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The effects of deposition temperature on structure and dielectric properties of $Ba_{0.6}Sr_{0.4}TiO_3$ thin films produced by pulsed laser deposition

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Abstract

The effects of deposition temperature on orientation, surface morphology and dielectric properties of the thin films for $Ba_{0.6}Sr_{0.4}TiO_3$ thin films deposited on $Pt/Ti/SiO_2/Si$ substrates by pulsed laser deposition were investigated. X-ray diffraction patterns revealed a (2 1 0) preferred orientation for all the films. With rising substrate temperature from 650 °C to 700 °C, the crystallinity and crystal grain size of the films increase, the relative dielectric constant increases, but the dielectric losses have not obvious difference. The film deposited at 350 °C and annealed at 700 °C has strongly improved roughness and dielectric permittivity compared with the film only deposited directly at 700 °C. Three distinct relaxation processes within tan(δ) were found for the $Ba_xSr_{1-x}TiO_3$ film: a broadened process of the film relaxation, an intermediate peak which originates from Maxwell–Wagner–Sillars polarization, and an extremely slow process ascribed to leak current. The complex dielectric permittivity and loss can be fitted by an improved Cole–Cole model corresponding to a stretched relaxation function.

Keywords: Pulsed laser deposition; BST thin film; Oxygen pressure; Dielectric relaxation

1. Introduction

$Ba_xSr_{1-x}TiO_3$ (BST) thin film is a continuous solid solution between $BaTiO_3$ and $SrTiO_3$ over the whole composition range. The solid solution of BST is known to show a decrease in transition temperature with increasing strontium content. In ceramics the rate of decrease of transition temperature with strontium content has been reported as 3.75 °C/mol% of $SrTiO_3$ [1]. In pulsed laser ablated films Gim et al. has reported this rate as 4.59 °C/mol% of $SrTiO_3$ [2]. Because of their potential applications, BST thin films have been attracting a great deal of attention in decoupling capacitors, storage capacitors, giga-bit dynamic random access memories and tunable microwave devices. The large electric field-dependent dielectric constant can be used for devices such as tunable oscillators, filters and phase shifters [3–6]. In such devices, it is desirable to have a high dielectric tunability in a certain electric field range and low dielectric loss. The dielectric constant and tunability of capacitance are sensitive to the relative crystal orientation of the films [7]. There are various methods for changing the orientation of the ferroelectric films, such as the control of heat treatment conditions and the deposition ambience [7–10].

In this work, $Ba_{0.6}Sr_{0.4}TiO_3$ thin films were fabricated by pulsed laser deposition (PLD) on $Pt/Ti/SiO_2/Si$ substrates at different growth temperatures. The effects of growth temperature on structure, surface morphology and dielectric properties of PLD-derived thin films are presented and discussed.

2. Experimental details

The $Ba_{0.6}Sr_{0.4}TiO_3$ thin films were grown on $Pt/Ti/SiO_2/Si$ substrates produced by pulsed laser deposition using the KrF (248 nm wavelength) excimer laser system (Lambda Physik LPX 300 cc) with a repetition rate of 4 Hz and 25 ns in pulse duration. The laser beam was focused by a quartz lens to a fluency of approximately 2.5 J/cm^2 and directed at an angle of 45° on the target. The target, a stoichiometric BST ceramic disc of 25 mm diameter × 5 mm thick, was rotated during the ablation process to reduce non-uniform erosion. The deposition rate was 20 nm/min. The substrate of 5 mm × 15 mm was placed parallel to the target at a distance of 40 mm.

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At first, in order to study the deposition temperature effects, three films with the thickness of 300 nm were deposited in oxygen pressure of 0.01 Pa and at substrate temperature of 650 °C, 680 °C and 700 °C. At last, for the study of annealing effects, films with the same thickness were deposited in oxygen pressure of 0.01 Pa (1) at substrate temperature of 700 °C (BST700) directly and (2) at substrate temperature of 350 °C and annealed at 700 °C for 30 min (BST350).

