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The effect of deposition power on the micro-structure and dielectric response of $Pb_{0.4}Sr_{0.6}TiO_3$ thin films

Kui Li[a], Denis Rémiens[b], Gang Du[a], Tao Li[a], Xianlin Dong[a], Genshui Wang[a,*]

[a]Key Laboratory of Inorganic Functional Materials and Devices, Shanghai Institute of Ceramics, Chinese Academy of Sciences, 1295 Dingxi Road, Shanghai 200050, People's Republic of China

[b]Institute of Electronics, Microelectronics and Nanotechnology (IEMN)—DOAE, UMR CNRS 8520, Université des Sciences et Technologies de Lille, 59652 Villeneuve d'Ascq Cedex, France

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Abstract

We report the fabrication of $Pb_{0.4}Sr_{0.6}TiO_3$ thin films with different microstructures and dielectric responses deposited on $LaNiO_3$ buffered silicon substrate via the RF magnetron sputtering method with various deposition powers from 40 W to 120 W. Effects of the power on deposition rate, orientation, surface morphology and dielectric response were investigated. X-ray diffraction patterns indicated that the crystal orientation of thin films changes from (110) preferential orientation to random orientation with decreasing power, and finally to perfect (100) orientation. Moreover, the thin films prepared at lower power show more homogeneous grain size distribution and denser microstructure. The capacitance–voltage analysis revealed that the films deposited at lower powers show larger dielectric response and better tunability performance. Especially, large dielectric constant and tunability of 947 and 80.88% (@400 kV/cm), respectively, were obtained under a deposition power of 40 W.

Keywords: Deposition power; Lead strontium titanate; Microstructure; Tunability

1. Introduction

The ferroelectric perovskite films have been the subject of studies in a vast range of applications due to their unique properties, such as dynamic random access memories, power-supply decoupling, and tunable microwave devices/radio frequency components [1–4]. $(Ba_xSr_{1-x})TiO_3$ (BST) thin film has long been considered to be one of the most promising candidates for these applications because of its large electric-field dependent and adjustable Curie temperature. However, its large insertion loss, especially in high frequency range, and relatively high processing temperature restrict its practical applications. Among the potential ferroelectric thin films for tunable device applications, thin film of $Pb_xSr_{1-x}TiO_3$ (PST) has recently been extensively studied because of its variable Curie temperature, smaller grain size effect [5], excellent dielectric response and tunability performance. Moreover, its processing temperature is lower [6] in comparison to that of BST films (typically 650–800 °C) [3], which makes it a promising candidate for the applications mentioned above.

A plethora of methods, such as sputtering [3,7], chemical vapor deposition, pulsed laser deposition [8], and sol–gel [9,10], are commonly used to fabricate ferroelectric thin films. Among which, radio frequency (RF) magnetron sputtering is one of the most promising choices for the commercial process, because this method can produce highly uniform films with good adherence to the substrate and offer the advantage of depositing films with a large area. Moreover, this technique is now well compatible with the microelectronics technologies. For the tunable microwave devices, it is very important to prepare thin film with both high tunability and low dielectric loss. Hitherto, extensive studies have been focused on increasing the dielectric constant and dielectric tunability via adopting various single-crystal substrates, such as $LaAlO_3$, MgO and $NdGaO_3$ [11–13]. The adoption of these substrates is contrary to their small-sized geometries and high cost. It is of commercial importance to integrate the ferroelectric films directly to silicon substrate because of its

*Corresponding author. Tel.: +86 21 52411160; fax: +86 21 52411104.
E-mail address: genshuiwang@mail.sic.ac.cn (G. Wang).

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low cost, large area, and high-volume production. It is well known that the structure and performance of the films deposited on silicon substrates are influenced by processing parameters such as the deposition rate, argon to oxygen ratio (OMR) [14], annealing temperature [15], and seeding layers [16]. Moreover, the effect of RF power has been studied for some lead free thin films and strong correlation between RF power and microstructure as well as electrical properties has been revealed for different thin films [17,18]. As for PST thin film, the lead particle is very heavy, which demonstrates different behaviors during the sputtering process. Unfortunately, there has not been a systematic investigation on the effect of RF power on the structure and electrical property of PST films.

