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Effect of Annealing Temperature of Sol-Gel TiO_2 Buffer Layer on Microstructure and Electrical Properties of $Ba_{0.6}Sr_{0.4}TiO_3$ Films

(Kesan Suhu Sepuhlindap Lapisan Penimbal TiO_2 Sol-Gel Terhadap Mikrostruktur dan Sifat Elektrik Filem $Ba_{0.6}Sr_{0.4}TiO_3$)

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ABSTRACT

$Ba_{0.6}Sr_{0.4}TiO_3$ (BST) thin films were prepared on TiO_2 buffer layers. The buffer layers were prepared using sol-gel method, followed by annealing process at different temperature from 300 to 550 °C with 50 °C interval for 30 min in air. The microstructure and electrical properties of BST were then investigated. Increasing the annealing temperature increased. The buffer layer thickness BST films prepared on thicker buffer layer showed improved crystallinity. Without the buffer layer, BST crystallization cannot occur at 700 °C. However with buffer layer, 700 °C is sufficient for the process to occur. The BST grain size increased with the buffer grains increment. The existence of TiO_2 buffer layer increased the current density. The dielectric constant, $\varepsilon_r{}'$ and dielectric loss were not affected much by the buffer layer except at frequency around 1 kHz that showed an increment in the $\varepsilon_r{}'$ value with the increment of the annealing temperature.

Keywords: Annealing; buffer layer; electrical properties; sol-gel

ABSTRAK

Filem nipis $Ba_{0.6}Sr_{0.4}TiO_3$ (BST) telah disediakan di atas lapisan penimbal TiO_2. Lapisan penimbal disediakan dengan kaedah sol-gel, diikuti dengan proses sepuh lindap pada suhu yang berbeza daripada 300 hingga 550 °C dengan sela 50 °C selama 30 min dalam udara biasa. Mikrostruktur dan sifat elektrik BST telah dikaji. Kenaikan suhu sepuh lindap meningkatkan ketebalan lapisan penimbal. Filem BST yang disediakan di atas lapisan penimbal yang lebih tebal mempunyai penghabluran yang lebih sempurna. Tanpa lapisan penimbal, penghabluran BST tidak boleh berlaku pada suhu 700 °C, namun begitu dengan adanya lapisan penimbal, 700 °C sudah mencukupi untuk membenarkan proses penghabluran berlaku. Saiz butiran BST meningkat dengan peningkatan butiran penimbal. Kewujudan lapisan penimbal TiO_2 juga meningkatkan ketumpatan arus. Namun pemalar dielektrik, $\varepsilon_r{}'$ dan kehilangan dielektrik tidak begitu dipengaruhi oleh lapisan penimbal kecuali pada frekuensi lebih kurang 1 kHz yang menunjukkan penambahan $\varepsilon_r{}'$ dengan peningkatan suhu sepuh lindap.

Kata kunci: Lapisan penimbal; sepuh lindap; sifat elektrik; sol-gel

INTRODUCTION

Barium strontium titanate (BST) is the most important ferroelectric material as it has various applications such as in hydrogen gas sensor (Jain et al. 2007), high density dynamic random access memories (DRAM), microwave and radio frequency devices (Ruckenbauer et al. 2004) and distance sensor (Dewi 2009). BST thin films can be prepared using various methods such as sol-gel method (Zhang et al. 2002), pulsed laser deposition (Zhu et al. 2003), and metal-organic deposition method (Yan et al. 2000). It has been reported that its dielectric properties depend on the composition, stoichiometry, microstructure, thickness and also the homogeinity (Ezhilvalan & Tseng 2000).

Recently it has also been reported that the physical properties of some ferroelectric films can be altered by controling its buffer layer. For example, crystallized TiO_2 buffer layer with 5 nm thickness improved the crystallinity and morphology of (Pb,Sr)TiO_3 (PST) ferroelectric films (Chen et al. 2008). It increased the dielectric constant and its tunability by dc voltage. The buffer layer decreased the dielectric loss and leakage current density of PST. The microstructure and dielectric constant of $Ba_{0.5}Sr_{0.5}TiO_3$ (BST) were also improved with buffer layer (Fan et al. 2009). The leakage current of BST reduced with La_2O_3 as buffer layer. At room temperature BST films shows a ferroelectric behaviour instead of a paraelectric behaviour for films without La_2O_3 layer.

