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Low Temperature Processing of $SrBi_2Ta_2O_9$ Thin Films

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$SrBi_2Ta_2O_9$ thin films were deposited at room temperature on the usual (111) oriented Pt bottom electrodes using r.f. magnetron sputtering, and then post-annealed at 650-800°C for 30 min in oxygen flow. Low temperature processing which shows the preferred oriented SBT thin films was obtained by controlling the sputtering pressure and/or Sr content in target. The orientation and grain growth behavior of SBT thin films were dependent on Sr contents in films. With increasing the excess Bi content up to 50% in SBT thin films, it was possible to lower the onset temperature of grain growth. The c-axis preferred oriented SBT thin films were well-grown under the condition of low post-annealing(650°C) by lowering post-annealing pressure. After 10^{11} switching cycles, no polarization degradation was observed in both preferred oriented SBT capacitors.

Key words: Ferroelectric, $SrBi_2Ta_2O_9$, Sr content, Post-annealing Pressure

I. Introduction

Ferroelectric thin films have been widely investigated for nonvolatile ferroelectric random access memory (FRAM) application. $SrBi_2Ta_2O_9$ (SBT) thin films have received considerable attention due to their potential application in FRAM as an alternative to $PbZr_{1-x}T_xO_3$ (PZT) thin films, which have a serious fatigue problem, when used in conjunction with Pt electrodes, during electric field cycling[1-12]. Although SBT thin films exhibited no fatigue in ferroelectric polarization even after 10^{12} switching cycles, a well-defined hysteresis curve of SBT capacitors can be obtained at high annealing temperature (700-800°C) only[2,8]. However, it is necessary to lower processing temperature to avoid interlayer diffusion and other problems.

Grain growth was reported to be a critical process for SBT thin films to have ferroelectric properties[2]. However, SBT grains grow at 700-800°C after formation of the layered perovskite structure, which occurred at 550-650°C[2]. Although a large number of studies have been made on SBT thin films, as yet, it is not fully understood why grain growth is inhibited. It has only been observed that the temperature needed to obtain a well-defined hysteresis curve is lowered by increasing the Bi content up to 50%, with controlled Sr content in conjunction with Bi content during the sputtering or under lowering post-annealing pressure[3].

It is therefore of interest to understand how the compositions of SBT thin films and post-annealing pressure have influence on the processing temperature and ferroelectric properties of SBT thin films.

In this study, the role of the composition of SBT thin films and post-annealing pressures in the low temperature processing will be discussed. The effect of crystallographic orientation on the ferroelectric properties was also reported.

II. Experimental Details

The SBT thin films were deposited at room temperature using r.f. magnetron sputtering system. The substrates used in this study were platinized silicon wafers, Pt (150 nm)/Ti (50 nm)/SiO_2 (1,000 nm)/Si (100) made by Silicon Quest International Inc. Pt layer was (111) preferred oriented. The targets were composite $SrBi_2Ta_2O_9$ pellets which have different Sr content mole ratio (Sr : Bi : Ta=1 : 2.6 : 2, 1.1 : 2.6 : 2) with a diameter of 5.08 cm and a purity of 99.9% (Seattle Specialty Ceramics Inc.). The mixture of two different gases (Ar/O_2=1/1) was used in the sputtering process. The sputtering pressures were 250 and 300 mTorr. The deposited thin films were post annealed at 650~800°C for 30 min in oxygen flow.

To confirm the influence of Bi content on the oriented growth, SBT/Bi_2O_3/SBT heterosturcture was fabricated and then post annealed at 750°C for 30 min in oxygen flow. The Bi content of SBT thin films was controlled by changing the thickness (100~200 Å) of the sandwiched Bi_2O_3 using r.f. magnetron sputtering from Bi_2O_3 target(Seattle Specialty Ceramics Inc., 99.999%). Details of the Bi control using sandwiched Bi_2O_3 layers are given elsewhere.

The phase and orientation of the films were characterized by the standard θ-2θ x-ray diffraction (XRD, PW1825, philips) with Cu K_α radiation. Rocking curve scan was also performed to determine the degree of the c-axis preferred orientation. The microstructure of SBT thin films was observed by scanning electron microscope (SEM, S-4200, HITACHI). The composition of thin films was determined by inductively coupled plasma atomic emission spectrometer (ICP-AES, polyscan61E, Thermo-Jarrell-ash). The characterization of the ferroelectric properties of the capacitors was performed by using a RT66A ferroelectric tester (Radiant technologies). Patterned platinum top electrodes were produced by using dc magnetron sputter deposition in conjunction with a lift-off method.