The structure of the BST thin films were analyzed by X-ray diffractometer (XRD, d/max ultima iii, 1.5406 nm) using a characteristic X-ray of Cu Kα. The microstructure and surface roughness characterizations were performed by atomic force microscopy (AFM) (type: HL-II, China) using a contact mode. Pt electrodes (1 mm in diameter) were deposited on top of the BST films by dc sputtering through a metallic mask. Dielectric complex permittivity of measurements for the Pt/BST/Pt system was performed using the HP 4192A LF impedance analyzer.

3. Results and discussion

The XRD patterns of the BST thin films deposited in oxygen pressure of 0.01 Pa and at different substrate temperatures are shown in Fig. 1a. The standard (1 1 0) peak of 2θ for $Ba_{0.6}Sr_{0.4}TiO_3$ ceramic (PDF Number: 34-0411) is at 31.892° (λ = 1.54178 nm). The (1 1 0) peak of 2θ in Fig. 1a is at 31.981, 31.829 and 31.887 for the BST thin films deposited at substrate temperature 650 °C, 680 °C and 700 °C, respectively. Therefore, $Ba_{0.6}Sr_{0.4}TiO_3$ thin films and ceramics have the same cubic perovskite structure at room temperature. The crystallinity and grain size of the films increase with rising substrate temperature. In Fig. 1b the (1 1 0) peaks of 2θ for BST350 are larger than the peak of BST700 about 0.7°. The orientation factor based on Lotgering's theory [11] is defined as

$$F = \frac{P - P_0}{1 - P_0}, \quad P = \frac{\sum I_{(a\,b\,c)}}{\sum I_{(h\,k\,l)}}$$

where F denotes the orientation factor with respect to the reference plane ($a\,b\,c$), where $a\,b\,c$ represents the Miller indices, P means the ratio of the sum of intensities of the interested family of plane ($a\,b\,c$) to the sum of all reflections for the textured thin film, and P_0 stands for the equivalent ratio for ceramic powder of the target with random orientation. The orientation factor of plane (2 1 0) of the thin films deposited at substrate temperature of 650 °C, 680 °C and 700 °C is 0.6598, 0.6637 and 0.7389, which shows that the crystallinity and

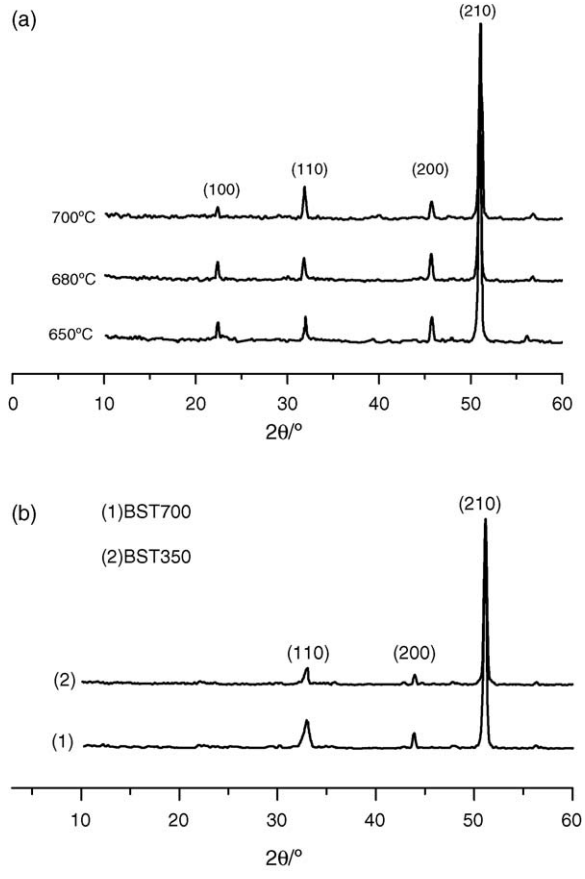

Fig. 1. XRD patterns of BST thin films deposited (a) in oxygen pressure of 0.01 Pa at different substrate temperatures and (b) deposited directly at 700 °C, and deposited at 350 °C then annealed at 700 °C.

