Effect of working pressure and annealing temperature on microstructure and surface chemical composition of barium strontium titanate films grown by pulsed laser deposition

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Abstract. Barium strontium titanate (BST, $\text{Ba}_{1-x}\text{Sr}_x\text{TiO}_3$) thin films have been extensively used in many dielectric devices such as dynamic random access memories (DRAMs). To optimize its characteristics, a microstructural control is essential. In this paper, $\text{Ba}_{0.6}\text{Sr}_{0.4}\text{TiO}_3$ thin film has been deposited on the SiO_2/Si substrate by the pulsed laser deposition (PLD) technique at three different oxygen working pressures of 100, 220 and 350 mTorr. Then the deposited thin films at 100 mTorr oxygen pressure were annealed for 50 min in oxygen ambient at three different temperatures: 650, 720 and 800°C. The effect of oxygen working pressure during laser ablation and thermal treatment on the films was investigated by using X-ray diffraction (XRD), atomic force microscopy (AFM) and scanning electron microscopy (SEM) analysis methods. X-ray photoelectron spectroscopy analysis was used to determine the surface chemical composition of the samples. The results indicate that the deposited BST film at low working pressure (100 mTorr) in PLD chamber shows a lower surface roughness than other working pressures (220 and 350 mTorr). The as-deposited films show an amorphous structure and would turn into polycrystalline structure at annealing temperature above 650°C. Increase of temperature would cause the formation of cubic and perovskite phases, improvement in crystalline peaks and also result in the decomposition of BST at high temperature (above 800°C). In addition, rising of temperature leads to the increase in size of grains and clusters. Therefore more roughness was found at higher temperatures as a result of a more heterogeneous growth and less tensions.

Keywords. Barium strontium titanate; thin film; pulsed laser deposition; ferroelectric.

1. Introduction

Perovskite barium strontium titanate (BST) thin films are promising candidates for dynamic random access memory (DRAM) owing to their excellent ferroelectric and dielectric properties. DRAM applications of BST thin films require the ferroelectric film to have high dielectric constant, high tunability and low dielectric loss. Also BST materials display a linear relationship between polarization and electric field, they have a low Curie temperature and lack problems related to fatigue and aging.^{1,2} $\text{Ba}_{1-x}\text{Sr}_x\text{TiO}_3$ has a perovskite structure ABX_3 , which exhibits complete solid solubility over all compositions, with a cubic structure at room temperature for $0.3 < x < 1$, becoming tetragonal for $0 < x < 0.3$.³ The tetragonal distortion of BST is associated with the paraelectric-to-ferroelectric transition. For DRAM applications, the cubic form of BST with high dielectric constant is preferred.² Several methods are used for the

fabrication of BST films. They include RF-sputtering,^{4,5} sol-gel,⁶ metal organic deposition⁷ and pulsed laser deposition (PLD).⁸ PLD technique has been used extensively as it can maintain the stoichiometry of the target in the deposited film and also has high coverage ability, which both are important in capacitors.⁹ By the PLD method a film with desirable properties could be obtained by controlling the deposition process such as working pressure, substrate temperature and post-annealing temperature. In this work, BST films have been deposited by the PLD method and the effect of working pressure (oxygen gas) and post-annealing temperature on microstructure and surface chemical composition of the BST films have been investigated.

2. Experimental

BST films were deposited using the PLD technique from $\text{Ba}_{0.6}\text{Sr}_{0.4}\text{TiO}_3$ target. The substrate was Si (100) and it was cleaned ultrasonically in ethanol. In the PLD system, a high vacuum chamber with a base pressure of 1×10^{-5} Torr has been used. BST target was made by $\text{Ba}_{0.6}\text{Sr}_{0.4}\text{TiO}_3$ powder

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and shaped into cylindrical sample with diameter of 14 mm and thickness of 10 mm. The temperature of silicon substrates was kept at 300°C. The deposited films at this temperature are amorphous. The PLD process was carried out at three oxygen working pressures (purity 99.999%) 100, 220 and 350 mTorr. It was used 9000 pulses of an eximer laser ($\lambda = 248$ nm, laser energy 300 mJ pulse⁻¹ and R.R. = 10 Hz). To obtain a crystalline structure, the as-deposited films were annealed in oxygen ambient at 650, 720 and 800°C for 50 min.

