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Influence of substrate temperature on morphological and ferroelectric properties of $Ba_{0.75}Sr_{0.25}TiO_3$ thin films deposited on nichrome substrates by Rf sputtering

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Abstract

$Ba_{0.75}Sr_{0.25}TiO_3$ (BST) thin films have been deposited by Rf-sputtering on nichrome substrates that have been heated in the range from 400 °C to 747 °C. The films were characterized morphologically and ferroelectrically. The microstructure of thin films was observed using an atomic force microscope to determine rugosity and grain size. The growth of grain size observed was 75 nm and 95 nm at substrate temperatures from 549 °C to 747 °C, respectively. The ferroelectric properties were determined by hysteresis loops applying an electric field of 110 kV/cm. The films grown at substrate temperatures from 549 °C to 747 °C show a decrease of the remnant polarization P_r, from 9.87 $\mu C/cm^2$ to 2.23 $\mu C/cm^2$, and of the coercive field strength E_c, from 59.75 kV/cm to 19.86 kV/cm. The films deposited on nichrome had uniform grain size distribution and relatively low surface roughness.

Keywords: B. Grain size; C. Ferroelectric properties; D. $BaTiO_3$ and titanates; Rf-sputtering process

1. Introduction

Barium strontium titanate (BST) thin films have created special interest due to their great potential in applications such as non-volatile ferroelectric random access memories (NVFRAM) and dynamic random access memories (DRAM) [1–5]. The most studied ferroelectric materials with perovskite-like structures are lead zirconate titanate (LZT), lead titanate (LT) and barium titanate (BT). However, these materials exhibit serious degradation, fatigue and polarization retention limitations. The first $Ba_xSr_{1-x}TiO_3$ films were studied by Francombe [6], in a composition range of $0.15<x<0.475$. A tetragonal cubic structure was found at 560 °C. Rupprecht et al. [7] described the dielectric constant variation as a function of Curie temperature (T_C) in the paraelectric state ($T<T_C$) of BST ($x=0.5$). Kuroiwa et al. [4] reported the dependence of dielectric constant on substrate temperature (520–750 °C) and grain size for $Ba_{0.75}Sr_{0.25}TiO_3$ deposited by magnetron sputtering. Li et al. [8] studied BST ($x=0.65$) films that were deposited using Rf-sputtering on silicon substrate at temperatures of 27–747 °C. The films were ex situ heat treated at 705 °C having the (110) + (200) preferential orientation. Nasser and Payne [9] deposited BST ($x=0.75$) by sol–gel and applied ex situ heat treatments from 500 to 675 °C. The dielectric constants reported with and without heat treatment were nearly comparable. Horikawa et al. [10] studied the dependence of dielectric constant on grain size of $Ba_{0.65}Sr_{0.35}TiO_3$ films prepared by Rf-sputtering at substrate temperatures of 500–700 °C. The films that exhibited grain sizes of 45 nm showed a dielectric constant of 190, while that of 220 nm showed a dielectric constant as large as 700. Cole et al. [11] prepared $Ba_{0.6}Sr_{0.4}TiO_3$ films deposited on MgO and Pt–Si substrates by metalorganic solution deposition technique using carboxylate–alkoxide precursors and ex situ annealing at 900 °C (film/MgO substrate) and 750 °C (film/Pt–Si substrate). Cole et al. [11] found that grain growth of doped and undoped films is proportional to an increase of annealing temperature.

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In this work, thin films of $Ba_{0.75}Sr_{0.25}TiO_3$ were grown by heating in situ the substrates of nichrome at temperatures that varied from 400 to 750 °C, using a furnace incorporated to the sputtering chamber [12]. A rotatory substrate holder was also used to promote a more uniform and homogeneous film thickness. The characterization of the superficial morphology was done using an atomic force microscope to measure mean grain size. Ferroelectric properties such as dielectric constant, remnant polarization, and coercive field, were measured with respect to substrate temperature.

