The Korean Journal of Ceramics, **6**[4] 333-338 (2000)

Microstructural Investigation of $Ba_{0.7}Sr_{0.3}TiO_3$ (BST) Thin Films on Various Electrodes and Buffers

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(Received February 16, 2000)

$Ba_{0.7}Sr_{0.3}TiO_3$ (BST) thin films were deposited simultaneously on various electrodes and buffers by the sputtering technique. When the substrate temperature was varied, the BST thin film on each electrode showed good crystallinity above 550°C as revealed by X-ray diffraction measurements. The surface morphology, determined by atomic force microscopy, indicated that the roughness of BST thin films on RuO_2 was substrate dependent. However, BST thin films on Ru electrodes are smoother and showed no substrate dependence, probably because the precursor surface diffusion length was greater than the sinusoidal perturbations of the wavelength.

Key words: Surface morphology, Eletrodes, Butter layer

I. Introduction

In recent years, materials with a high dielectric constant have been in demand for insulators in dynamic random access memory (DRAM) applications. Many materials, such as lead zirconate titanate (PZT), lead lanthanum zirconate titanate (PLZT), and $Ba_xSr_{1-x}TiO_3$ (BST), have been studied extensively for this purpose. Among these materials, BST is the most promising, because it has desirable properties such as a high dielectric constant. In addition a low Curie temperature can be obtained in BST by controlling the molar ratio of barium to strontium. BST can be produced by RF magnetron sputtering,[1-3] sol-gel processing,[4] metalorganic chemical vapor deposition (MOCVD),[5,6] or laser ablation.[7,8] The RF magnetron sputtering method has particular merit because it enables easy thickness control and results in low contamination.

In determining the performance of a ferroelectric thin-film capacitor, electrodes (especially the bottom electrodes) play an important role since the microstructures of films grown on them can be distorted. Consequently, the properties of the films can be affected significantly. Many researchers have reported that the dielectric and electrical properties of films depend on the bottom electrodes.[9] Because an electrode can affect the performance of a device, it must be chosen carefully. First, the electrode must have electrical stability supplied by a barrier layer. Because most of the ferroelectric materials considered for DRAM applications are oxide compounds, some electrodes can be oxidized during the fabrication process.[1,5] In addition, electrodes with Ag or Au coating can react with thin-film materials because they exhibit solid-solubility in the perovskite structure. Until now, Pt has been the conventional electrode material for such devices, and several oxide compound electrodes are also being investigated.[10-13]

For the present study, we deposited BST thin films onto various electrodes on silicon wafers, with buffer layers, in order to investigate the effects on the film properties. Structural analyses were conducted using different electrodes with buffer layers.

II. Experiment

The Pt (150 nm), Ru (100 nm) and RuO_2 (100 nm) films were sputter-deposited over a diffusion barrier and a buffer layer. The sputtering gas was Ar for the metal electrodes, and a mixing gas (Ar/O_2=1.5) was used for the RuO_2 electrode. The substrate temperature was room temperature. The sputtering conditions for BST thin films were as follows. In order to avoid run-to-run variations, we used clean substrates (1.0×1.0 cm^2) of $Pt/SiO_2/Si$, $Pt/TiN/SiO_2/Si$, $Ru/SiO_2/Si$, $Ru/Si_3N_4/Si$, $RuO_2/Ru/SiO_2/Si$ and $RuO_2/Ru/Si_3N_4/Si$ simultaneously for each deposition. The distance between the target and substrates was 60 mm, and the working gas was an equal mixture of Ar and O_2. The base pressure was maintained at 2.5×10^{-5} Torr, and the gas flow rate was 10 sccm. Presputtering was performed for 30 min each time to remove the contaminated materials from the target surface.

The crystal structure of the films was analyzed by X-ray diffracion (XRD), and the thickness of the films and the size of the top Pt electrodes were measured using a mechanical stylus profilometer and scanning electron microscopy (SEM). The depth profiles of the films were analyzed by auger electron spectroscopy (AES). The surface morphologies of the films and electrodes were also investigated by atomic force microscopy (AFM) and scanning tunneling microscopy (STM).