In this work, the effect of RF power on the microstructure and electrical properties of $Pb_{0.4}Sr_{0.6}TiO_3$ thin films deposited on $LaNiO_3$ (LNO) coated Si substrates by RF magnetron sputtering was investigated. The nominal Pb/Sr composition ratio of 40/60 is chosen because of its better dielectric response and tunability near room temperature [7]. PST films were deposited with pure Argon and fixed deposited pressure of 30 mTorr with various RF powers from 40 to 120 W (denoted as PST-40 to PST-120 respectively).

2. Experimental procedure

$Pb_{0.4}Sr_{0.6}TiO_3$ ceramic with 25 wt% lead excess and 6 wt% strontium excess was used as the target. A large lead excess in the target was adopted to compensate the essential loss of lead during the deposition and post-annealing process. The ceramic target was prepared by the traditional solid-state reaction process. The starting materials were batched with agate balls for 12 h, the mixture was then calcined at 800 °C for 2 h in air. Then the powder was re-milled for 24 h and then pressed at 100 MPa into a disk of 90 mm diameter using polyvinyl acetate (PVA) as adhesive. The target was sintered at 900 °C for 2 h in air. After sintering, the target was burnished to a diameter of 3 in. The (100)-oriented LNO bottom electrode with a thickness of 300 nm was prepared by RF magnetron sputtering on the SiO_2/Si substrate at 450 °C and post-annealed at 700 °C for 1 h to improve the electrical conductivity and the crystallization [19]. The $Pb_{0.4}Sr_{0.6}TiO_3$ thin films with a thickness of nearly 400 nm were prepared by a radio frequency magnetron sputtering system using (100)-orientated LNO bottom electrodes. PST target attached to a metallic Cu back plate positioned 8 cm from the substrate holder. The PST thin films were deposited with the off axis RF magnetron sputtering method without heating the substrate. The target was tilted 30° from the normal direction to the substrate, that is the distance between the normal directions of the substrate and the target was nearly 4 cm. The substrate was rotated at a constant velocity of 15 r/min. Details of the thin films deposition conditions are listed in Table 1. The as-deposited PST thin films showed amorphous phase, which transformed to a crystalline phase through a post-annealing process at 650 °C for 1 h in air. The increasing and decreasing speeds of the post-annealing temperature were 2 and 1 °C/min respectively. The Pt top electrode with a diameter of 150 μm was prepared with traditional photolithography and lift-off process. Top Pt electrodes were deposited by direct current (DC) magnetron sputtering. Then the top electrode was annealed at 500 °C for 1 h after the preparing of Pt top electrode to improve the interface and the conductivity.

The crystal quality and mean grain sizes of PST thin films were examined by X-ray diffraction (XRD) analysis (Siemens D5000 diffractometer) in the θ–2θ scan mode with CuKα1 radiation ($\lambda = 1.5406$ Å) at 40 kV and 40 mA. The surface morphology was observed by a scanning electronic microscope (SEM) Hitachi S4700 (Hitachi, États-Unis, TX). The dielectric constant and loss tangent dependences on the electric field in the range of ± 400 kV/cm were tested by a HP4192A LCR meter under ac voltage of 0.1 V at a frequency of 10 kHz and room temperature.

3. Results and discussion

The XRD patterns of PST thin films prepared with different RF powers ranging from 40 to 90 W are demonstrated in Fig. 1. As depicted in the figure, all the films display the pure perovskite phase and no second phase is detected within the accuracy of measurement. The films deposited with RF powers ranging from 40 to 70 W on (100)-oriented LNO bottom electrode are found to be perfectly oriented in (100) direction because of the similar perovskite structure and well matched lattice parameter [20] between PST thin films and the LNO bottom electrodes. However, even on the same perfect (100)-oriented LNO bottom electrodes, the PST thin films prepared with RF powers ranging from 90 W to 120 W show random

Table 1
Typical deposition conditions for PST thin films.