III. Results and Discussion

A. Effects of Sr content

SBT thin films were deposited on Pt (111) electrodes from targets having different Sr content (Sr : Bi : Ta=1 : 2.6 : 2, 1.1 : 2.6 : 2), and post-annealed at 750°C for 30 min in oxygen flow. The XRD patterns shown Fig. 1 were indexed by assuming an orthorhombic cell. Fig. 1(a) and (b) shows the XRD patterns of post-annealed SBT thin films deposited at 250 mTorr and 300 mTorr from stoichiometric Sr target (Sr : Bi : Ta=1 : 2.6 : 2). With increasing sputtering pressure from 250 to 300 mTorr, (00*l*) peaks corresponding to the c-axis oriented SBT were strongly enhanced and (115) peak, the major XRD peak at the randomly oriented state, was decreased. Fig. 1(c) and (d) shows the XRD patterns of post-annealed SBT thin films deposited at 250 mTorr and 300 mTorr from 10 mol% SrO excess target (Sr : Bi : Ta= 1.1 : 2.6 : 2). (00*l*) peaks of c-axis oriented SBT were not observed and intensity of (200) peak corresponding to the a-axis oriented SBT was enhanced with increasing sputtering pressure from 250 to 300 mTorr. According to the XRD patterns shown in Fig. 1, specimens were designated as poly-c, c-axis, poly-a, and a-axis. In this study, these designations were used for all specimens that have same target composition and sputtering pressure. Table 1 shows the sputtering pressure and target composition of each specimen.

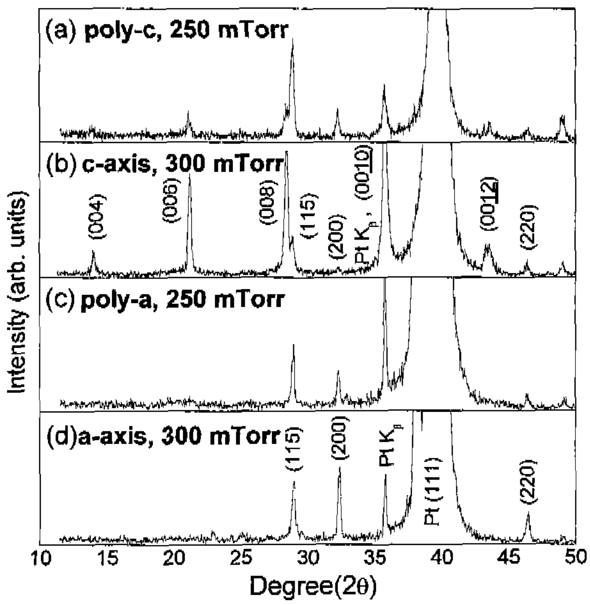

Fig. 1. XRD patterns of SBT thin films post-annealed at 750 °C for 30 min. in oxygen flow which were deposited at sputtering pressures of 250 mTorr (for (a), (c)) and 300 mTorr (for (b), (d)). (a), (b) were deposited from Sr : Bi : Ta=1 : 2.6 : 2 target and (c), (d) were deposited from Sr : Bi : Ta=1.1 : 2.6 : 2 target.

Table 1. Specimens were Designated by Their XRD Patterns in Fig. 1. In this Paper, these Designations were used for all Specimens that have Same Target Composition and Sputtering Pressure

Specimens	Composition of target (Sr : Bi : Ta,mole ratios)	Sputtering pressure (mTorr)
poly-c	1.0 : 2.6 : 2.0	250
c-axis	1.0 : 2.6 : 2.0	300
poly-a	1.1 : 2.6 : 2.0	250
a-axis	1.1 : 2.6 : 2.0	300

In our previous reports, the degree of the c-axis preferred orientation was enhanced with increasing Bi content in SBT thin films by control of sputtering pressure,[13-15] and/or annealing atmosphere.[15] The increase of Bi contents at high sputtering pressure is attributed to the different transport phenomena between the cathode and substrate during deposition. Compositions of SBT thin films were shown in Fig. 2. For the poly-c and c-axis specimens deposited from stoichiometric Sr target (Sr : Bi : Ta=1 : 2.6 : 2), Sr content were 10 mol% deficient from stoichiometric composition. On the other hands, for the poly-a and a-axis specimens deposited from 10 mol% SrO excess target (Sr : Bi : Ta=1.1 :2.6 : 2), Sr content was similar to stoichiometric composition. There was little difference in the Sr contents by increasing the sputtering pressure and post-annealing temperature. However, Bi content in SBT thin films was increased with increasing sputtering pressures and decreased 10~15 mol% from that of as-deposited films with post-annealing. Since poly-a and a-axis specimens (or poly-c and c-axis speci-