In this paper we report the effect of different annealing temperature of TiO_2 buffer layer prepared via sol-gel method on the physical properties of $Ba_{0.6}Sr_{0.4}TiO_3$ films.

EXPERIMENTAL DETAILS

SUBSTRATE CLEANING

The p-type silicon substrates were cleaned using acetone, methanol and distilled water. Then SiO_2 (150 nm) and RuO_2 (100 nm) films were deposited successionly onto the substrates using electron gun (e-gun) evaporation technique.

PREPARATION OF TiO_2 FILMS BY SOL-GEL TECHNIQUE

Titanium butoxide was disolved in 5 mL ethanol and stirred for 6 h at room temperature. Without stopping the stirring process, 0.3 mL ion free water and 0.4 mL hydrochloric acid were added to the solution. The stirring process was continued for another hour. The composition of the obtained gel was $Ti(OC_4H_9)_4$:C_2H_5OH:H_2O:HCl with ratio of 1:26.5:1:1. Using a spin coater the gel was transferred into thin film form onto the $RuO_2/SiO_2/Si$ substrates. The spinning rate was 2500 rpm with 30 s duration. All of the films were then dried at 50 °C in air for an hour in order to get rid of the solvent, followed by the annealing process from 300 to 550 °C with 50 °C interval, for 30 min in air. Then $Ba_{0.6}Sr_{0.4}TiO_3$ (BST) were deposited onto the films by sol-gel process. The BST thickness measured from the cross section micrograph obtained using field emission scanning electron microscope (FE-SEM) is 240 nm.

The crystalline microstructure of the BST film was studied using X-ray diffractometer (XRD) Bruker D8 Advance and field emission scanning electron microscope (FE-SEM) model Supra 55VP. The FE-SEM was also used to measure the film thickness. For the electrical characterization, aluminium film (100 nm) which acted as the upper electrode was deposited by e-gun technique onto the BST film. Hence the final configuration obtained was $Al/BST/TiO_2/RuO_2/SiO_2/Si$. Current density measurements were done using 2 point probe method. The dielectric properties were measured at room temperature using Solarton-Schlumberger complex impedance spectroscopy model 1255 with frequency range from 1 Hz to 1 MHz.

RESULTS AND DISCUSSION

Figure 1 shows the XRD patterns of BST thin films with and without TiO_2 buffer layer. It can be seen that the annealing temperature of the buffer layers influence the BST relative intensities. The buffer layers thicknesses were measured from the cross section morphologies obtained from the FE-SEM and the results are shown in Table 1. The results showed that increasing the annealing temperature increased the buffer layer thickness. This implies that BST films prepared on thicker buffer layers have more perfect crystallization as thicker buffer layer could reduce the random nucleation of BST. Similar results have also been reported by Peng & Meng (2003) who studied on the effect of MgO buffer layer onto $Ba_{0.6}Sr_{0.4}TiO_3$ and Chen et al. (2008) who studied on the effect of TiO_2 layer onto $Pb_{1-x}Sr_xTiO_3$ films. To further clarify out statement we also show in Figure 1 the XRD pattern of BST film prepared onto $RuO_2/SiO_2/Si$ substrate (without the TiO_2 layer and the BST was also annealed at 700 °C similar as for BST with buffer layer). No BST peaks can be found in the pattern. These results also showed that without buffer layer, BST crystallization cannot occur at 700 °C, however with buffer layer, 700 °C is sufficient for the process to occur. Similar result has also been reported by Kil et al. (1999) who studied on the effect of self-buffering process onto $Ba_{0.5}Sr_{0.5}TiO_3$ films.