2. Experimental details

$Ba_{0.75}Sr_{0.25}TiO_3$ thin films were prepared by Rf co-sputtering technique using 2 in diameter magnetrons. $SrTiO_3$ (STO) and $BaTiO_3$ (BTO) targets were used, both 99.95% pure. Samples were prepared by fixing the Rf-power targets to 30 W and 90 W for STO and BTO, respectively. Substrate used was nichrome which has the advantages of diminishing micro-cracks and holes in the film surface [13,14]. Distance between the targets and the substrate was 0.085 m. A rotatory substrate holder was used at 100 min^{-1}. Deposition time was variable in order to keep constant the film thickness (240 nm). Thicknesses were measured using a Dektak^{3}ST Profilometer by Veeco Instruments. Prior to film deposition, the substrates were thoroughly cleaned by ultrasonic waves with neutral soap, deionized water, hexane, acetone, and isopropanol for 10 min each. Finally, the substrates were rinsed with deionized water and dried with nitrogen gas. The sputtering chamber was evacuated to a pressure of 0.53 Pa. The vacuum was 8×10^{-5} Pa. An Ar/O_2 (90/10) gas mixture of 6.67×10^{-4} Pa was injected into the chamber to remove any residual gases for 15 min, after that, the vacuum pressure was recovered. Impurities and residuals were removed by flushing argon at 6.67 Pa for 12 min. Working pressure of the chamber was kept at 4×10^{-3} Pa. Off-axis geometry was used with an angle of 30° between the target and the substrate holder to reduce the re-sputtering caused by negative ions from the plasma. The substrate holder was heated in the range of 400–750 °C every 50 °C.

The superficial morphology of the BST thin films was examined by using a contact-mode atomic force microscopy (AFM) Jeol JSPM-5200. Applying tapping contact and a scan area of 1 μm × 1 μm, the grain size distribution and the roughness root-mean-square (R.M.S.) were determined. The ferroelectric properties of the BST thin films were determined using a Sawyer-Tower circuit-mode EDU Radiant Technology Ferroelectric Device. The bias voltage V_b, electric field E, and frequency were 3 V, 100 kV/cm and 1 kHz, respectively. The dielectric constant ε of the thin films was calculated using Eq. (1) [15]

$$\varepsilon = \frac{Ct}{\varepsilon_0 A} \quad (1)$$

where C, t, ε_0 and A are the capacitance, film thickness ($= V_b/E$), permittivity of vacuum (8.854×10^{-12} F/m) and tip electrode area, respectively.

3. Results and discussion

Fig. 1 shows the two-dimensional atomic force micrographies for samples deposited at substrate temperatures of 600 °C (see Fig. 1(a)) and 700 °C (see Fig. 1(b)). Fig. 2 illustrates the particle diameter distribution of samples showed in Fig. 1. Mean grain sizes of samples in Fig. 1(a) and (b) were approximately 62 nm (see Fig. 2(a)), and 91 nm (see Fig. 2(b)), respectively. It is clear that the films surfaces were deposited without microcracks or holes.

As seen in Fig. 3, mean grain size of the BST films ranged from 64 nm to 95 nm, and grain size increased as the substrate temperature increased. These results exhibited the tendency showed by Kuroiwa et al. [4] (temperature range of 480–750 °C) and Cole et al. [11] (temperature range of 650–800 °C). The increase in grain size at higher substrate temperatures could be attributed to higher mobility of the deposited atoms.