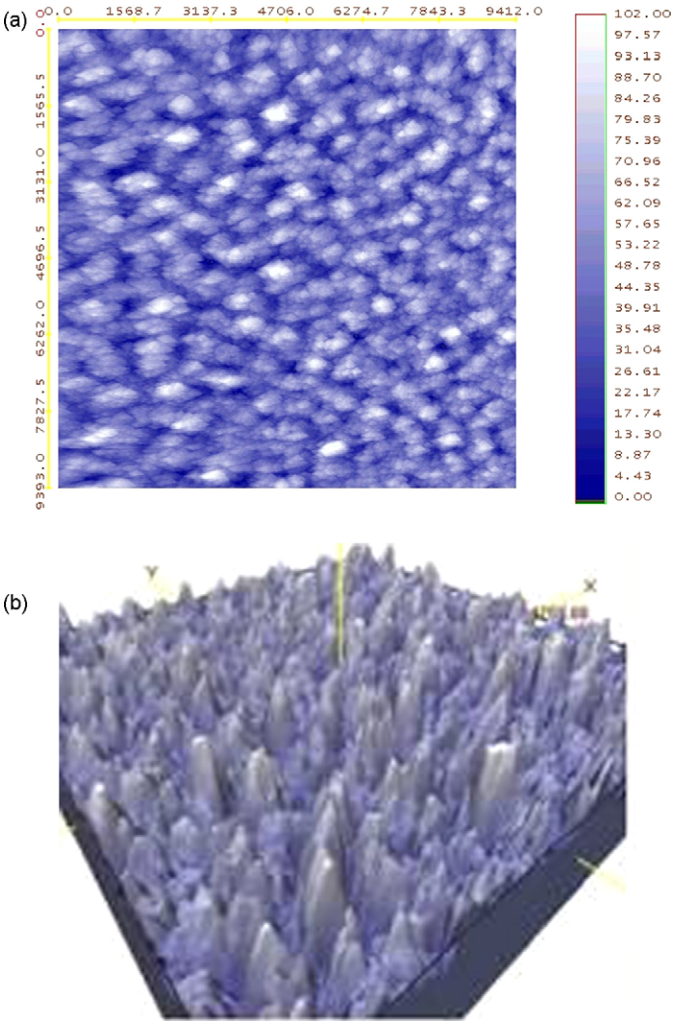

Fig. 2. (a) Two-dimensional and (b) corresponding three-dimensional AFM imagines of BST thin film deposited directly at 700 °C.

crystal orientation of the films increase. The average of the crystal grain size can be calculated from the Debye–Scherrer equation [12], $d = (K\lambda/\beta)\cos\theta$, where K is equal to 0.89, λ is equal to 0.154 nm, β denotes the full width at half maximum of the major peaks, and d is the crystal grain size. The obtained average of crystal grain size of the films deposited at temperature of 650 °C, 680 °C and 700 °C is 43.3 nm, 67.6 nm and 103.4 nm, respectively. The increase of the grain size can be related to the sintering, wherein small grains coalesce to form larger grains.

The XRD patterns of BST700 and BST350 are shown in Fig. 1b. As can be seen from the patterns, the crystal orientation and crystallinity of the film deposited at 350 °C and then annealing at 700 °C are strongly enhanced with orientation factor of 0.8574, compared with the one of 0.7389 deposited directly at 700 °C.

