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Ferroelectric $Ba_{1-x}Sr_xTiO_3$ Thin Films for DRAM's Applications

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Ferroelectric $Ba_{1-x}Sr_xTiO_3$ thin films were deposited by pulsed laser ablation on SiO_2/Si, RuO_2/Ta/SiO_2/Si and Pt/Ti/SiO_2/Si substrates. The films were weakly crystalline in the as-deposited condition and subsequent crystallization was induced by annealing the films in the range of 550-650ºC. The BST films deposited on Pt/Ti/SiO_2/c-Si substrates presented wide cracks that were promoted during the annealing process due to the thermal expansion mismatch between the BST films ($\alpha_{BST} = 4 \times 10^{-6}$ ºC^{-1}) and the Pt ($\alpha_{Pt} = 9 \times 10^{-6}$ ºC^{-1}). Smooth films showing slightly crackeded areas were obtained on SiO_2/c-Si and RuO_2/Ta/SiO_2/Si substrates. The ruthenium oxide thermal expansion coefficient is $\alpha_{RuO2} = 5.2 \times 10^{-6}$ ºC^{-1}. A cross-sectional analysis at the ferroelectric/substrate interface showed that for the lower annealing temperature (550ºC) a mixed amorphous/nanocrystalline microstructure is formed. For temperatures above 600ºC a randomly oriented polycrystalline material is obtained. However, an amorphous layer of 4-6 nm still remains on the substrate even after heat-treatments up to 650ºC. The dielectric constant of the BST films varied in the range of 30-325.

Keywords: pulsed laser ablation; ferroelectric films

1. Introduction

Ferroelectric oxide thin films with perovskite structure are currently of great technological interest due to their excellent properties for applications in dynamic random access memories (DRAM's)[1]. Barium strontium titanate (BST) has a simple cubic perovskite structure with a lattice parameter of a=0.39471 nm, space group Pm3m and possesses a high dielectric constant in the paraelectric state.

One of the main technological challenges is to find a suitable electrode material that could offer low electrical resistivity, good thermal stability, high resistance to oxidation and good adhesion both to the substrate and the ferroelectric film. Ruthenium oxide (RuO_2) is one of the most promising materials with only 35 -cm resistivity, thermodynamic stability up to 800ºC and chemically resistant to common acids and bases[2].

BST thin films have been deposited by radio-frequency (RF) sputtering[3,4], metallorganicchemical vapor deposition (MOCVD) [5,6], ion beam sputtering [7] and pulsed laser ablation [1,8,9]. PLD is known to be an excellent technique to produce thin films on various substrates with preserving the stoichiometry of multicomponent targets[10]. In the present study ferroelectric properties were measured on $Ba_{0.5}Sr_{0.5}TiO_3$ thin films grown by PLD and the crystallinity, morphology and microstructure were analyzed and compared with the target (bulk) properties

2. Experimental Procedure

Stoichiometric barium strontium titanate ($Ba_{0.5}Sr_{0.5}TiO_3$) targets were fabricated by combustion synthesized powders. The target for laser ablation experiments was made by isostatically pressing the ceramic powders and sintering in air at 1200ºC for 2 hr. BST films were grown by PLD on 400ºC SiO_2/Si, RuO_2/Ta/SiO_2/Si and Pt/Ti/SiO_2/Si substrates with a KrF laser (λ=248 nm) at a fluence energy of 2.0 J/cm^2.and 30 ns duration pulses. The separation between the rastered target and the rotated substrate was maintained fixed at 50 mm.

The BST/SiO_2/Si, BST/RuO_2/Ta/SiO_2/Si and BST/Pt/Ti/SiO_2/Si samples were cut into small pieces (2.0 x 2.0 cm^2) and post-annealed in air for 2 hr. in the temperature range of 550-650ºC.

The crystallinity of the films was determined by X-ray diffractometry (XRD) excited with Cu K$\propto$ radiation (λ=1.541 nm) and the surface morphology was examined by scanning electron microscopy (SEM).