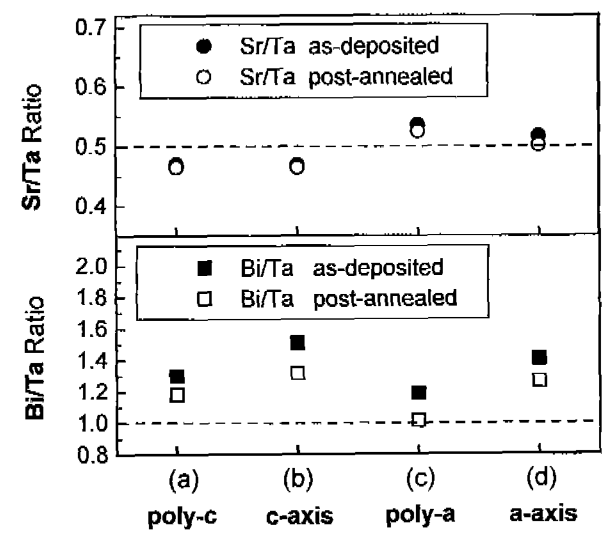

Fig. 2. Compositions of SBT thin films measured by ICP-AES which were as-deposited and post-annealed at 750°C for 30 min. in oxygen flow. (a), (b) were deposited from Sr : Bi : Ta=1 : 2.6 : 2 target and (c), (d) were deposited from Sr : Bi : Ta=1.1 : 2.6 : 2 target.

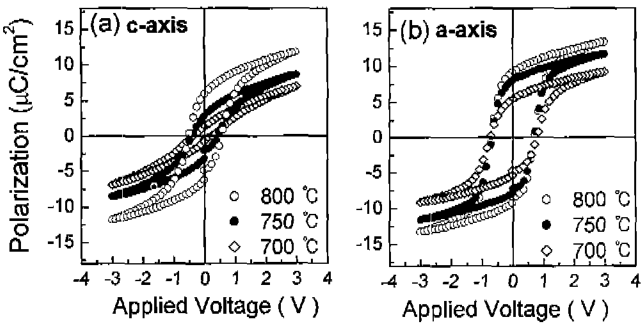

Fig. 3. P-E hysteresis curves of Pt/SBT/Pt thin films capacitor post-annealed at 700, 750 and 800°C for 30 min. in oxygen flow.

mens), which have same Sr content, were textured in the same direction, we could conclude that the direction of preferred orientation is determined by Sr content, and the degree of the preferred orientation was enhanced with increasing Bi content.

Fig. 3 shows the hysteresis curves for the capacitors of SBT thin films post-annealed at 700, 750 and 800°C for 30 min in oxygen flow. For the SBT thin film annealed at 650°C for 30 min, a good hysteresis curve could not be obtained. The remanent polarization of c-axis and a-axis specimens increased with increasing post-annealing temperature. Although c-axis and a-axis specimens have nearly same amount of excess Bi content, the remanent polarization and coercive field of c-axis specimen are always less than those of a-axis specimen. Therefore, the different ferroelectric properties between c-axis specimens and a-axis

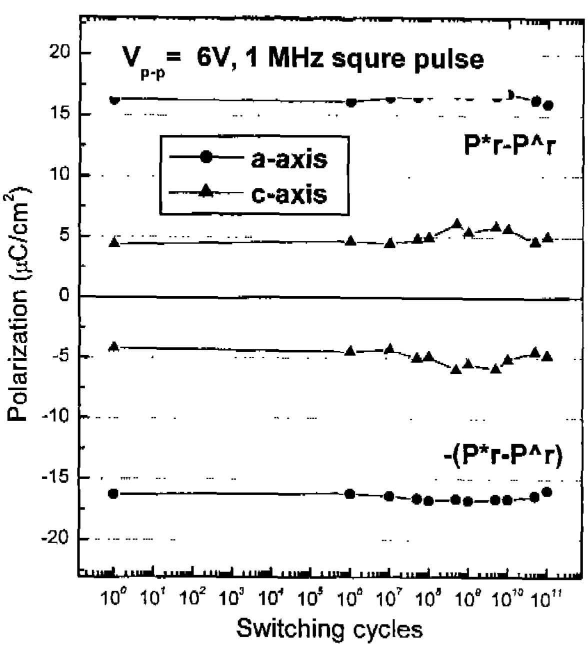

Fig. 4. Fatigue behavior of Pt/SBT/Pt thin films capacitor post-annealed at 750°C for 30 min. in oxygen flow up to 10^{11} switching cycles.

