nm with increasing annealing temperature from 700℃ to 900℃. When annealed at temperatures up to 800℃, the surface of SBT films was quite smooth and flat with RMS surface roughness of about 13nm and was changed little wit annealing temperarure. However, surface roughness of the films increased significantly by

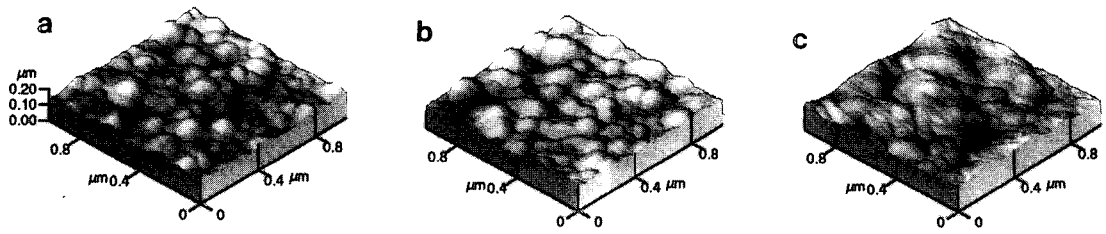

Fig. 3 AFM images of $SrBi_2Ta_2O_9$ thin films annealed at (a) 700℃, (b) 800℃, and (c) 900℃

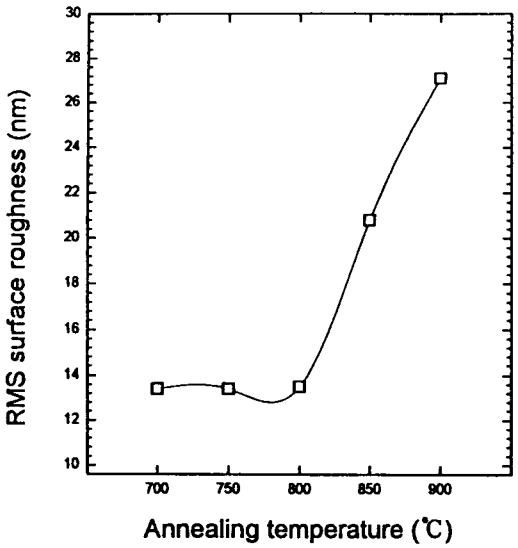

Fig. 4 Surface roughness of $SrBi_2Ta_2O_9$ thin films vs. annealing temperature.

annealing at temperatures above 800℃, and reached to ~28nm for the film annealed at 900℃. This increment of the surface roughness could be attributed to the grain growth at higher annealing temperature.

Bismuth oxide in SBT has relatively high vapor pressure compared with those of strontium and tantalum oxides. Thus, bismuth volatility occurs during annealing process of the as-deposited SBT thin films at elevated temperatures, resulting in non-stoichiometry of the film composition. As lead deficiency of sol-gel derived PZT films deteriorates ferroelectric properties of PZT films[1, 4, 5], remanant polarization of SBT thin films decreases with bismuth deficiency of the films. Addition of excess bismuth oxide precursor into coating solutions is helpful to realize the stoichiometric composition of SBT films[7]. If bismuth content in SBT thin films is enriched to a high level, however, formation of non-ferroelectric second phases and decrease of electrical resistivity have been reported[7]. Thus, bismuth content in coating solutions should be controlled to have proper stoichiometry of the annealed SBT films.

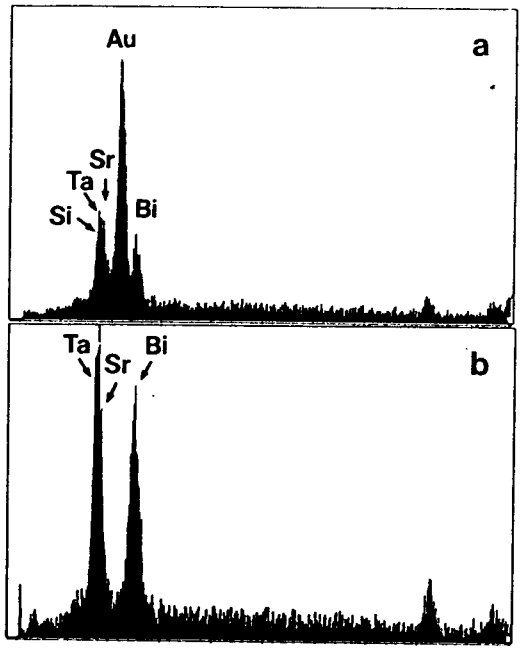

Fig. 5 EDS spectrum of (a) $SrBi_2Ta_2O_9$ thin films and (b) powders

SBT thin films were prepared by spin-casting of $SrBi_{2x}Ta_2O_9$ solutions ($0.8 \leq x \leq 1.6$) and annealing at 800℃ for 1 hour in oxygen atmosphere. To characterize the composition of $SrBi_{2x}Ta_2O_9$ films, EDS analysis was conducted for films fabricated on platinized silicon substrates. As shown in Fig. 5(a), however, $K_{\alpha 1}$ peak of silicon substrate (1.740 eV) is located close to Ta $M_{\alpha 1}$ (1.710 eV) and M $_{\beta 1}$ (1.766 eV) peaks[17]. Also $K_{\beta 1}$ peak energy of Si (1.832 eV) coincides withthose of Sr $L_{\alpha 1}$ (1.806 eV) and $_{\beta 1}$L (1.872 eV), resulting in the inability of the quantitative composition analysis[17]. To eliminate Si substrate peaks in EDS spectrum, $SrBi_{2x}Ta_2O_9$ powders were