Sputtering parameters	Conditions
Base pressure (Pa)	$< 2 \times 10^{-6}$
Deposition pressure (mTorr)	30
RF power (W)	40, 60, 70, 90, and 120
Target	PST ceramic with 25% lead excess and 6% Sr excess
Substrate temperature (°C)	Without heating (90 °C due to the plasma)
Deposition atmosphere	Pure argon
Target–substrate distance (mm)	80

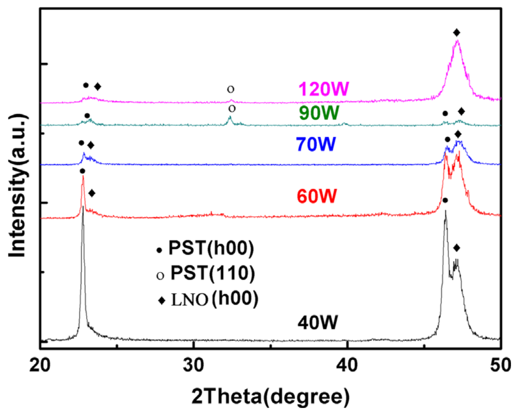

Fig. 1. X-ray diffraction patterns of the PST thin films grown on LNO buffered Si substrate with different RF powers.

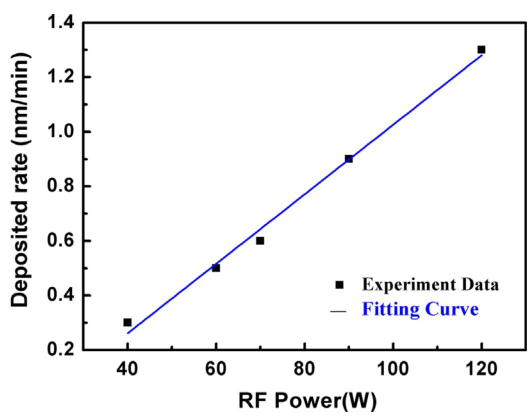

Fig. 2. Effect of RF power on the deposition rate of PST thin films.

orientation demonstrated as a mixture of (100) and (110) PST peaks, and the intensity of the PST (100) peak decreases with higher RF power. It is worthwhile to note that there is a obvious dependence of the orientation on the different RF powers using the same deposition and post-annealing parameters. This interesting phenomenon can be explained by the different deposition rates under different RF powers which will affect the epitaxial growth of PST thin films on (100)-orientated LNO bottom electrode. We will discuss it in detail later.

The deposition rate of the PST thin films grown at various RF powers while similar deposition and post annealing parameters, is shown in Fig. 2. The growth rate of the thin films is calculated by the thickness of thin film and deposition time. It is clearly shown that the deposition rate of the thin films by magnetron sputtering increases with higher RF power. This can be explained by the increasing rate of arrival of the adatoms which dominates the deposition rate in our case [21]. Moreover, the kinetic energy of the atoms sputtered with higher RF power would also be increased, resulting in an enhancement of adsorption of the atoms that would help the atoms to have more chances to move to the lowest energy state.

Scanning electron microscopy (SEM) is used to characterize the microstructure morphology of the PST thin films and the results are presented in Fig. 3. It can be observed that the PST

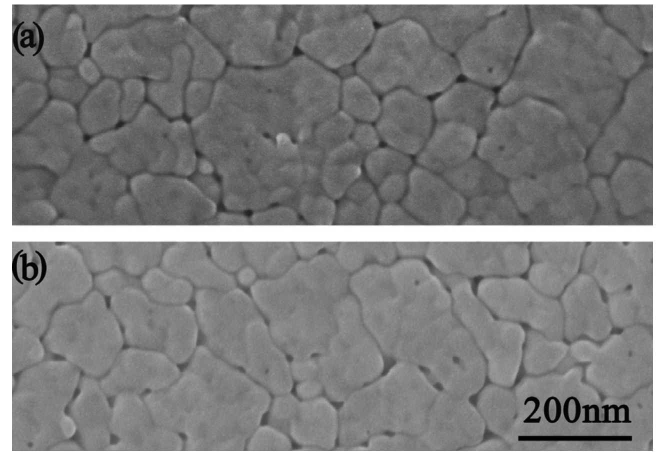

Fig. 3. Scanning electron microscope (SEM) photographs of the PST thin films prepared with RF powers of (a) 90 W and (b) 60 W.