III. Results and Discussion

Fig. 1 shows the rms roughness of the BST thin films and the associated bottom electrode layers. BST thin films on metals (Pt: filled and open squares, Ru: filled and open circles) exhibited smooth surfaces compared with those on RuO_2 (filled and open triangles). The roughness of the BST thin films on RuO_2 exhibited substrate dependence: That is, the RuO_2 electrodes deposited onto Si_3N_4 were rougher than those deposited onto SiO_2. Concomitantly, BST thin films on $RuO_2/Ru/Si_3N_4/Si$ were rougher than those on $RuO_2/Ru/SiO_2/Si$. Meanwhile, BST thin films deposited on Ru were smoother and exhibited no substrate dependence. These results are explained by the evolution of surface profiles in response to sinusoidal perturbations of the wavelength, λ_r.[14] In models of ballistic deposition, for example, effects of finite atomic size[15] and shadowing[16] have been reported to enhance these perturbations, whereas adatom surface diffusion supposedly damps them. Thus, perturbations with wavelengths smaller than the diffusion length λ_0 are smoothed by surface diffusion, whereas long-wavelength perturbations grow unstably and result in a strongly modulated surface profile with columnar microstructure.

The deposition of BST thin films at 600°C might have caused an annealing effect on the electrode. Thus, we performed STM studies on each electrode before and after deposition of the BST thin film at 600°C. Fig. 2 shows the STM images of (a) $Pt/SiO_2/Si$, (b) $Ru/SiO_2/Si$ and (c) $Ru/Si_3N_4/Si$ bottom electrodes before (left column) and after (right column) annealing. Overall, the electrode grains became larger because of the coalescence effect, and the rms roughness varied according to the electrode and buffer layer. A comparison of Figs. 2(a) and 2(b) reveals that the increase in grain size measured by the linear intercept method was greater in Ru than in Pt. The grain size of $Pt/SiO_2/Si$ thin

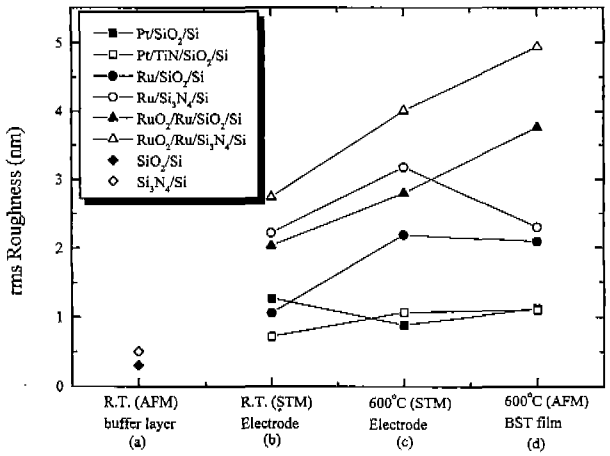

Fig. 1. The variation of roughnesses after depositing a layer and annealing. (a): The rms roughnesses of buffer layers at room temperature (AFM), (b): The rms roughnesses of electrodes on buffer layers at room temperature (STM), (c): The rms roughnesses of electrodes after annealing (STM) and (d): The rms roughnesses of BST thin films on electrodes (AFM).

films changed by less than 1 nm for the average grain size of about 12 nm, but in the case of Ru/SiO_2 thin films, it increased from 11 nm to 18 nm. If the surface energy of the thin film is greater than that of the substrate, to minimize the surface energy it tends to form cruster on the low surface energy substrate. Thus a coalescence effect can be increased. Furthermore, minimizing the internal grain boundary energy can lead to morphological changes by grain growth and grooving. In Figs. 2(b) and 2(c), the grain size of Ru on different buffer layers can be easily seen before and after annealing.