High resolution transmission electron microscopy (HRTEM) was performed on cross-sectioned specimens in order to study the microstructure and thickness of the films. For capacitance measurements, platinum electrodes (0.1 mm in diameter) were deposited on top of the BST/substrate films by DC sputtering through a metallic mask. The dielectric constant was calculated from the capacitance measured at 10 kHz with a LCR meter by using the following equation:

$$= Cd/\;_{0}A \qquad (1)$$

Where C is the capacitance (farads),ε_o the free space dielectric constant value (8.85 X 10^{-12} F m), A the capacitor area (m^2) and d. (m) the thickness of the ferroelectric film.

3. Results

Figures 1(a)-1(c) show the XRD patterns for the films grown on SiO_2/Si substrates and subsequently annealed at 550ºC, 575ºC and 600ºC. The films were amorphous in the as-deposited condition and full re-crystallization was obtained at 550ºC.

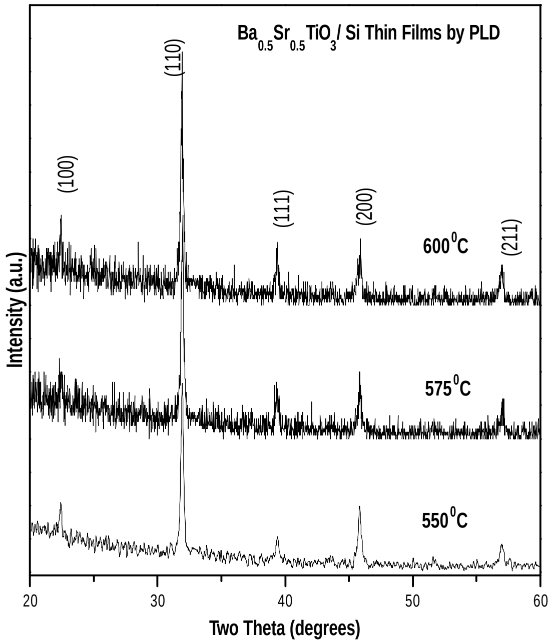

Figure 1. XRD patterns of BST/SiO_2/Si films post-annealed in the range 550-600ºC for 2 hr

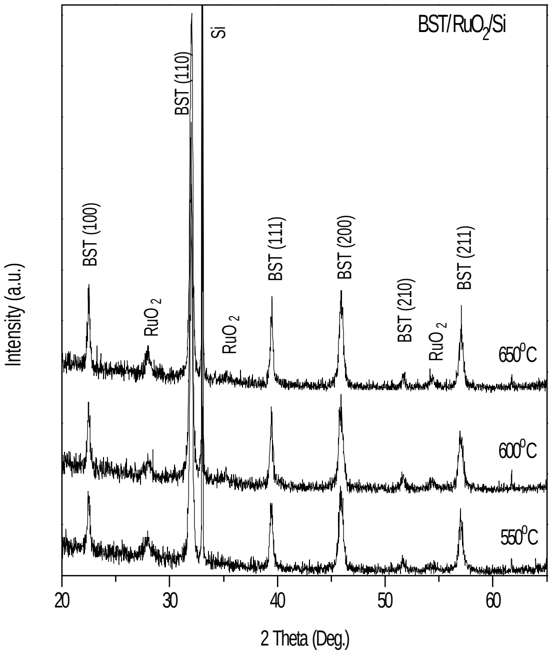

Fig. 2. XRD patterns of BST/ RuO_2/Ta/SiO_2/Si post-annealed at different temperatures in air for 2 hr.

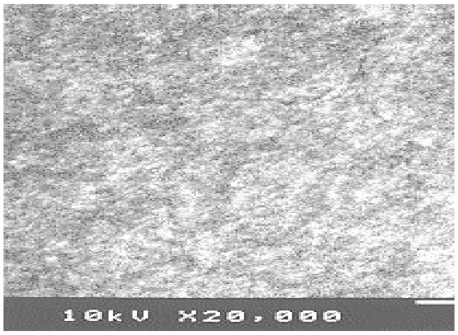

Fig. 3. SEM micrograph of BST/SiO_2/Si annealed at 600ºC in air for 2 hr.