The microscopic surface morphology of the BST films was studied by the AFM. Figs. 2 and 3 show the AFM micrographs indicating that the BST thin films are well-crystallized, crack-free and pinhole-free. The unit on the top and left sides of Figs. 2a and 3a is nanometer. Fig. 2 shows the two-dimensional (Fig. 2a) and corresponding three-dimensional (Fig. 2b) AFM images of the BST700. The surface roughness is relatively high with root mean square (RMS) roughness of 15.81 nm. AFM images of the BST350 are shown in Fig. 3. The film exhibits a better crystallized, uniform and dense microstructure. The RMS roughness was reduced to 10.55 nm. It can be explained that direct deposition at high temperature of 700 °C would cause the homogeneous gas phase reaction near the heated substrate, and active intermediate species might undergo decomposition and are subjected to chemical reactions to form big grain clusters on the film surface [13]; but at low temperature active species are only absorbed onto the heated substrate, surface and thus produced a uniform adherent layer which at high annealing temperature start the diffusion processes and/or migration of cluster [14] to form the nuclei for subsequent crystal growth of films during annealing at high temperature [15].

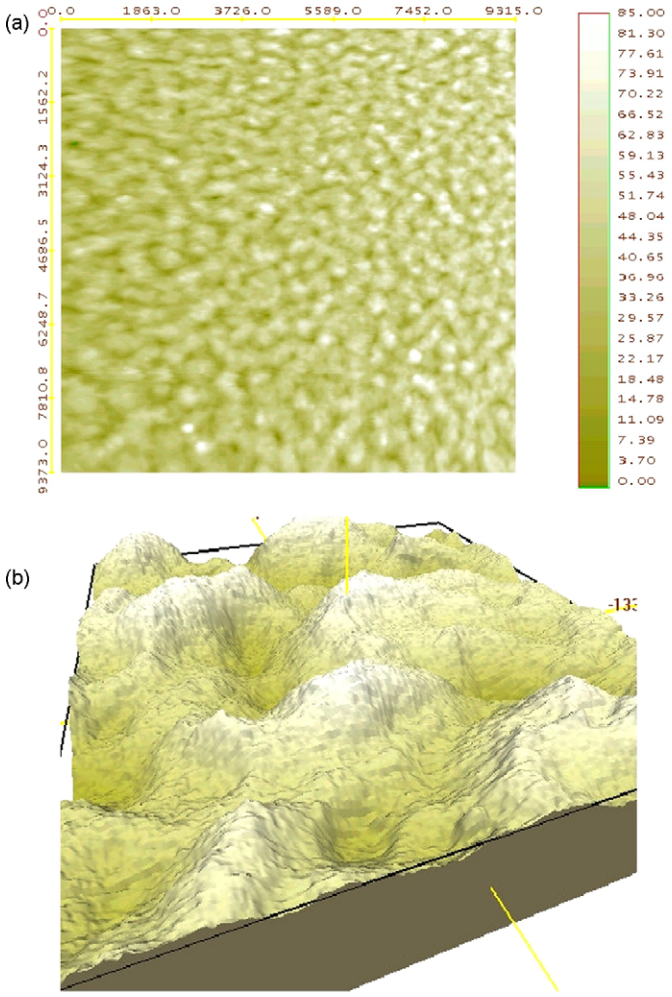

Fig. 3. (a) Two-dimensional and (b) corresponding three-dimensional AFM imagines of BST thin film deposited at 350 °C and then annealed at 700 °C.

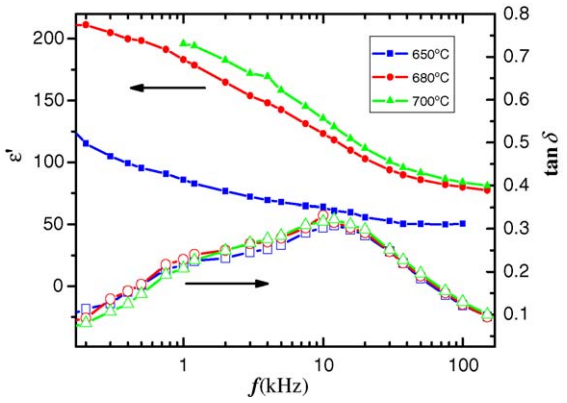

Fig. 4. Dielectric properties of BST thin films deposited at different temperatures.