The surfaces of BST thin films were investigated by SEM and AFM. Fig. 3 shows SEM images of the BST thin films simultaneously deposited on different electrodes at 600°C with a 0.7 Ba molar ratio. As shown in Table 1, the surface roughness and grain size of BST thin films depends strongly on the bottom electrode. (a) and (b) are the films grown on Pt electrodes, without and with a TiN adhesion layer on SiO_2, respectively. Morphological changes on Pt electrodes may be caused by the differences in surface roughness of the Pt layer, as may be concluded based on the STM measurements (Fig. 2 (a)). (c) and (d) are BST thin films grown on Ru electrodes. (e) and (f) are BST thin films on Ru/RuO_2 electrodes. The grain sizes of the BST thin film on Ru/RuO_2 are larger than those other films. SEM images of BST thin films on Pt electrodes are poor in spite of the larger grain size. Surface roughness due to the grain size in oxide materials can be interpreted in terms of facets[18] and lattice matching. If the grain size is small, so is the individual facet. Therefore, the average depth of the grooves formed by microfacets on the surface becomes smaller as the grain size decreases. BST thin films deposited on the smooth surface of Pt electrodes have fine-grained, smooth surfaces. This result agrees well with BST thin films on metal and oxide electrodes. Lattice matching is the other parameter influenced by the surface morphology. Since the electrode is the substrate in the BST thin film growth, the electrode has control of the orientation and crystallinity of the BST thin film. The misfits f[17] between BST thin films and electrode are −0.012, −0.32, and 0.13 for Pt, Ru, and RuO_2, repectively. Since the misfits of BST thin films on Ru, RuO_2 are larger than those on Pt, the lattice mismatching causes poor growth of the BST thin film. This result can be confirmed in BST thin films on Pt and Ru. These results can explain the possible interface problem between the electrode and BST thin film.

Table 1. Surface Roughness and Grain Size of BST Thin Films on Various Electrodes

Substrate	Roughness (Å)	Grain size (nm)
$Pt/SiO_2/Si$	11.2	61.1
$Pt/TiN/SiO_2/Si$	11.0	55.8
$Ru/SiO_2/Si$	20.9	48.2
$Ru/Si_3N_4/Si$	23.0	57.5
$RuO_2/Ru/SiO_2/Si$	37.6	91.6
$RuO_2/Ru/Si_3N_4/Si$	49.4	96.4