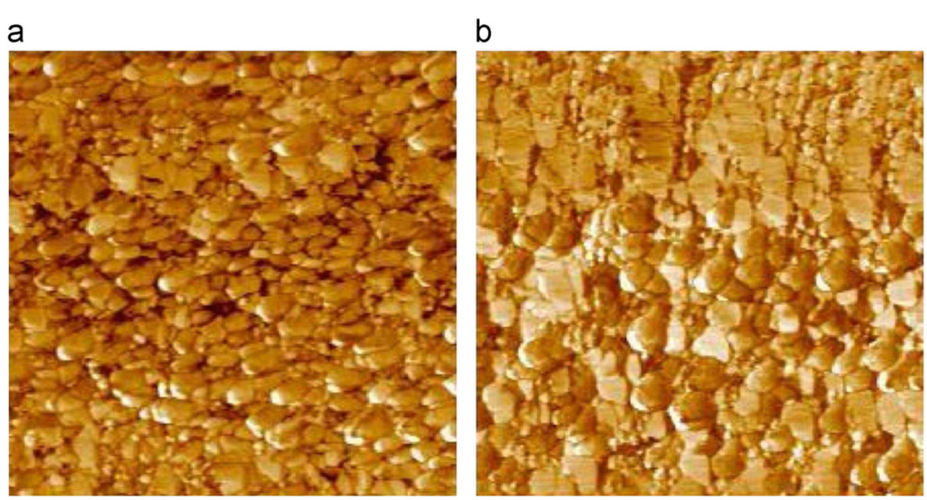

Fig. 1. 2-D atomic force micrograph of $Ba_{0.75}Sr_{0.25}TiO_3$ films deposited at substrate temperatures of (a) 600 °C and (b) 700 °C.

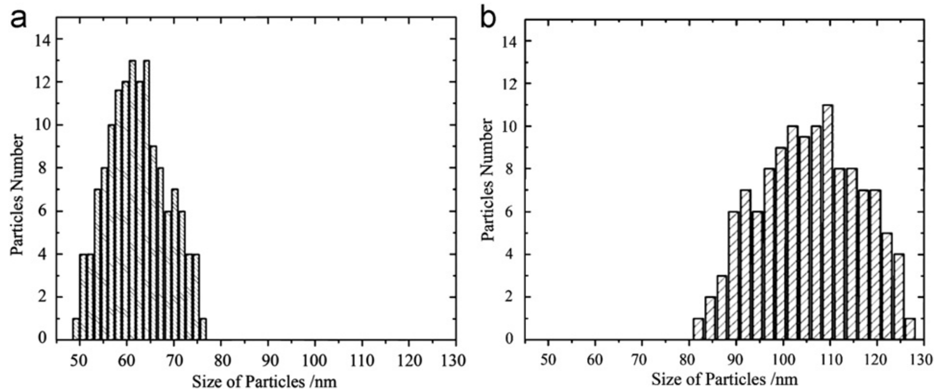

Fig. 2. Histograms of the particle diameter distribution of $Ba_{0.75}Sr_{0.25}TiO_3$ films deposited at substrate temperatures of (a) 600 °C and (b) 700 °C.

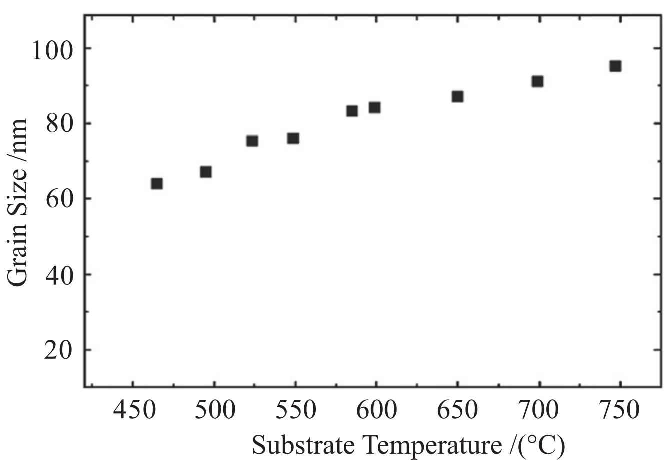

Fig. 3. Variation of the mean grain size for a $Ba_{0.75}Sr_{0.25}TiO_3$ thin film as a function of the substrate temperature.