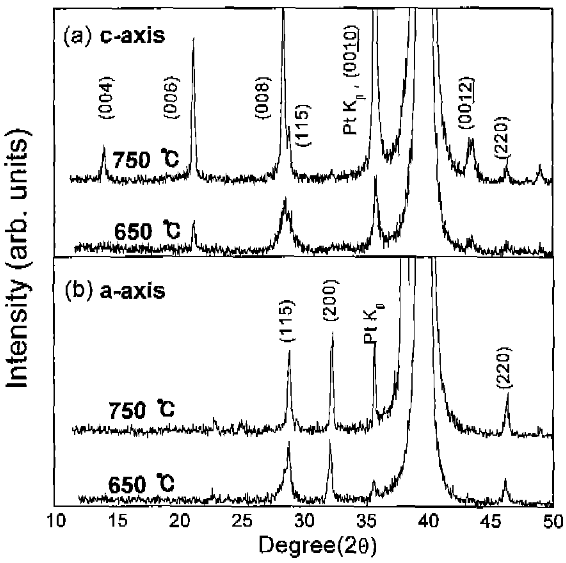

Fig. 5. XRD patterns of SBT thin films post-annealed at 650, and 750°C for 30 min. in oxygen flow. (a) c-axis specimens, and (b) a-axis specimens.

specimens were mainly attributed to the anisotropic ferroelectric properties related with crystallographic orientation due to Sr content. To check the fatigue characteristics, as shown in Fig. 4, bipolar square pulses of 1 MHz frequency were applied with the peak-to-peak voltage of 6 V. No polarization degradation was observed after 10^{11} switching cycles.

For the c-axis and a-axis specimens, Sr content has also influence on the phase formation and grain growth temperature along with preferred orientation. Fig. 5(a) shows the XRD patterns of c-axis and a-axis specimens post-annealed at 650°C, and 750°C for 30 min in oxygen flow. For the c-axis specimen post-annealed at 650°C, small (00*l*) peaks of c-axis oriented SBT were observed simultaneously with broad peak, which was suggested as fluorite structure.[16] In contrary, a-axis specimen shown in Fig. 5(b) was almost completely crystallized to SBT phase and fluorite structure peak disappeared. Fig. 6 shows SEM surface morphologes of c-axis and a-axis specimens post-annealed at 650°C, and 750°C for 30 min in oxygen flow. The c-axis specimen post-annealed at 650°C shows bimodal grain size distribution, consisting of elongated grains and small globular grains.[8,10,13,14] Small globular grains in the matrix were completely changed to uniform elongated grains with increasing temperatures. On the other hands, for the a-axis specimens, the surface morphology post-annealed at 650°C consisting of elongated grains only and no bimodal grain size distribution was observed at lower temperature than 650°C(not included in the Figs).

Considering that c-axis and a-axis specimens have nearly same amount of excess Bi content, it is concluded that the grain growth of SBT thin films is inhibited by Sr deficiency. Since the perovskite layer of SBT is $(SrTa_2O_7)_2$- and the temperature of phase formation and grain growth was lowered by excess Bi, which have the lowest melting point in