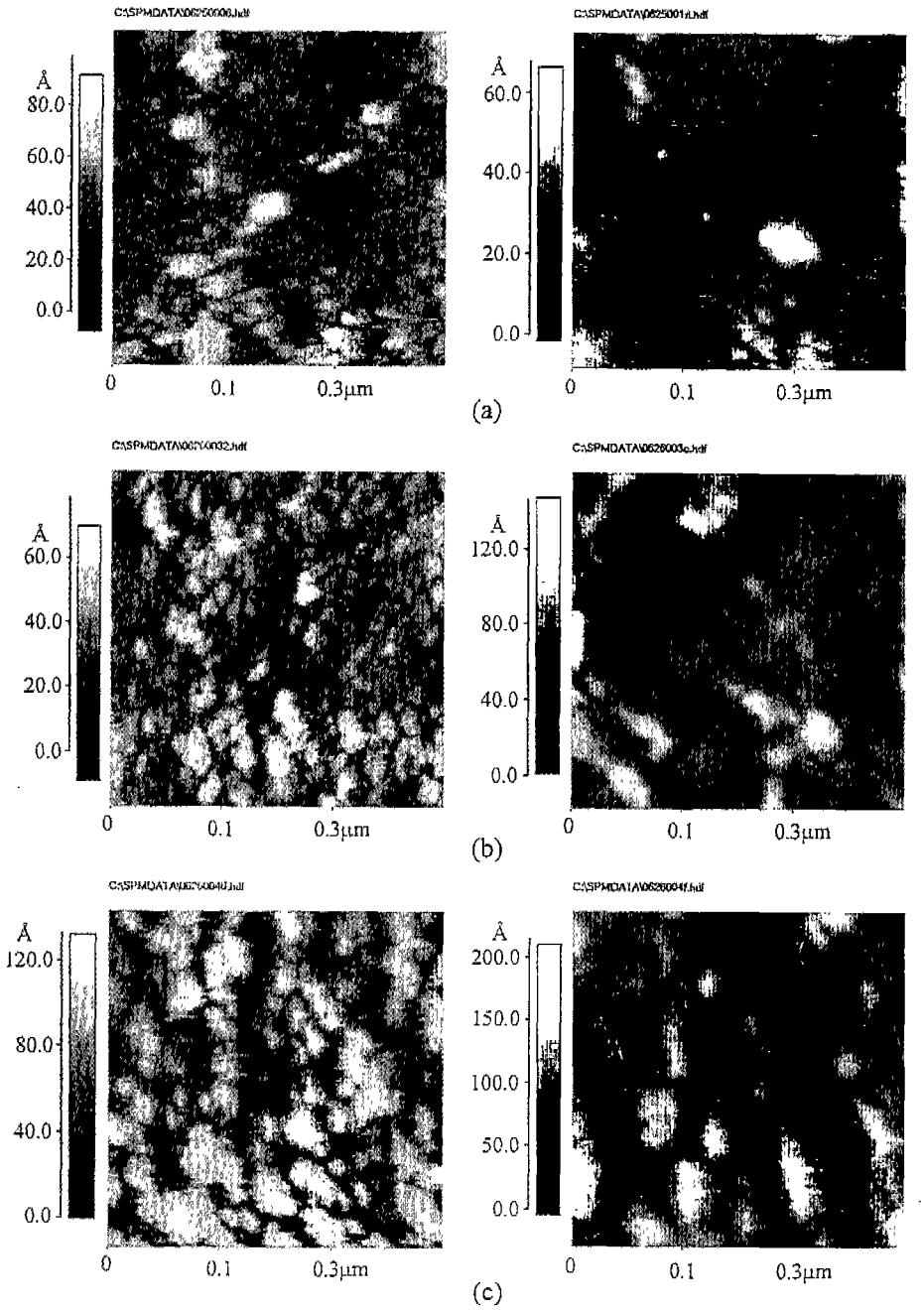

Fig. 2. STM images (scan size: **0.3×0.3** μm^2) of electrodes before (left column) and after (right column) annealing. (a) $Pt/SiO_2/Si$, (b) $Ru/SiO_2/Si$ and (c) $Ru/Si_3N_4/Si$.

Fig. 4 shows the XRD patterns of BST thin films on (a) $Ru/SiO_2/Si$ and (b) $Ru/Si_3N_4/Si$ prepared at different substrate temperatures. Because perovskite peaks become stronger in films deposited at a higher substrate temperature, all of the samples for the present study were prepared at 600°C. The BST film peak intensities are almost the same, but the Ru peak intensities are very different. The Ru peak on SiO_2/Si is much weaker than that on Si_3N_4/Si. The Ru peak intensity on the different buffer layer can be interpreted in terms of oxidation of the Ru metal. Many researchers have reported that the surface of Ru is oxidized under exposure to O_2 atomosphere[5] and that Ru bottom electrodes at high-temperature deposition are oxidized by oxygen diffusion.[19] In particular, the possibility of oxidation of the Ru film is greater in the SiO_2 buffer layer than in the Si_3N_4 buffer layer.

The XRD patterns of the target and the films with a 0.7 molar ratio of Ba on each electrode are depicted in Fig. 5. The XRD patterns of the target in Fig. 5 shows growth as a typical perovskite structure for BST. The as-deposited BST thin films exhibit (110) peaks for all electrode materials. We note that the (110) peak for the films on RuO_2/Ru exhibits a