Fig. 4(a) and (b) shows three-dimensional atomic force images of thin films surfaces obtained from film samples deposited at substrate temperatures from 600 °C and 700 °C. The scan area was 5 μm × 5 μm. The root-mean-square surface roughness were 4.8 nm and 6.1 nm from 600 °C and 700 °C, respectively. As seen in Fig. 5, a correlation between roughness and substrate temperature was observed. This correlation is similar to those previously reported [16,17]. It is well known that the roughness parameter is one of the most important factors that influence the dielectric properties because it not only depends on a well-defined microstructure but also on electrode and film interactions [18,19].

The ferroelectric properties of the BST (x=0.75) deposited at different substrate temperatures were determined using hysteresis curves. Fig. 6 shows the P–E plots for specimens deposited at 400, 435, 465, 495 and 525 °C. Ferroelectric behavior was not observed at substrates temperatures below 435 °C. This is due to amorphous regions in films. Fig. 7 shows that the ferroelectric behavior began at substrate temperatures above 465 °C. The maximum polarization was obtained when the substrate temperature was 600 °C. At higher substrate temperatures, polarization gradually decreased. This ferroelectric behavior suggests that for polarization there was an optimal substrate temperature of

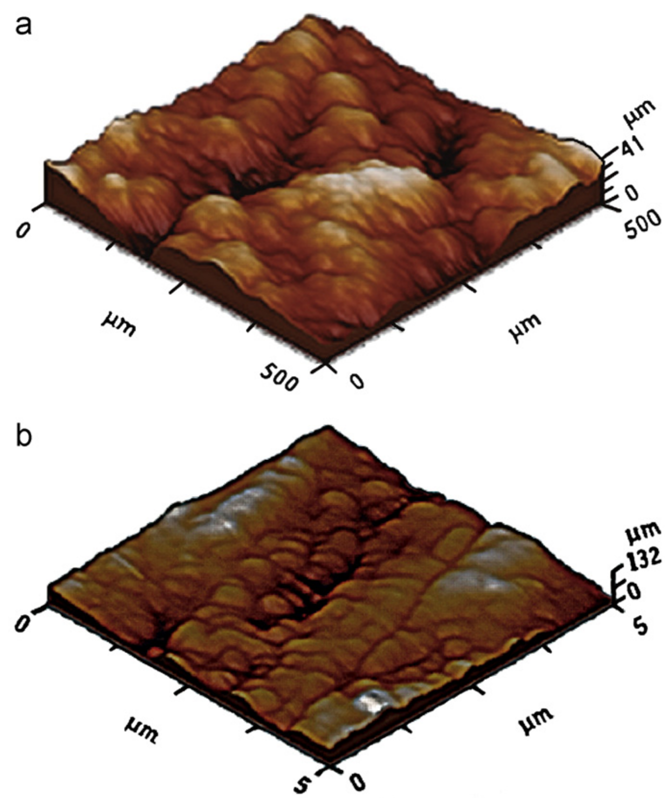

Fig. 4. 3-D atomic force micrograph of a $Ba_{0.75}Sr_{0.25}TiO_3$ thin film at substrate temperatures of (a) 600 °C and (b) 700 °C.

549 °C because amorphous material was found at lower temperatures, and at higher temperatures than 750 °C the material starts to degrade.

The ferroelectric properties of the BST thin films strongly affect the dielectric constant and the dielectric loose [20]. Fig. 8 shows the substrate temperature dependence of the dielectric constant ε_r. The values of dielectric constant of the BST thin films ranged from 436 to 671. Fig. 9 shows a correlation between dielectric constant and mean grain size, in accordance with the dielectric constant evolution reported in the literature [4,10]. The results indicate that the dielectric constant increases with temperature. We found that a maximum dielectric constant was obtained when the substrate