Figs. 4 and 5 show the dielectric properties of BST thin films deposited at different heat treatments. In Fig. 4 the dielectric constant of BST thin films decreases rapidly with frequency in the lower frequency region and increases as the substrate temperature increases, especially when the temperature increases from 650 °C to 680 °C. The enhancement of dielectric properties of the films attributes to the increases of the crystallinity and the crystal grain size. Fig. 4 shows the

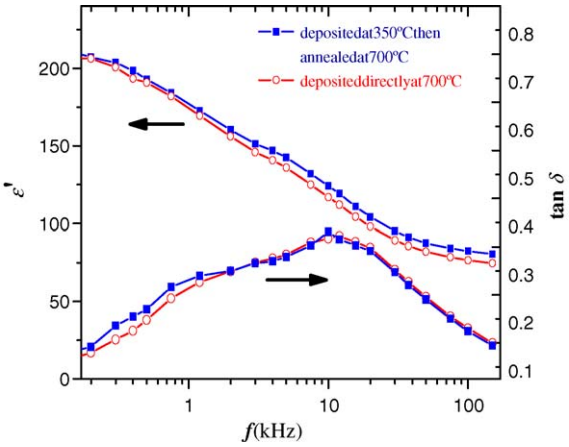

Fig. 5. Dielectric properties of BST thin films deposited at 700 °C and 350 °C and annealed at 700 °C for 30 min.

dielectric loss curves of the BST thin films deposited at different substrate temperatures. The dielectric loss (tan $\delta(\omega)$) reveals two typical dielectric peaks. There are unconspicuous changes in dielectric loss for the films at different substrate temperatures. Fig. 5 shows that the dielectric properties of the film BST350 have an unconspicuous variation compared to the film BST700.

Fig. 6 demonstrates the dependence of dielectric losses of the BST thin films on frequency. The whole loss curve can be separated to three sections. One is caused by the BST thin film at a resonance frequency about 10 kHz. Another is interfacial reaction near 1 kHz. As clearly shown, the function of dielectric loss of BST thin films can be fitted to an improved Cole–Cole model. The fitted functions of two respective losses curves are

$$\tan\delta(f) = \frac{0.330\,f}{f^{1.70}+0.95} + \frac{2.50\,f}{f^{1.66}+54} \quad \text{(BST700)} \tag{1}$$

$$\tan\delta(f) = \frac{0.334\,f}{f^{1.67}+1.0} + \frac{2.48\,f}{f^{1.66}+54} \quad \text{(BST350)} \tag{2}$$

The curves of the dielectric permittivity of the BST thin films as a function of frequency are shown in Fig. 7. The function of dielectric permittivity of BST thin films can be also fitted to the improved Cole–Cole model. The fitted functions of two respective dielectric permittivity curves can be expressed by

$$\varepsilon'(f) = \frac{68}{f^{1.70}+1.1} + \frac{4500}{f^{1.58}+65} + 74 \quad \text{(BST700)} \tag{3}$$

$$\varepsilon'(f) = \frac{53}{f^{1.70}+1.0} + \frac{3900}{f^{1.66}+54} + 82 \quad \text{(BST350)} \tag{4}$$

From the above fitting, the improved Cole–Cole model can be expressed as

$$\tan\delta(f) = \frac{A\,f}{f^{1+\alpha_1} + {f_1}^{1+\alpha_1}} + \frac{B\,f}{f^{1+\alpha_2} + {f_2}^{1+\alpha_2}} \tag{5}$$

and

$$\varepsilon'(f) - \varepsilon_0 = \frac{C}{f^{1+\alpha_1} + {f_1}^{1+\alpha_1}} + \frac{D}{f^{1+\alpha_2} + {f_2}^{1+\alpha_2}2} \tag{6}$$

where α_1 and α_2 are nearly equal to 0.70 and 0.66, respectively. In standard Debye equation α is equal to 1, while $0 < \alpha < 1$ denotes the stretched Debye equation, and there is a stronger the interaction between the dipole–dipole in the films. The high frequency peak of dielectric spectroscopy is considered due to the dipoles in growing directions, while the low frequency effect is the Maxwell–Wagner–Sillars (MWS) polarization, a result of electric charges gathering at the boundaries between