The effect of buffer layers on BST morphologies were studied using FE-SEM. The micrographs in Figure 2 show that all of the BST films are cracked free. The

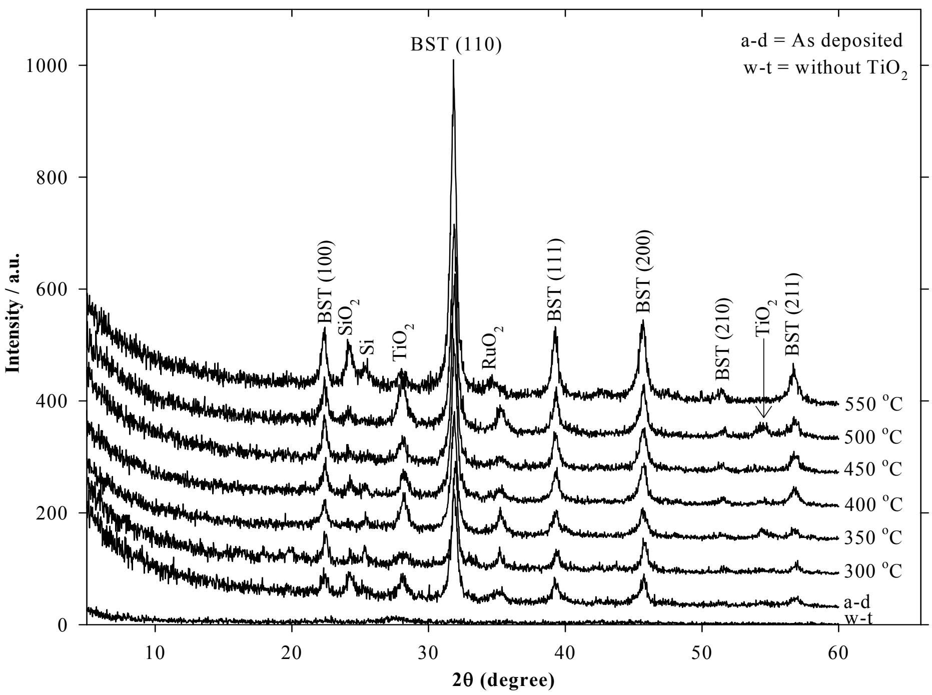

FIGURE 1. The XRD patterns of BST thin films with and without TiO_2 buffer layers

TABLE 1. Annealing temperature, thickness and grain size of buffer layer and BST film average grain size

Buffer layer annealing temperature (°C)	Buffer thickness (± 0.1) nm	Buffer average grain size (± 0.1) nm	BST average grain size (± 0.1) nm
As deposited	191.0	13.2	27.2
300	218.1	17.0	28.8
350	222.8	18.1	29.2
400	230.1	19.3	31.3
450	289.3	21.9	39.9
500	300.2	24.2	40.9
550	312.2	27.6	43.6
Without buffer layer	-	-	23.9