fabricated by drying each coating solution at 250℃ and annealing at 800℃ for 1 hour in oxygen ambient. As shown in Fig. 5(b), EDS analysis was performed on $SrBi_{2x}Ta_2O_9$ powders with carbon coating Since Ta $M_{\alpha 1}$ 1 and Sr $L_{\alpha 1}$ peaks are detected together at narrow energy range, it would be still difficult to analyze the content of each element accurately even with deconvolution of the peaks[18]. Compared to strontium and tantalum oxides, bismuth oxide is volatilized more easily during annealing of MOD derived SBT films, and compositional variation of the films is caused mainly by bismuth-oxide volatility. Thus, the composition of $SrBi_{2x}Ta_2O_9$ powders was determined as Bi/(Sr+Ta) mole ratio, and is illustrated in Fig. 6 as a function of Bi content x in coating solutions. Bi/(Sr+Ta) mole ratio increased almost linearly from 0.24 to 0.48 with increase of Bi content x from 0.8 to 1.6. Overall mole ratio of Bi/(Sr+Ta) in Fig. 6 is lower than the expected value in the annealed thin films, which may be due to the heavy vaporization of bismuth oxide in $SrBi_{2x}Ta_2O_9$ powders to larger surface area compared with thin films.

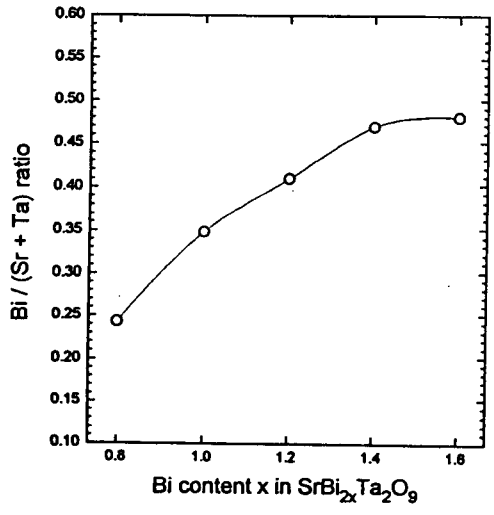

Fig. 6 Bi/(Sr+Ta) mole ratio of $SrBi_2O_9$ powders vs. Bi content x.

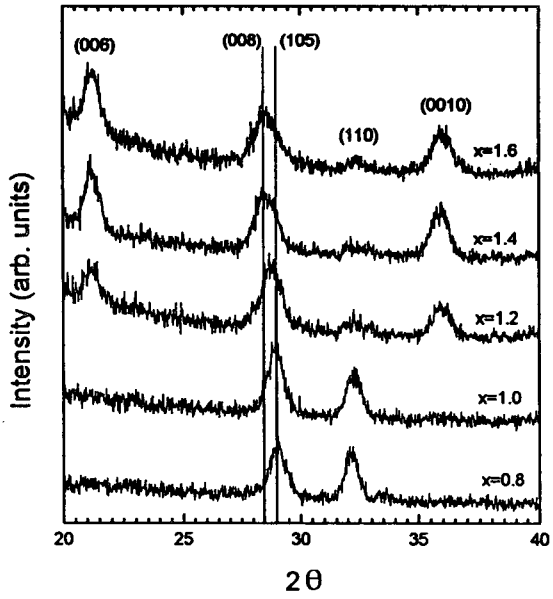

Fig. 7 XRD patterns of $SrBi_{2x}Ta_2O_9$ thin films vs. Bi content x.

XRD patterns of $SrBi_{2x}Ta_2O_9$ films are illustrated in Fig. 7. For all composition x ranging from 0.8 to 1.6, SBT phase of the bismuth layered perovskite structure was formed by annealing at 800℃ for 1 hour. For SBT thin films with $x \leq 1.0$, only (105) and (110) diffraction peaks were observed. In contrast, (006), (008) and (0010) diffraction peaks newly appeared at $x=1.2$ and their intensities increased with increasing bismuth con tent x, indicating films were preferentially oriented along the c-axis.