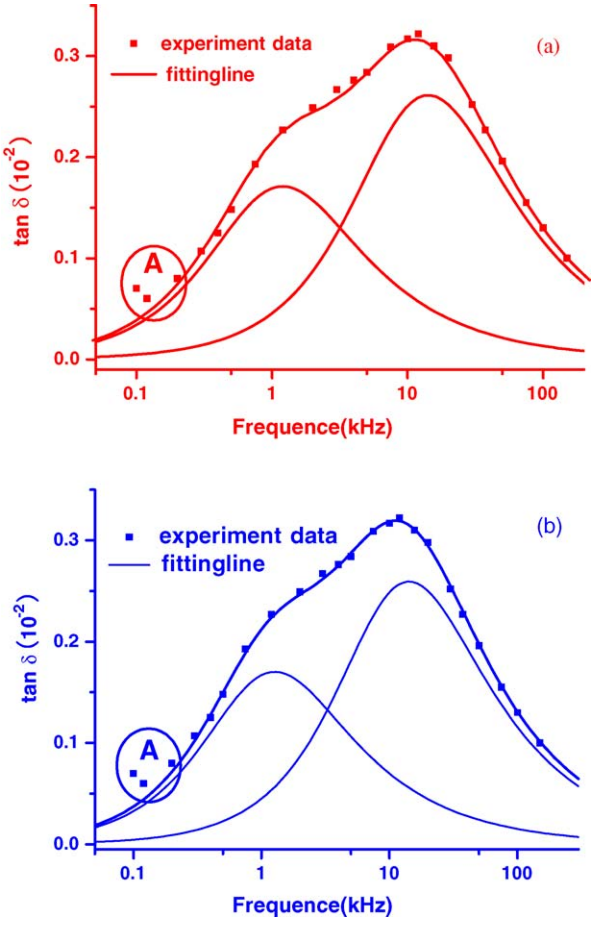

Fig. 6. Fitting of dielectric loss of BST thin films deposited at (a) 700 °C and (b) 350 °C and annealed at 700 °C for 30 min.

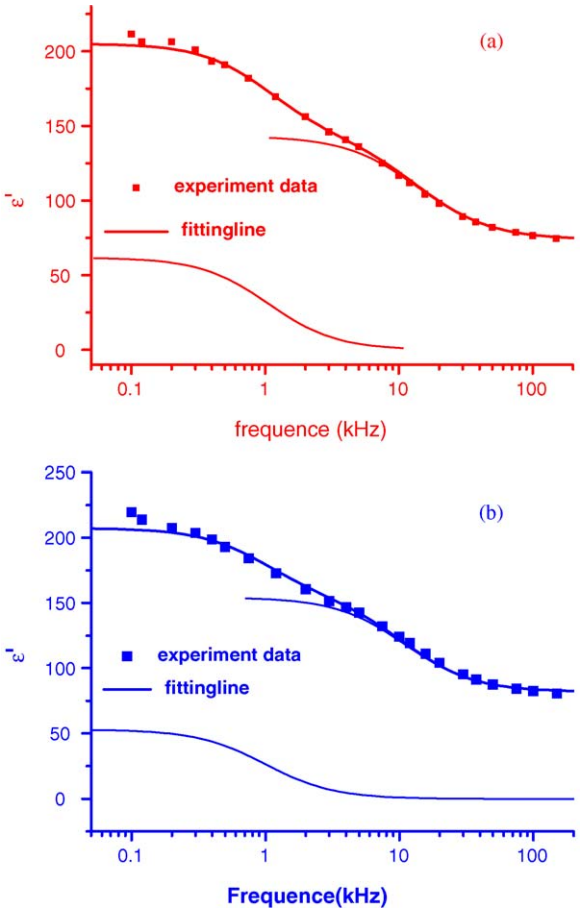

Fig. 7. Dielectric permittivity of BST thin films deposited at (a) 700 °C and (b) 350 °C and annealed at 700 °C for 30 min.