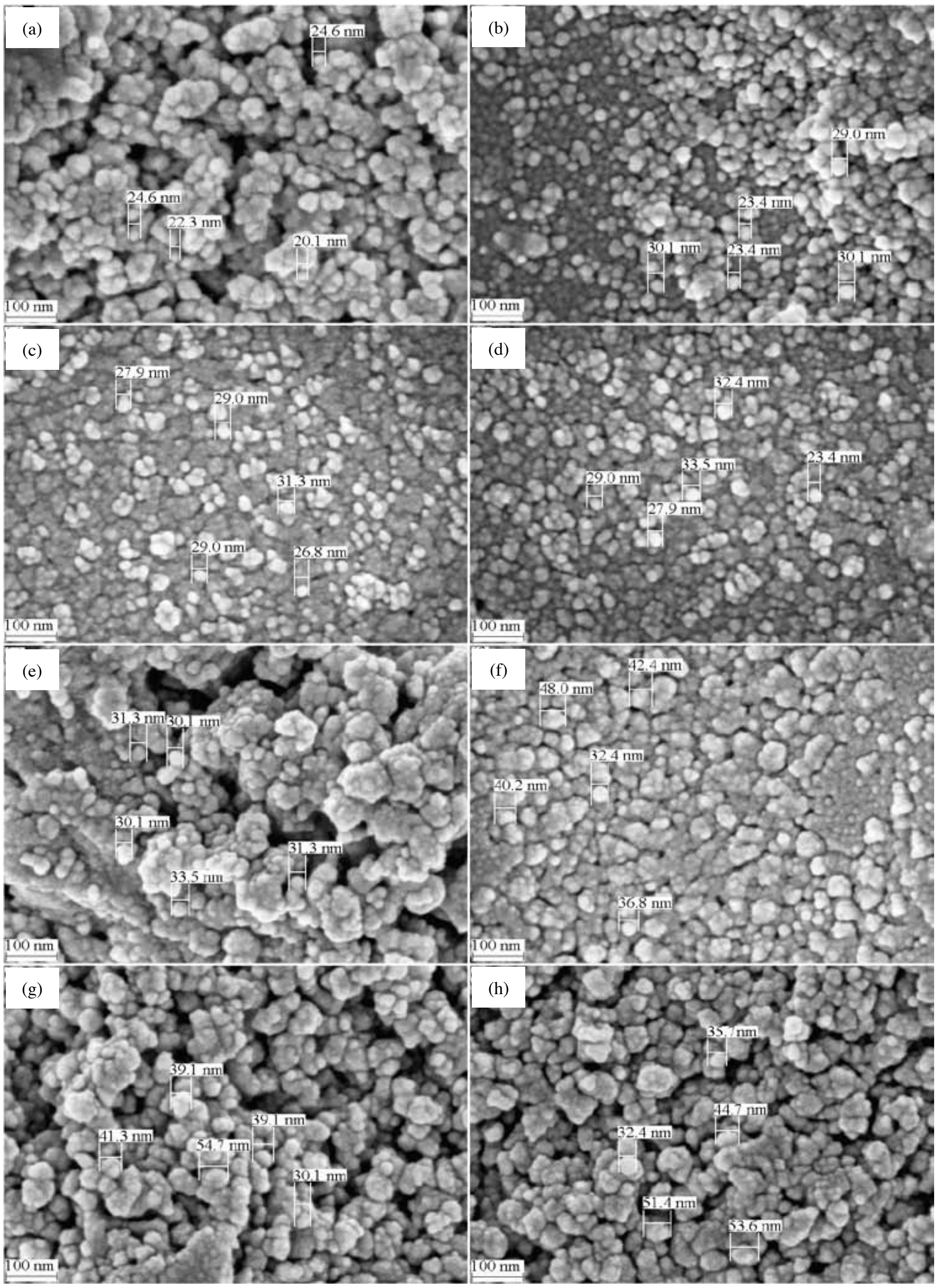

FIGURE. 2: FE-SEM micrographs of BST film (a) without buffer layer, with buffer layer (b) as prepared, annealed at (c) 300ºC , (d) 350 ºC , (e) 400 ºC, (f) 450 ºC , (g) 500 ºC and (h) 550 ºC

average grain sizes were measured from the micrographs and the results are shown in Table 1. The average grain size of buffer layers measured using the same technique prior to the BST preparation are also shown in Table 1. The buffer layers average grain size increased with the annealing temperature. Kingery et al. (1991) reported that increasing the annealing temperature increased the films atomic mobility, resulting in combination of small grains. Table 1 also shows that BST grain size increases with buffer grains. BST without buffer layer has smaller grain size. Fan et al. (2009) has also reported similar results for BST films prepared with and without La_2O_3 buffer layers. This could be due to the possible crystals defect of their copper substrates such as splitting dislocation and twinning dislocation which suppress the nucleus and growth of BST film (Fan et al. 2009). In our case the defect could occur at the RuO_2 layers.

In order to measure the electrical properties of the BST films, Al electrodes were deposited onto the BST using e-gun technique. Figure 3 shows that the current densities increased with the applied voltage. BST without buffer layer gives the smallest current density. This could be due to the direct contact of the BST with the negative electrode (RuO_2). Above 1.5 V, increasing the buffer annealing temperature to 350°C increased the current density. This could be due to the closed packed of the grain as shown in Figure 2. However in general further increment of the temperature from 400 to 550°C decreased the current density which could be due the existence of pores as shown in Figure 2, leading to the direct contact between upper electrode and TiO_2. Direct contact of BST to the lower electrode could also happen as grain size of TiO_2 increased with the annealing temperature.