The effect of working pressure and thermal treatment on surface morphology of the films was investigated by atomic force microscopy (AFM) (Veeco CP-research model) and scanning electron microscopy (SEM) (TESCAN VEGA model). The crystal structure was characterized by X-ray diffraction (XRD). This analysis was carried out by a Philips Xpert instrument operating with Cu K α radiation ($\lambda = 1.54$ Å) at 40 kV/40 Ma. X-ray photoelectron spectroscopy (XPS) was employed to characterize the surface chemical composition of the films. For the XPS experiment, an Al anode X-ray source was employed with a concentric hemispherical analyzer (Specs Company, model EA10 plus) to analyse the energy of the emitted photoelectron from the surface. The chamber pressure during the XPS experiment was 7.5×10^{-10} Torr. The energy scale was calibrated by adjusting the carbon peak C(1s) at 284.8 eV. All the peaks were deconvoluted using an SDP software (version 4.1).

3. Results and discussion

3.1 Effect of working pressure

XRD analysis was used to investigate the effect of oxygen pressure deposition ambience on crystalline structure of the BST films. XRD data of the as-deposited films revealed an amorphous structure (not shown here). To obtain a crystalline film, the as-deposited films have been annealed at 720°C at three different working pressures. Figure 1 shows XRD

Figure 1. XRD patterns of BST thin films deposited at three different oxygen pressures.

patterns of deposited films at 100, 220 and 350 mTorr oxygen pressure. This figure indicates that all films show a polycrystalline structure and that a cubic perovskite phase has been obtained in all three samples. The strongest peak in all samples is related to (110) that is the prominent diffraction peak in the perovskite structure.¹⁰ From the XRD results, it has also been found that the crystallinity of BST films increases by decreasing the working pressure. In addition, at 350 mTorr O₂ deposition ambience, the (100) peak can hardly be observed. The reason is that the (100) are the slowest growing planes in the perovskite structure, because the (100) are closely packed oxygen planes; then these surfaces have the lowest surface energy.¹¹ Hence at lower oxygen pressure, the particles that ablated from the target usually have more energy for rearrangement on the substrate surface. In other words, as the oxygen pressure is enhanced, the collisions between ablated particles within plume and oxygen gas also increase, thus the kinetic energy of particles becomes low resulting in a higher intensity of (100) planes for deposited BST films at 100 mTorr oxygen pressure.¹²

Figure 2a shows the SEM image of as-deposited BST film at 100 mTorr oxygen working pressure. As mentioned this micrograph indicates that the as-deposited film has an amorphous structure. To obtain a crystalline film the as-deposited films have been annealed at 720°C at different working pressure (100, 220 and 350 mTorr; figure 2b–d). These figures indicate that post-annealing temperature leads to the formation of a polycrystalline structure. It has been observed that the films deposited at a lower working pressure (100 mTorr) have a smooth surface. High working pressure leads

Figure 2. SEM images of deposited films at (a) 100 mTorr without post-annealing and deposited film at (b) 100 mTorr, (c) 220 mTorr and (d) 350 mTorr after post-annealing at 720°C.

Figure 3. Two- and three-dimensional AFM images of BST thin films deposited at three different oxygen pressures.

Table 1. RMS value of BST thin films at three different oxygen pressures.

Oxygen pressure (mTorr)	RMS (nm)
100	3.640
220	6.345
350	8.915

to formation of clusters within the gas phase. Such clusters may condense on the film surface, which is not desirable for most applications. This reduces the film quality, damages the microstructure and enhances the surface roughness of the BST films.

Figure 3 shows the two- and three-dimensional AFM images of the BST thin films prepared at different oxygen pressures. As it can be observed, the films have a nanograin size structure, and the root-mean-square (rms) value of surface roughness of BST thin films at three different oxygen pressures are shown in table 1. Less roughness is more appropriate for capacitors because this leads to a better contact between the thin film and electrodes. According to table 1, an increase in roughness with the increase in oxygen pressure could be related to the relaxation of intrinsic stress developed during film deposition. Another reason is that the high working pressure leads to the formation of clusters within the gas phase. In addition, interactions between ablated particles from target and oxygen gas results in kinetic energy loss of particles and reduction in their rearrangement on the substrate. Therefore the ablated particles tend to locate in the vicinity of other particles, and finally lead to increasing the surface roughness.⁴

According to the above results, the deposited film at 100 mTorr oxygen pressure shows a low surface roughness. It is expected that such films which have been formed at mentioned conditions are likely better than the two other

Figure 4. XRD patterns of BST thin films post-annealed at three different temperatures.

types for capacitor applications. Therefore, for investigating the best annealing temperature, the films deposited at 100 mTorr oxygen pressure have been annealed at three different temperatures: 650, 720 and 800°C.