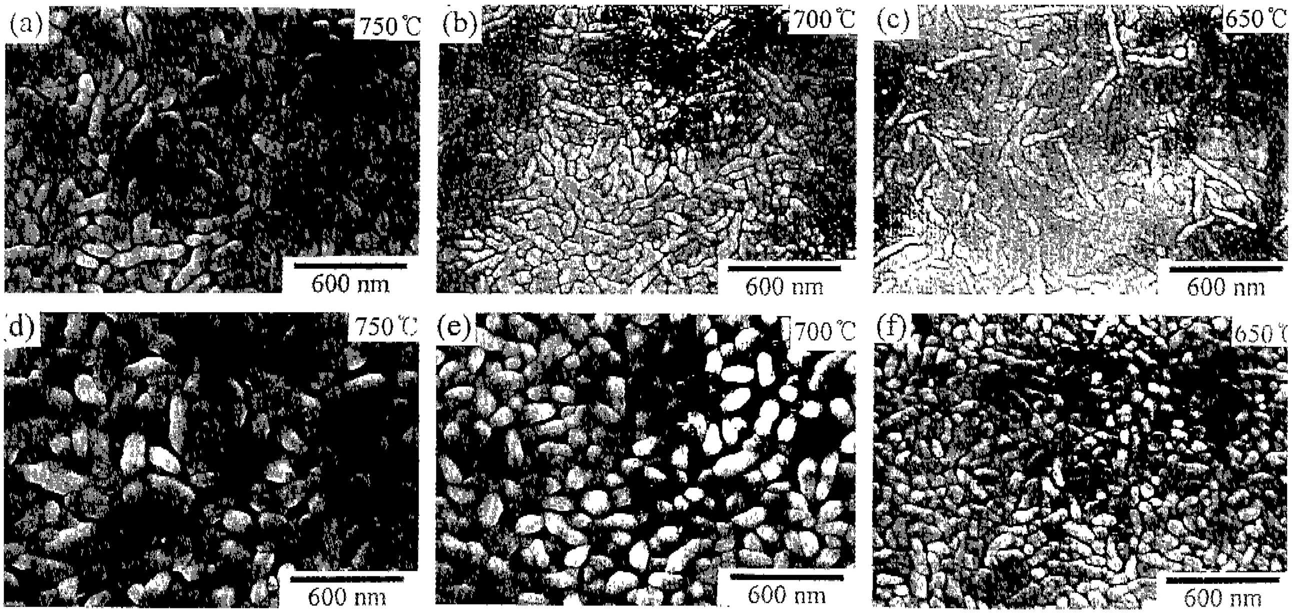

Fig. 6. SEM morphologies of SBT thin films post-annealed at 650°C, 700°C and 750°C for 30 min. in oxygen flow. (a), (b) and (c) are c-axis specimens, and (d), (e) and (f) are a-axis specimens.

the three elements of SBT, the grain growth inhibition due to the nonstoichiometry of SBT thin films could be attributed to only Sr/Ta mole ratio. If the ions consisting of perovskite layers of the Bi-layered structure are deficient, the growing rate in the c-axis direction is more lowered since more perfect arrangement is needed in the direction of the c-axis compared with the direction of the a-b axis. In addition, the grain growth of SBT phase more inhibited by the remained small globular grains of fluorite, which do not grow to the large grains due to the stresses.[16)]

B. Low post-annealing pressure processing

Fig. 7 shows the XRD patterns of c-axis and poly specimens post-annealed at 650°C, and 800°C for 30 min in oxygen flow. And each specimen was post-annealed at 760 Torr, 15 Torr, and 5 Torr. For poly specimens, as the annealing pressure is decreased, the intensities of all XRD peaks are decreased. In contrary, the c-axis thin oriented films are a strong (00*l*) texture as indicated by reflections

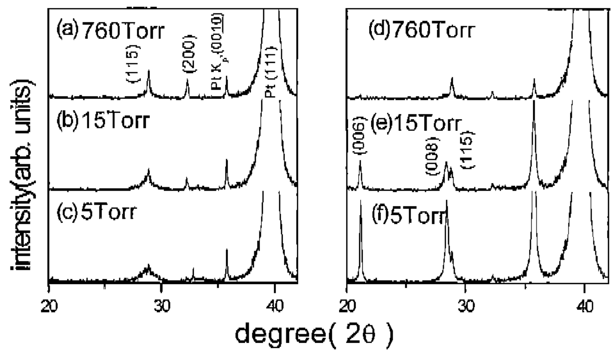

Fig. 7. XRD patterns of c-axis and poly oriented SBT thin films post-annealed at 760 Torr, 15 Torr, and 5 Torr. (a), (b) and (c) are poly specimens, and (d), (e) and (f) are c-axis specimens.

from (006)and (008) planes. For the intermediate case of the films, the predominant orientation in the ferroelectric is still (00*l*). In effect, these results indicate that simply by decreasing the annealing pressure, the degree of c-axis orientation in the ferroelectric can be increased for the same processing condition.

The surface morphology of SBT thin films annealed at 760 Torr exhibits somewhat porous grain structure with elongated grains while those annealed at 5 Torr show dense grains with large grains as shown Fig. 8. Based on the above results, it is assumed that the grain size of c-axis oriented SBT films increases with decreasing the annealing pressure.

Therefore, we suggest that it is possible to obtain the low temperature processing by lowering post-annealing pressure. But further work is needed to obtain the adequate remanent polarization and coercive field.