Dielectric constant, ε_r' and loss, ε_r" of BST as a function of frequency at room temperature for films with TiO_2 buffer layer at different annealing temperature and without TiO_2 buffer layer are shown in Figures 4 and 5, respectively. It can be seen that the insertion of buffer layer did not significantly improved the dielectric constant and dielectric loss of the BST films. All of the ε_r' curves seem to converge at around 1 kHz with an increasing ε_r' value from 1332 to 1464 when the TiO_2 buffer layer annealing temperature was increased from 300 °C to 550 °C. However at higher frequencies BST film with buffer annealed at 500°C has the highest dielectric constant follows by the 350 °C annealed buffer. They also show very high dielectric loss (> 300). However it is difficult to determine the exact mechanism which contributed to the high dielectric constant and loss at these annealing temperature due to the complex microstructure of the films. BST films with the as-prepared buffer and buffers annealed at 300, 400, 450 and 550°C exhibit a large dispersion of dielectric constant within the low frequency range (<10000) Hz and a slight dispersion at higher frequencies. The strong dispersion is due to the large space charge or interfacial polarization at lower frequencies and can be explained by the accumulation of charge at the film-electrode surface or at the grain boundaries of the BST or TiO_2 (Adikary & Chan 2003; Lahiry & Mansingh 2008). The small dispersion of the dielectric constant of the films at higher frequencies show the absence of internal interfacial barriers (Adikary & Chan 2003). Even though there is a possible direct contact for a few films as discussed