Fig. 8 shows SEM micrographs of $SrBi_{2x}Ta_2O_9$ thin films with various bismuth content x. Contrary to equiaxed grains of non-oriented $SrBi_{2x}Ta_2O_9$ films ($x=0.8$ and 1.0), elongated grains have been observed on the films with c-axis orientation ($x \geq 1.2$), as reported by

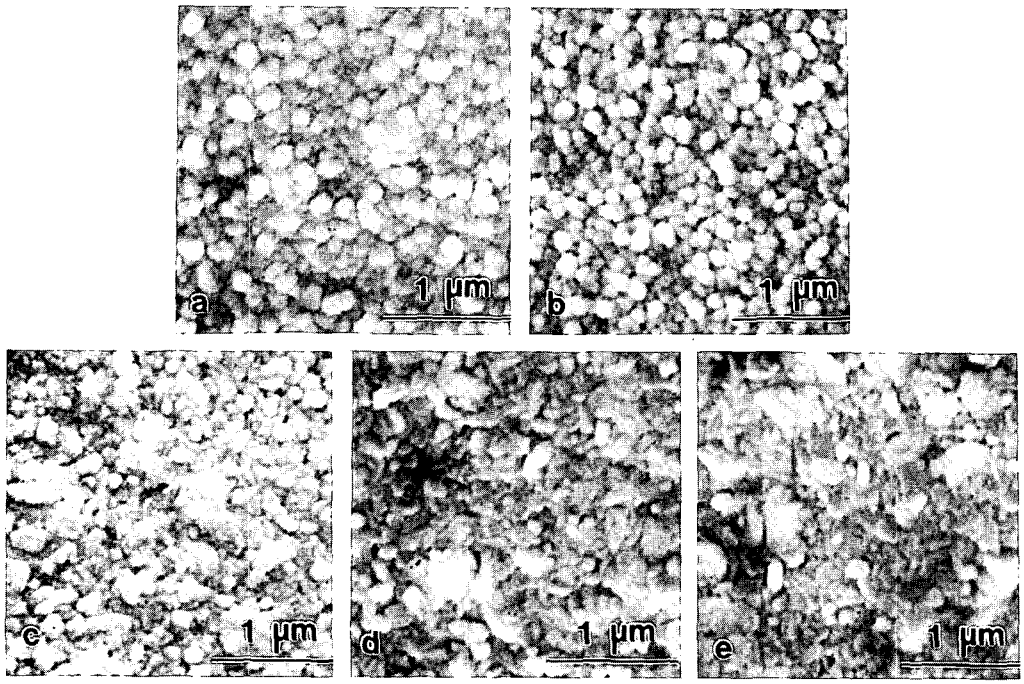

Fig. 8 SEM micrographs of $SrBi_{2x}Ta_2O_9$ thin films with Bi content x of (a) 0.8, (b) 1.0, (c) 1.2, (d) 1.4, and (e) 1.6.

others[16]. The amount of the elongated grains in-creased with bismuth content x. From these results, it could be suggested that these elongated grains are oriented along the c-axis which is perpendicular to the film surface. Surface roughness of $SrBi_{2x}Ta_2O_9$ thin films was 13nm~16nm, and was not changed with bismuth content.

Polarization of the compounds with bismuth layered perovskite structure is largely dependent on the crystal orientation. $SrBi_2Ta_2O_9$ may be written as $(Bi_2O_2)^{2+}(SrTa_2O_7)^{2-}$ consisted of two perovskite-like $(SrTa_2O_7)^{2-}$ layers, alternating with a non-ferroelectric layer of $(Bi_2O_2)^{2+}$, along the c-axis[7,13]. As ferroelectric properties of $SrBi_2Ta_2O_9$ depend on O-Ta-O chains in the perovskite layer perpendicular the c-axis, remanant polarization clecreases with c-axis preferred orientation[7,13,15]. Howeuer, it has been reported that the coerciue field and electrical conductioiity of layered perouskites are lcwer in the c-axis[14] Since strong ⟨00l⟩ orientation was obtained for MOD derived $SrBi_{2x}Ta_2O_9$ films with x ranging from 1.2 to 1.6, electrical prcperties for fram application is expected to be optimum in this range.

CONCLUSIONS

$SrBi_{2x}Ta_2O_9$ thin films ($0.8 \leq x \leq 1.6$), prepared on platinized silicon substrates using MOD process, were crystallized without formation of second phases by annealing at 800 ℃ for 1 hour in oxygen ambient. Preferred orientation in $SrBi_{2x}Ta_2O_9$ thin films was largely affected by bismuth content x in the coating solutions, i.e., stoichiometry of the an

nealed films. Thin films with $x \leq 1.0$ did not exhibit the preferred orientation. However, c-axis orientation could be observed for films with $x \geq 1.2$, and was enhanced with increasing bismuth content x. Contrary to the non-oriented films, $SrBi_{2x}Ta_2O_9$ thin films with c-axis orientation were composed of elongated grains of which amount increased with bismuth content x. Thus, it could be suggested that these elongated grains were oriented along the c-axis perpendicular to the film surface.

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