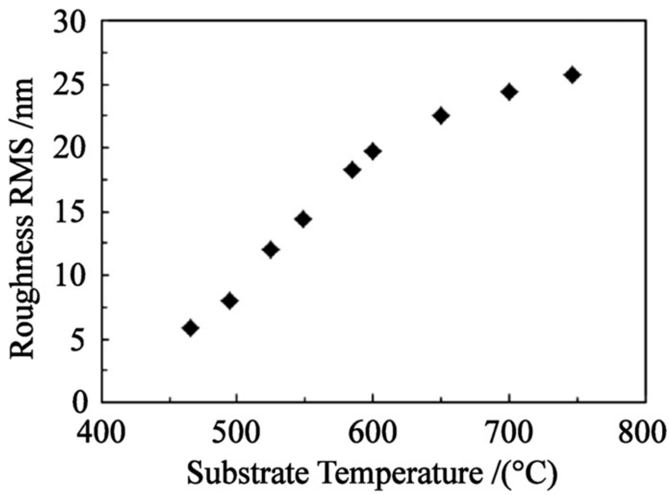

Fig. 5. Variation of the surface rugosities of a $Ba_{0.75}Sr_{0.25}TiO_3$ thin film as a function of the substrate temperature.

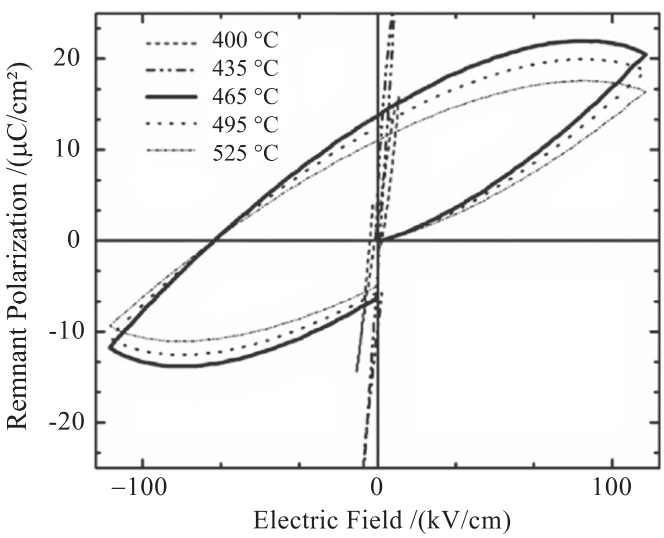

Fig. 6. Variation of the P–E hysteresis loops for $Ba_{0.75}Sr_{0.25}TiO_3$ thin film as a function of the substrate temperature from 400 to 525 °C.

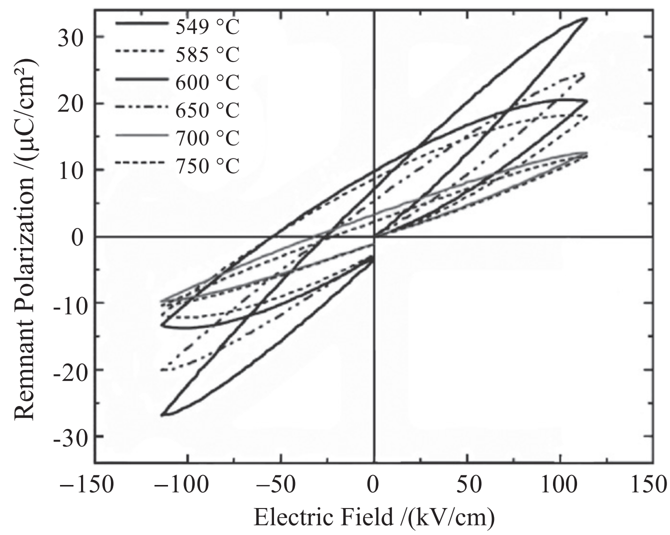

Fig. 7. Variation of the P–E hysteresis loops for $Ba_{0.75}Sr_{0.25}TiO_3$ thin films as a function of the substrate temperature from 549 to 750 °C.