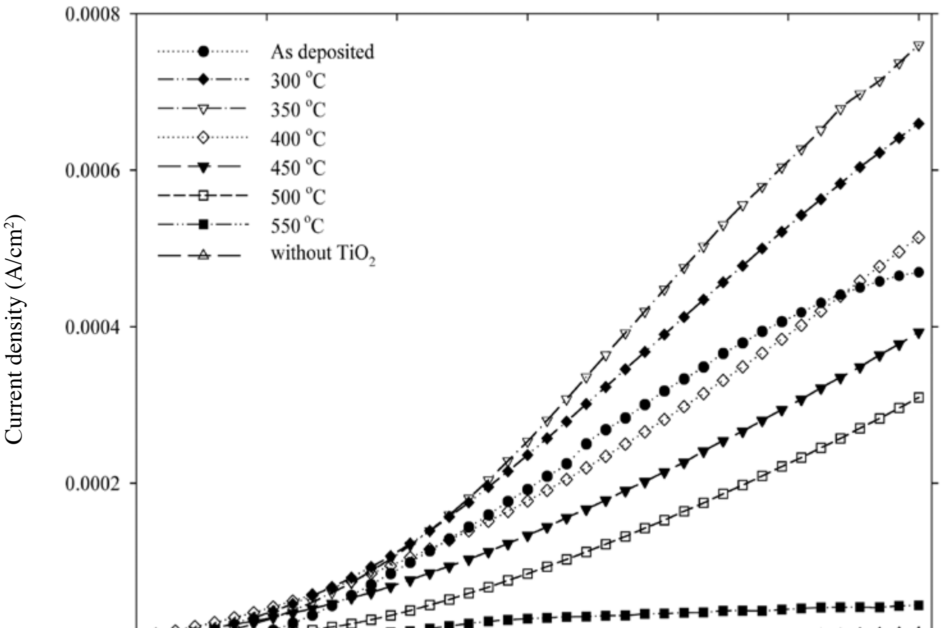

FIGURE 3. Current density of BST devices with and without TiO_2 buffer layers

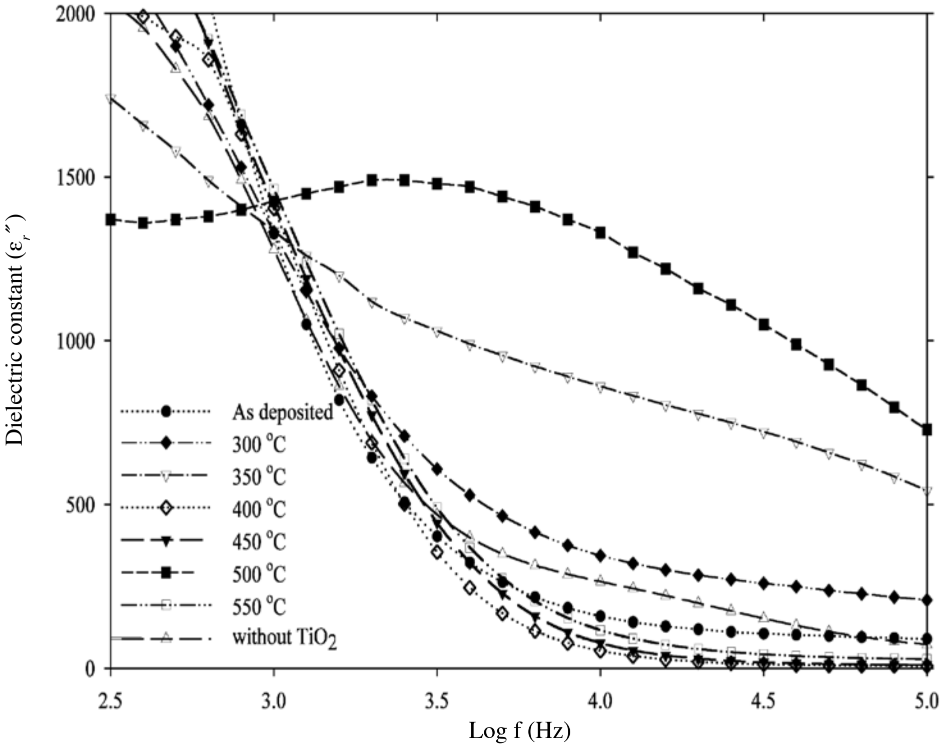

FIGURE 4. Dielectric constants as function of frequency of BST thin films with and without TiO_2 buffer layers

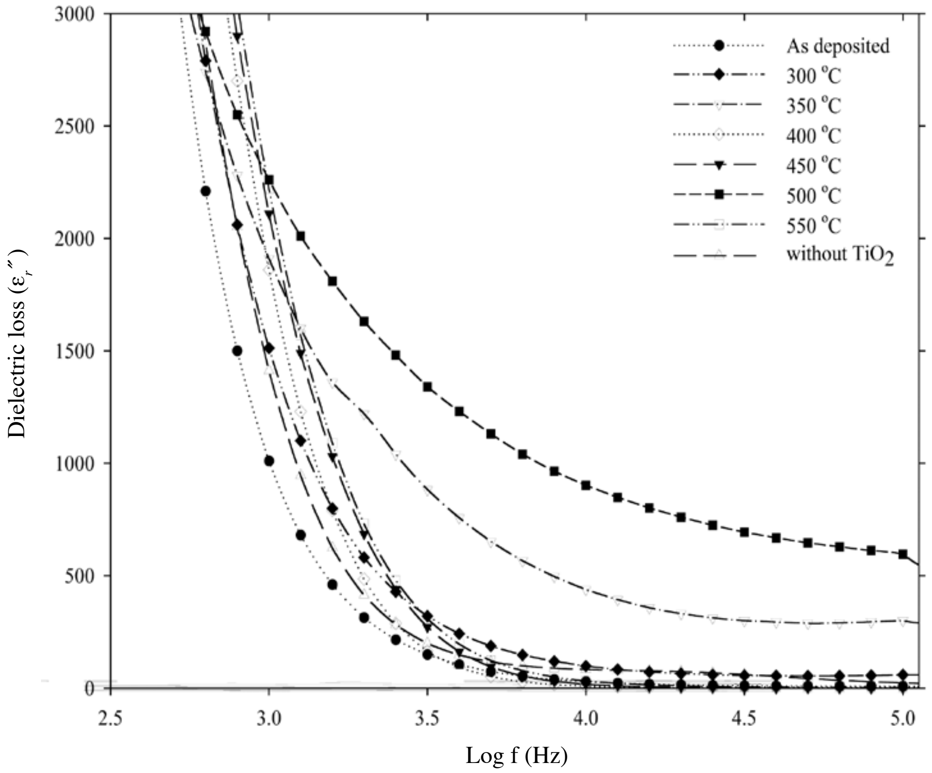

FIGURE 5. Dielectric loss as function of frequency of BST thin films with and without TiO_2 buffer layers

in the previous paragraph, accumulation of charge could occur due to the TiO_2 buffer layer which is an insulative material.

CONCLUSION

The effect of annealing temperature of sol-gel TiO_2 buffer layer on the microstructure and electrical properties of $Ba_{0.6}Sr_{0.4}TiO_3$ films have been studied. Increasing the annealing temperature increased the buffer layer thickness. BST films prepared on thicker buffer layers have more perfect crystallization and the grain size increased with buffer grain. The existence of TiO_2 buffer layer improved the current density. However the dielectric constant and dielectric loss are not affected much by the buffer layer.

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