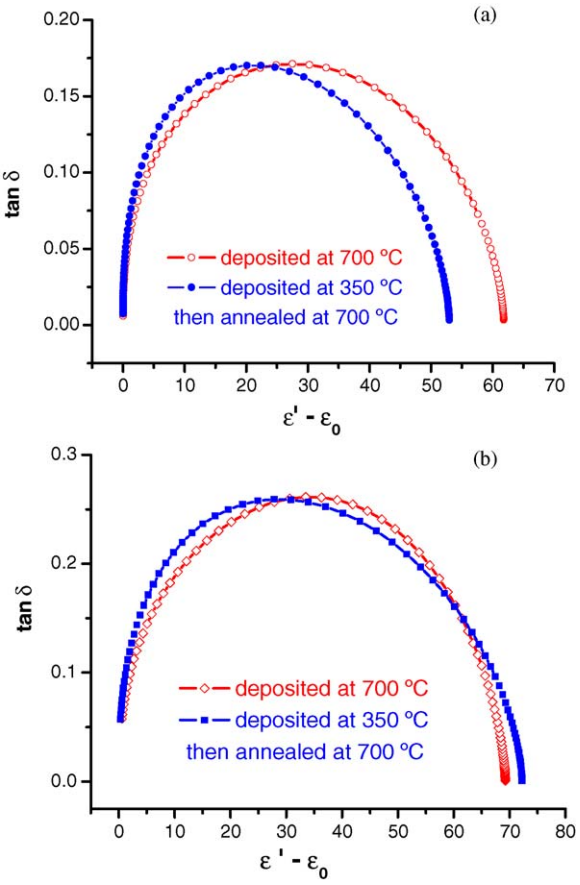

Fig. 8. Cole–Cole circle of BST thin films at (a) low frequency and (b) high frequency.

the material and the substrate electrode and depending on a sample's texture and the conductance of the involved phases. The MWS polarization usually occurs at high temperatures and low frequencies.

The Cole–Cole diagram consists of real and imaginary parts of complex dielectric constant. Fig. 8a and b demonstrates two semicircles of loss and real part of complex dielectric constant. This result is similar to the explanation given by Hedvig [16].

The low frequency loss, the circle 'A', in Fig. 6a and b is due to leak current following an approximate relation:

$$\tan\delta \doteq \frac{\varepsilon_s - \varepsilon_\infty}{\varepsilon_\infty w\tau} + \frac{\gamma}{w\varepsilon_0\varepsilon_\infty} \rightarrow \frac{1}{w} \quad (7)$$

This explanation has a good agreement with the results of Fig. 6a and b for frequency lower than 0.1 kHz.

4. Conclusion

$Ba_{0.6}Sr_{0.4}TiO_3$ thin films were fabricated by pulsed laser deposition. The influence of substrate temperature on the growth of BST thin films on $Pt/Ti/SiO_2/Si$ substrate has been investigated. It is revealed that the crystal orientation, crystal grain size and surface roughness are dependent on the substrate temperature and annealing temperature. X-ray diffraction patterns show that all the films have a (2 1 0) preferred orientation. The major effects of substrate temperature on the growth of thin films can be concluded that the crystallinity, and crystal grain size of the films increase. The dielectric constant increases and the dielectric loss decreases with increasing substrate temperature. At last, the crystal orientation and crystallinity of the film deposited at 350 °C and then annealed at 700 °C were enhanced. The film deposited directly at 700 °C has larger orientation factor of 0.8574 and smaller the RMS roughness. The dielectric losses are attributed to the relaxation of the polarization of the dipoles and MWS polarization, respectively.

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