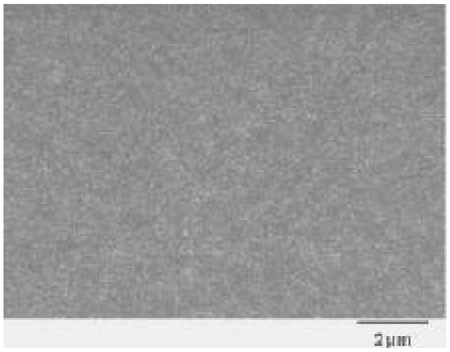

Figure 4. SEM micrograph of BST/RuO_2/Ta/SiO_2/Si annealed at 600ºC in air for 2 hr.

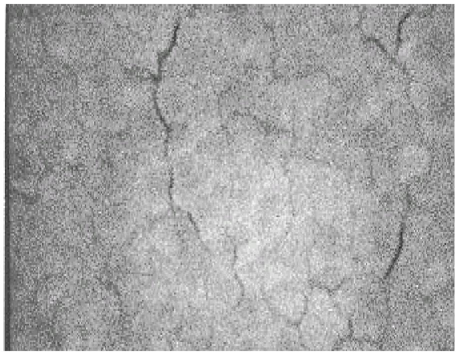

Fig. 5. SEM micrograph of BST/Pt/Ti/SiO_2/Si annealed at 600ºC in air for 2 hr.

Figures 2(a)-2(c) correspond to BST films grown on RuO_2/Ta/SiO_2/Si substrates and post-annealed in air for 2 hr .in the range 550-650ºC. The XRD patterns of the films match exactly with those obtained from the ablation target.

In this narrow temperature range (550-650ºC) the films crystallized with a random orientation on both substrates. Similar results were obtained for BST films deposited on the Pt coated substrates.

Figures 3 and 4 show SEM micrographs for films grown on SiO_2/Si RuO_2/Ta/SiO_2/Si substrates, respectively. Smooth and uniform surfaces for both BST films that were post-annealed at 600ºC in air for 2 hr can be observed. However for films grown on Pt/Ti/SiO_2/Si the surface area is cracked after the heat treatment, as can be seen in Figure 5.

The thermal expansion coefficients for SiO_2, RuO_2 and Pt are $\propto_{SiO2}$= 3.5 x 10^{-6} ºC^{-1}, $\propto_{RuO2}$= 5.2 x 10^{-6} ºC^{-1}. and $\propto_{Pt}$= 9 x 10^{-6} ºC^{-1}, respectively. Assuming a thermal expansion coefficient value for BST to be similar to that reported for $BaTiO_3$ thin films[11] ($\propto_{BaTiO3}$ = 4 x 10^{-6} ºC^{-1}) it is reasonably to expect larger cracks on the Pt coated substrates due to a larger thermal expansion mismatch.

The as-deposited amorphous films crystallized with grain sizes between 50-200 nm after the post-annealing treatment. A cross-sectional HRTEM analysis at the

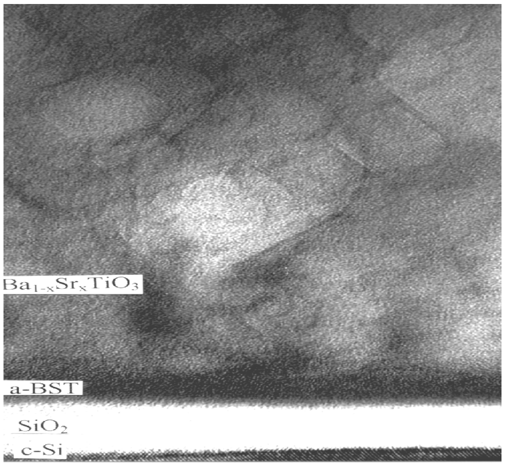

Fig. 6.Cross-sectional image taken from the BST/SiO_2/Si film post-annealed in air at 550ºC for 2 hr.