3.2 Effect of annealing temperature

Figure 4 shows XRD patterns of annealed films at 650, 720 and 800°C. As it can be seen in figure 4, the crystal orientation and crystallinity of the films strongly depends on the annealing temperature, such that as the annealing temperature rises, a better crystalline film is formed. We observed that a cubic perovskite structure of that polycrystalline BST films was typically obtained under all three temperatures. At 650°C, the strongest peak is related to (110) XRD peaks. Large lattice mismatch between BST thin films and substrate results in less intensity of (100) XRD peaks.^{13–15} As the post-annealed temperature increases from 650 to 720°C and 800°C, both samples display an improvement in (100)

Figure 5. XPS spectra of Ba3d at (a) 650°C, (b) 720°C and (c) 800°C.

Figure 6. XPS spectra of Sr3d at (a) 650°C, (b) 720°C and (c) 800°C.

and (110) orientations. With enhancement of the annealing temperature, as it was expected, the amount of crystalline phase (perovskite phase) rises up, but despite the fact that at 800°C more crystallinity is observed, the appearance of two new peaks on the XRD pattern (shown by arrow) which are related to the BaTiO₃ means the BST thin films are unstable at above 800°C.

To determine the surface chemical composition of the annealed films at three different temperatures, XPS analysis was used. Figure 5a shows high-resolution XPS spectra of Ba3d peak of the BST thin film post-annealed at 650°C. A fit to the measured data was performed and three separate peaks centred at 779.77, 781.35 and 778.70 eV for Ba3d_{5/2} and two separate peaks centred at 794.63 and 796.33 eV for Ba3d_{3/2} were observed. The peaks at 794.63 and 779.77 eV, named Ba₁, correspond to the Ba atoms in perovskite structure BST, while the peaks at 796.33 and 781.35 eV, named Ba₂, correspond to the Ba atoms in non-perovskite structure BST, which is also called decomposed perovskite structure BST.¹⁶ The additional peak at lower binding energy of 778.61 eV (named Ba₃) could be caused by weaker Ba–O bonds related to oxygen deficiency.^{11,17–19} This strong Ba₃ peak confirms the existence of oxygen deficiency in the film. It has been reported that oxygen vacancies on BST films have a negative effect that causes a high leakage current of Pt/BST/Pt capacitors.²⁰ Figure 5b and c shows the Ba3d XPS peaks for BST thin film, post-annealed at 720 and 800°C, respectively. These figures show that after annealing at temperatures above 650°C Ba₃ peaks disappear. This can

be related to the reduction of oxygen vacancies due to the following reaction:

On the other hand, at 800°C the peak intensity of Ba₁ (perovskite structure) has decreased extremely compared to the Ba₂ peak (non-perovskite structure) which can be attributed to the formation of barium carbonate. These results confirm that Ba in BST thin films are unstable at temperatures above 800°C, which is in agreement with the aforementioned XRD data.

Figure 6a shows high-resolution XPS spectra of Sr3d peaks for post-annealed BST films at 650°C. The binding energy of Sr3d_{5/2} peaks is centred at 133.13 and 132.30 eV; combining these peaks with the peaks of Sr3d_{3/2} (at 135.46 and 134.22 eV) results a broad peak of the SrO spectrum. As shown in figure 7a, the Sr3d peaks can be fitted with four peaks. The peaks at 134.22 and 132.30 eV are known as Sr₁ and correspond to Sr atoms in perovskite structure BST, while the peaks at 135.46 and 133.13 eV are known as Sr₂ and correspond to Sr atoms in non-perovskite structure BST and can also be related to Sr3d peak in SrCO₃.^{17–21} Figure 6b and c shows the Sr3d XPS peaks for post-annealed BST thin films at 720 and 800°C, respectively. These figures show that after annealing at temperatures above 650°C, Sr₂ peaks (non-perovskite structure of Sr) disappear.