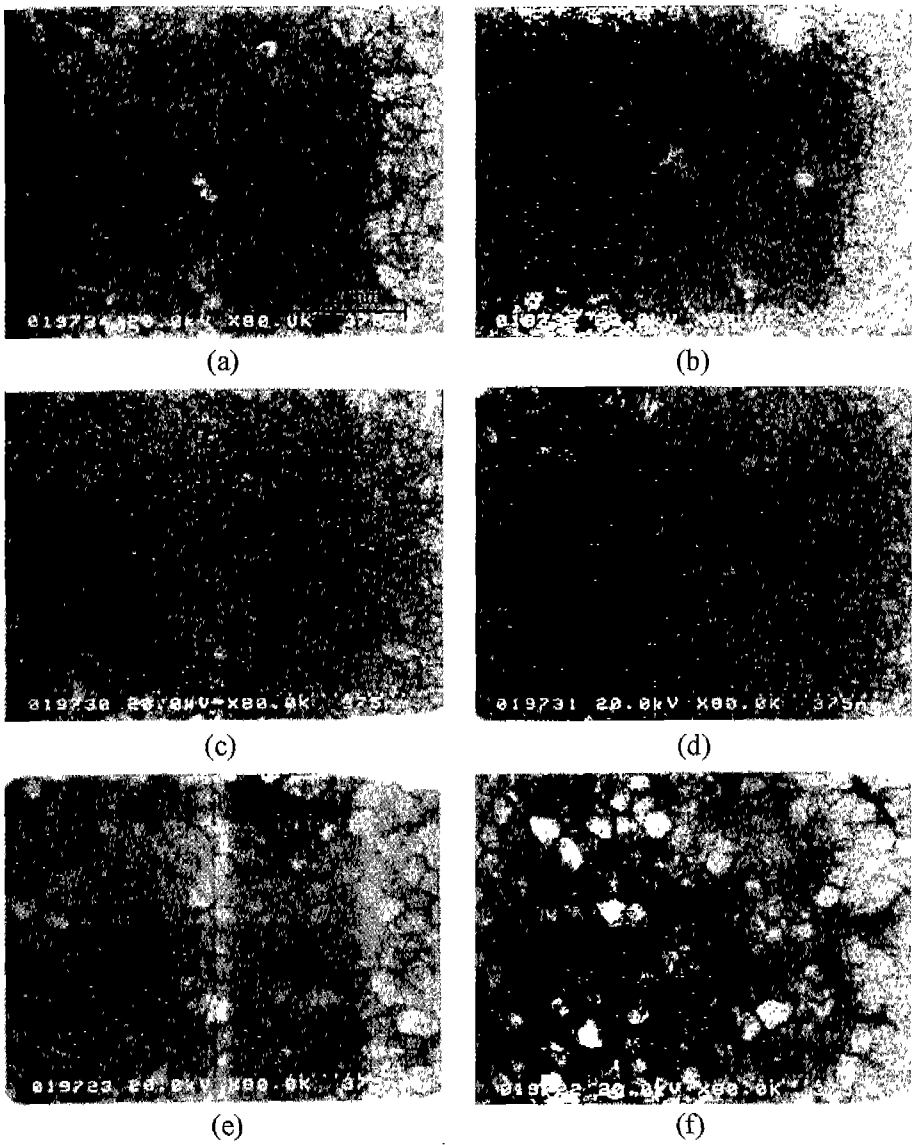

Fig. 3. SEM images of BST films on various electrodes. (a) $Pt/SiO_2/Si$, (b) $Pt/TiN/SiO_2/Si$, (c) $Ru/SiO_2/Si$, (d) $Ru/Si_3N_4/Si$, (e) $RuO_2/Ru/SiO_2/Si$ and (f) $RuO_2/Ru/Si_3N_4/Si$.

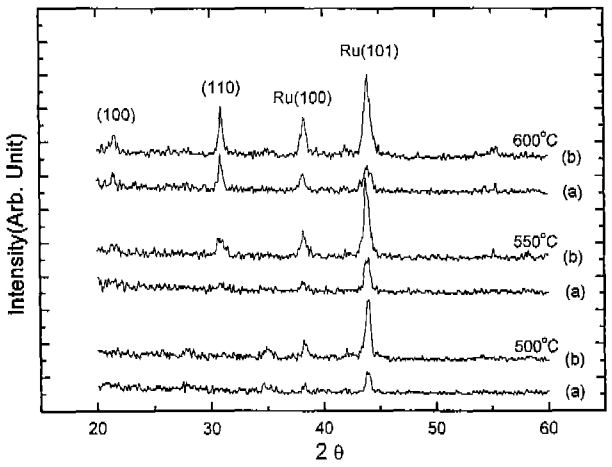

Fig. 4. XRD patterns of BST thin films on $Ru/SiO_2/Si$ (a) and $Ru/Si_3N_4/Si$ (b) for different substrate temperatures.

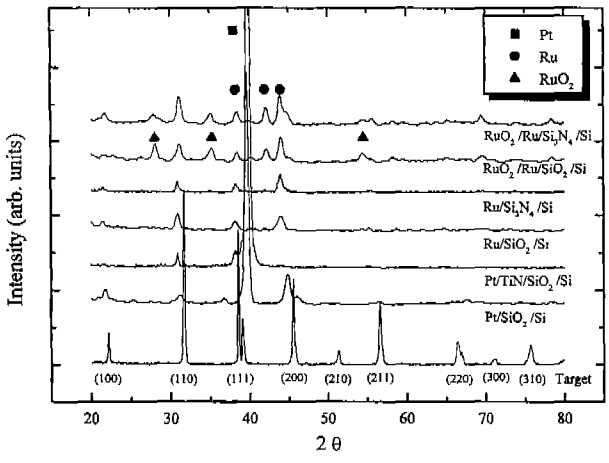

Fig. 5. XRD patterns of samples sputtered on various electrodes and a buffer layer at 600°C for a Ba molar ratio of 0.7.