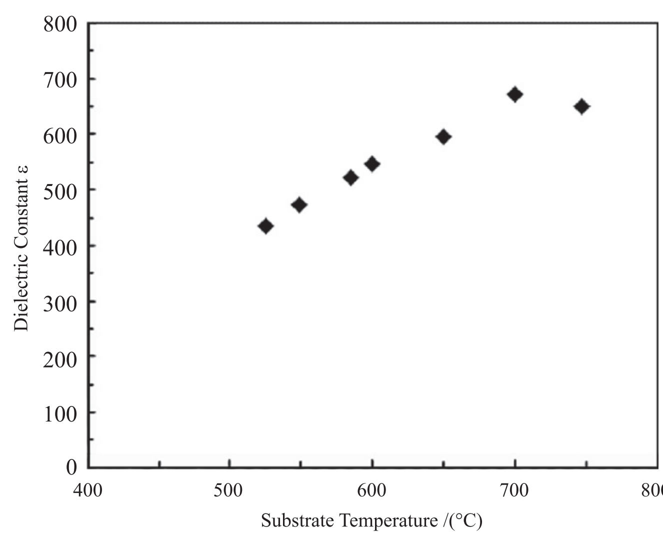

Fig. 8. Variation of the dielectric constant of $Ba_{0.75}Sr_{0.25}TiO_3$ thin films as a function of the substrate temperature.

temperature was 700 °C. The ε_r values obtained were similar to those derived by Quan et al. [21] for $Ba_{0.9}Sr_{0.1}TiO_3$ films deposited on fused quartz and $Pt/TiN/Si_3N_4/Si$ substrates via magnetron sputtering. They found ε_r values of 591, 696, and 758 at 1 MHz when the films were annealed at 650, 700 and 750 °C, respectively [21].

An exponential model may describe remnant polarization P_r data very well within the investigated substrate temperature as

$$P_r = -6.57 + 82.16\, exp\left(\frac{-T_s}{337.35}\right) \quad (2)$$

Fig. 10 shows a fit of P_r with T_s given by Eq. (2). The remnant polarization decreased from 14 $\mu C/cm^2$ to 2.3 $\mu C/cm^2$ in the range from 465 °C to 750 °C, respectively.

An inverse sigmoidal model may describe coercive field strength E_c data very well within the investigated substrate temperature as

$$E_c = 20.76 + 48.71\left[1 + exp\left(\frac{T_s - 582.79}{22.27}\right)\right]^{-1} \quad (3)$$

Fig. 11 shows a fit of coercive field strength with T_s by Eq. (3). E_c decreases from 59.75 kV/cm to 19.86 kV/cm in the substrate temperature range studied. This behavior is similar to that reported in the literature [15,22–24].

The magnitude of the coercive field is large when the substrate temperature is from 454 to 525 °C. E_c decreased suddenly in the temperature range from 525 to 700 °C. This behavior is related to the hysteresis loops which did not present conduction mechanisms, pointing towards an increment in the maximum polarization. It is also related to an increment of the grain size towards a maximum at 525 °C, as can be seen in Fig. 3, behavior also reported by Chen et al. [25]. The exact mechanism is not fully understood, and further investigation is required.

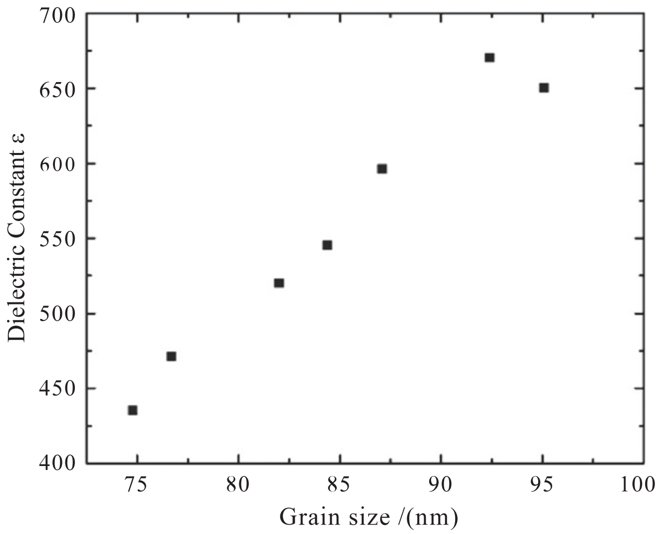

Fig. 9. Variation of the dielectric constant as a function of the mean grain size for thin films samples areas of 5 μm × 5 μm.