Figure 7a shows high-resolution spectra of O1s XPS peak. The O1s peak is deconvoluted into three components. The

Figure 7. XPS spectra of O1s at (a) 650°C, (b) 720°C and (c) 800°C.

Figure 8. SEM images for BST thin films post-annealed at (a) 650°C, (b) 720°C, (c) 800°C and (d) cross-section image of b.

main peak at 530.03 eV (O_L) ascribes to oxygen atoms in perovskite structure BST. Two other peaks can be observed at 531.39 and 532.76 eV. The chemisorption oxygen (O_C) is presented in the range of ~ 532.5 – 530.5 eV and corresponds to oxygen atoms in Ti_2O_3 . In addition, the observed peak at 532.76 eV (O_H) is related to oxygen in OH-groups, free oxygen or a contamination. The two latter oxygen species can be possibly related to oxygen deficiency.^{17,22} Figure 7b and c shows the O1s XPS peaks for post-annealed BST thin films at 720 and 800°C, respectively. These data show that after annealing at temperature above 650°C, the O_C peak also disappears. This shows a reduction in oxygen vacancies which are mostly responsible for a high leakage current.²¹

Figure 8 shows SEM images of annealed BST films at different annealing temperatures. According to these images, it can be observed that the average grain size of the polycrystalline films increases with the increase in temperature and due to the sintering, coalescence of small grains to form larger grains is expected. The average grain size for annealed BST thin films have been shown in table 2. Increasing the size of grains means a reduction in the number

Table 2. Average grain size and RMS value of BST thin films post-annealed at three different temperatures.

Annealing temperature (°C)	Average grain size (nm)	RMS (nm)
650	43.90	3.500
720	57.52	3.640
800	64.81	4.661

of grain boundaries which has a negative effect on dielectric leakage.¹² In figure 8d the cross-section SEM image of deposited film at 100 mTorr is shown, the film thickness is ~ 500 nm and the sample has a columnar structure that has already been observed for the deposited films by the PLD method.²³ It is expected that this type of structure is the reason for the enhancement of the films' dielectric constant.²⁴

The rms surface roughness of BST thin films annealed at three different temperatures derived from AFM data (not shown here) is shown in table 2. The surface roughness of the polycrystalline BST film increases slightly when the annealing temperature is changed from 650 to 720°C, whereas there is a sharp increase of surface roughness for annealed films at 800°C. This sharp increase of roughness could be attributed to non-uniform growth of grains; also above this temperature, abnormal growth is observed. When BST thin films are exposed to an electric field, it is usually considered that higher electric field density exists at the summit of sharp valleys than the smoother surface. Therefore it is expected that the abnormal growth can have a negative effect and lead to the increase in the current leakage.

4. Conclusion

In this study, BST films were deposited by the PLD technique. The results showed that oxygen working pressure and post-annealing temperature play crucial roles in the crystalline phase and microstructure of the films. The as-deposited films have an amorphous structure. XRD results of deposited films at three different working pressures after post-annealing at 720°C indicate that the crystallinity of

films increases by decreasing the working pressure (from 100 to 350 mTorr) during laser ablation. It has also been confirmed that by increasing the annealing temperature from 650 to 800°C the intensity of crystalline peaks increase, but these films become unstable at/above 800°C. AFM and SEM pictures indicate that the surface of deposited films at lower working pressure (100 mTorr) is smoother than that others, whereas a raise in oxygen pressure leads to the formation of clusters on the film's surface. It was also observed that the average grain size and the surface roughness of the polycrystalline BST film decreases slightly with decrease in post-annealing temperatures from 800 to 650°C. XPS results confirm that Ba in BST thin films is unstable at temperatures above 800°C. On the other hand, by increasing the annealing temperature, oxygen deficiencies can be decreased which are mostly responsible for a high leakage current. In addition, because of the high crystallinity, nanograin size structure and less surface roughness of the deposited films at 100 mTorr working pressure and post-annealing temperature at 720°C, it is expected that these thin films to be better than those two other types of films for capacitor applications.

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