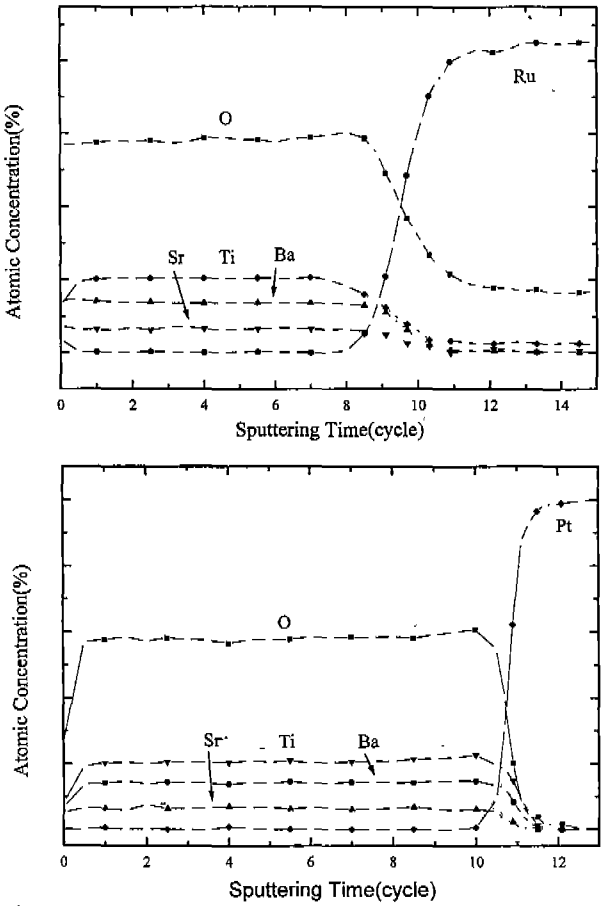

Fig. 6. AES depth profiles of (a) $Ru/SiO_2/Si$ and (b) $Pt/TiN/SiO_2/Si$.

stronger intensity, while that for the film on $Pt/SiO_2/Si$ exhibits a fairly weak intensity. Since the adhesion of Pt to SiO_2 is poor, we assume that this is due to the stress caused by thermal expansion mismatch.[20]

The AES depth profiles of BST thin films deposited onto different substrates were investigated in order to study the electrode stability. The depth profiles of three BST thin films deposited onto different substrates by AES are shown in Fig. 6. Fig. 6(a) shows the depth profiles of $Ru/SiO_2/Si$; oxygen diffusion to ruthenium is observed, which indicates the oxidation of Ru during deposition. This result is consistent with that of Lee *et al.*[19] According to the Mitsubishi Group, RuO_2 formation during deposition leads to an abrupt increase in surface roughness, which can influence the electrical properties of dielectric films.[19] This morphological difference in BST thin films is reflected in their electrical properties. The depth profiles of BST films on $Pt/TiN/SiO_2/Si$, as shown in Figs. 6(b) show no diffusion and have a very sharp gradient at the interfaces.

II. Conclusion

The structural and electrical properties of BST thin films grown on $Pt/SiO_2/Si$, $Pt/TiN/SiO_2/Si$, $Ru/SiO_2/Si$, $Ru/Si_3N_4/Si$, $RuO_2/Ru/SiO_2/Si$, and $RuO_2/Ru/Si_3N_4/Si$ electrodes were investigated. STM and AFM studies revealed that the roughness of BST films on RuO_2 was substrate dependent but that BST thin films on Ru and Pt exhibited no substrate dependence. A comparison of electrode surface morphologies before and after annealing revealed that the grains of Ru and RuO_2 electrodes became larger because of the coalescence effect and, thus, the rms roughness of the BST thin films varied according to the electrode and buffer layer. In particular, the surface morphology of an electrode and the variation of this morphology at high temperatures were significent factors causing for interfacial problems in BST thin films.

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