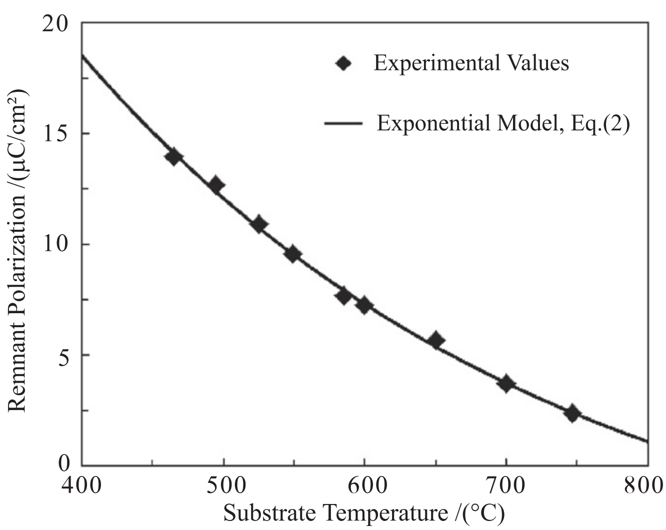

Fig. 10. Remnant polarization dependence of substrate temperatures in $Ba_{0.75}Sr_{0.25}TiO_3$ thin films, with fitted curve (Eq. ((2)).

4. Conclusions

In this study, $Ba_{0.75}Sr_{0.25}TiO_3$ (BST) thin films were deposited on nichrome substrates using Rf co-sputtering with two magnetrons, everyone for every target of BT and ST with different power. The substrate was heated in situ into the sputtering chamber in the range of 400–747 °C. The films deposited were characterized morphologically and ferroelectrically. A rotatory substrate holder was used to maintain the film thickness constant. The substrate holder was heated in situ to deposit films with more uniform grain size and low surface roughness. Grain growth was observed at temperatures of 549 °C and 747 °C, varying the grain size from 75 nm to 95 nm, respectively. This experimental procedure increases the magnitude of the dielectric constant and in general enhances the ferroelectric properties of this composition of BST

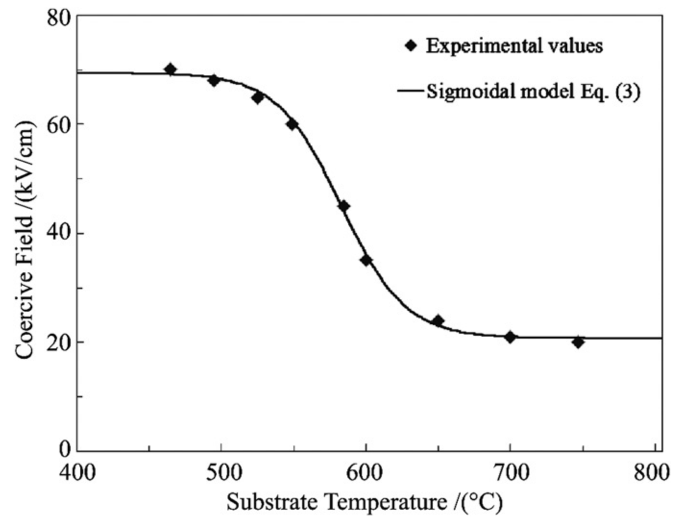

Fig. 11. Coercive field dependence of substrate temperatures in $Ba_{0.75}Sr_{0.25}TiO_3$ thin films, with fitted curve (Eq. (3)).

with respect to that reported in the literature. The results indicated that grain size uniformity and the dielectric constant both increased with the temperature increase. Additionally, the remnant polarization and the coercive field strength decreased with the increase in substrate temperatures.

Acknowledgments

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