V. Conclusion

We obtained the c-axis, and a-axis preferred oriented SBT thin films on (111) oriented Pt electrodes using r.f. magnetron sputtering. The preferred oriented direction is determined by Sr content and the degree of preferred orientation is enhanced with increasing the excess Bi content. SBT thin films with Sr deficient compositions showed c-axis preferred oriented growth. On the other hands, SBT thin films with stoichiometric Sr compositions showed a-axis preferred oriented growth. The degrees of preferred orientation are enhanced with increasing the excess Bi content. The a-axis preferred oriented SBT capacitors have lower phase formation and grain growth temperature and higher remanent polarization and coercive field than c-axis preferred oriented SBT capacitors.

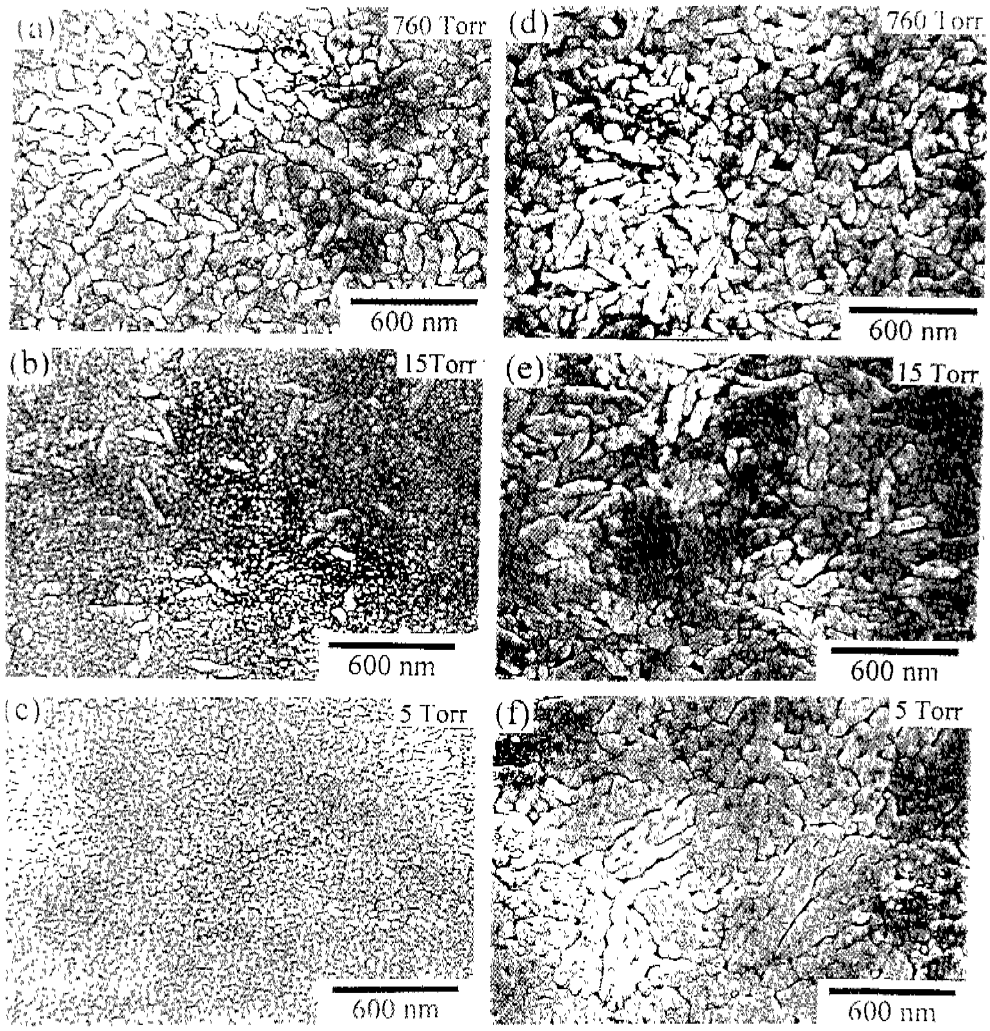

Fig. 8. SEM morphologies of SBT thin films post-annealed at 760 Torr, 15 Torr, and 5 Torr. (a), (b) and (c) are poly specimens, and (d), (e) and (f) are c-axis specimens.

On the other hand, even at low temperature, well-grown c-axis preferred oriented SBT capacitors were obtained by lowering post-annealing pressure.

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