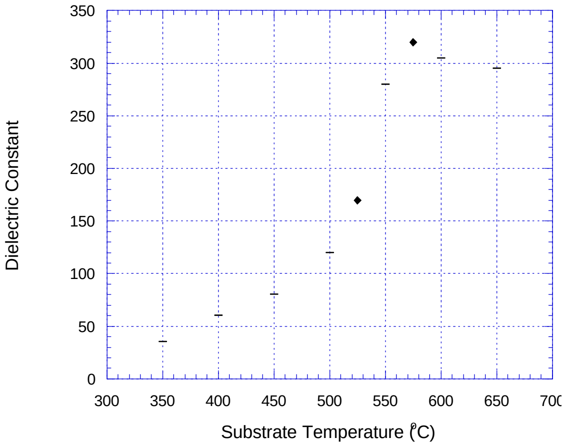

Fig. 7. Dielectric constant *versus* post-anneling temperature of BST/RuO_2/Ta/SiO_2/Si films.

film/substrate interface revealed that for samples annealed at 550ºC a mixed amorphous/nanocrystalline phase is formed as can be seen in Figure 6. The film thickness is 200 nm. For temperatures above 600ºC an amorphous layer of 4-6 nm is always observed at the BST/substrate interface.

The dependence of dielectric constant *versus* post-annealing temperature of BST films deposited on RuO_2/Ta/SiO_2/Si is shown in Figure 7. A maximum value of =325 can be obtained for films annealed at 575ºC. Similar values were obtained for films deposited on Pt.

4. Conclusions

Ferroelectric $Ba_{0.5}Sr_{0.5}TiO_3$ (BST) thin films were obtained by pulsed laser deposition. The BST films were amorphous in the as-deposited condition and crystallized randomly under low temperature annealing (full crystallization from 550ºC). The X-ray diffraction patterns of the films matched exactly with those obtained from the ablation target indicating the excellent stoichiometric preservation is attained by the pulsed laser deposition. Smooth and uniform films with minimal cracking were obtained on SiO_2/Si, BST/RuO_2/Ta/SiO_2/Si substrates, while films deposited on Pt/Ti/SiO_2/Si substrates presented pronounced cracks that were promoted during the annealing process due to the thermal expansion mismatch between the film and the Pt substrates.

The as-deposited films re-crystallized on an amorphous BST layer (4-6nm) after post-annealing treatments in the temperature range of 550-650ºC. A maximum dielectric constant =325 was obtained for BST samples post-annealed in air at 575ºC for 2 hr.

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References

[1] H.F. Cheng, *J. Appl. Phys.*, **79,** 7965 (1996).
[2] J. Vetrone, C.M. Foster, G-R. Bai, A. Wang, J. Patel and X. Wu, *J. Mater. Res.*, **13,** 2281 (1998).
[3] Y. Fukuda, H. Haneda, I. Sakaguchi, K. Numata, K. Aoki and A. Nishimura, *Jpn. J. Appl. Phys.*, **36,** L1514 (1997).
[4] K. Abe, S. Komatsu, N. Yanase, K. Sano and T. Kawakubo, *Jpn. J. Appl. Phys.*, **36,** 4125 (1997).
[5] T. Kawahara, M. Yamamuka and K. Ono, *Jpn. J. Appl. Phys.*, **34,** 5077 (1995).
[6] R. Tsu, H.Y. Liu, W.Y. Hsu, S. Summerfelt, K. Aoki and B. Gnade, Mater. Res. Soc. Symp. Proc., Vol. 361, (1995) 275.
[7] S. Yamamichi, H. Yabuta, T. Sakuma and Y. Miyasaka, *Appl. Phys. Lett.*, **64,** 1644 (1994).
[8] T. Nakamura, Y. Yamanaka, A. Morimoto and T. Shimizu, *Jpn. J. Appl. Phys.*, **34,** 5150 (1995).
[9.] Q.X. Jia, D.S. Zhou, X.D. Wu, S.R. Foltyn, P. Tiwari and T.E. Mitchell, *Integrated Ferroelectrics*, **10,** 73 (1995).
[10] D. Roy and S.B. Krupanidhi, *Appl. Phys. Lett.*, **62,** 1056 (1995).
[11] S. B. Desu, Mater. Res. Soc. Symp. Proc., Vol. 200, (1990), p. 199.