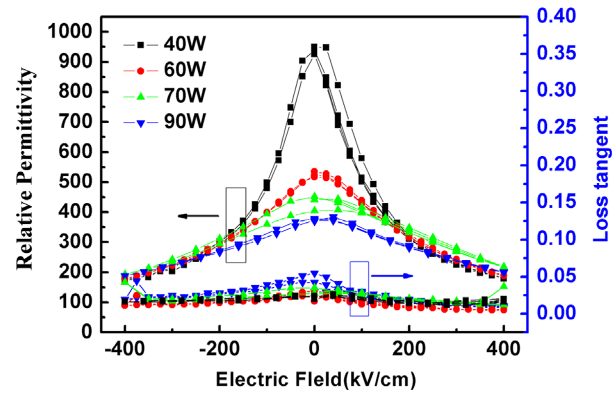

Fig. 4. The dielectric constant and the loss tangent of PST thin films prepared with different RF powers as a function of DC bias field tested at 10 kHz.

thin films prepared with RF powers of 60 W and 90 W possess crack-free micro-structure and smooth thin film surface, while PST-60 shows much denser micro-structure than that of PST-90 and some small pores in PST-90 can be observed from its surface morphology. Moreover, PST-60 shows more homogeneous grain size distribution and better crystallization. As shown in the figure, PST-60 demonstrates increased grain size. These dramatic differences of the microstructures as a function of the deposition RF powers may be attributed to the increasing deposition rate with higher RF powers, with associated poorer epitaxial growth of the PST thin films.

The direct current (DC) bias field dependence of dielectric properties for the thin films deposited with different powers is investigated via a HP4192A LCR meter under an electric field of 400 kV/cm and plotted in Fig. 4. It can be found that the dielectric constant under zero electric field which is mainly contributes to the extrinsic dielectric response increases gradually from 370 to 441 with the orientation changing from randomly orientation to perfect (100) orientation with decreasing RF power, and then increases dramatically to 947 with increasing intensity of PST

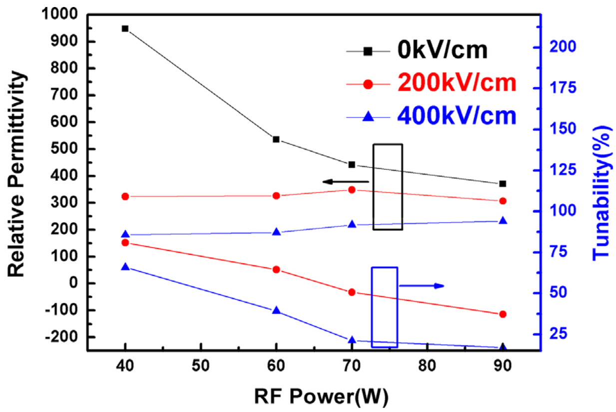

Fig. 5. Effect of RF power on the tunability and dielectric constant of the PST thin films.

(100) peak with lower power. While the dielectric constant under the maximum electric field of 400 kV/cm shows different trend with RF powers, all the thin films show a similar dielectric constant value. This strong correlation between the dielectric response and the deposition power may be attributed to different epitaxial crystallization qualities and deposition rates stemming from the different RF powers. Thanks to the better crystallization for the films prepared with lower RF powers, the loss tangent of the films decreases dramatically with decreasing RF powers, which is very advantageous for better figure of merit value. Moreover, the much denser micro-structure and better interface structure of the films derived from lower RF powers may be also the sources of drastically decreased loss tangent.

Fig. 5 displays the dielectric constant and tunability dependence on DC electric field as a function of RF power. The tunability can be defined by the following function:

$$\eta = \{[\varepsilon(0) - \varepsilon(E_{\max})]/\varepsilon(0)\}100\% \quad (1)$$

where $\varepsilon(0)$ and $\varepsilon(E\text{max})$ are the dielectric constants under zero and the maximum DC electric field of 400 kV/cm respectively. The former is mainly contributed by the extrinsic response stemming from the domain motion, while the latter is dominated by the intrinsic response because of the suppressed extrinsic response under an electric field higher than 200 kV/cm [22]. As shown in the figure, the $\varepsilon(0)$ decreased drastically with increasing RF power, indicating that PST-40 possesses larger extrinsic dielectric response, which is consistent with the analysis in Fig. 4. Consequently the RF power affects the tunability drastically and PST-40 shows a tunability value of 80.88% at an electric field of 400 kV/cm, which is much higher than those of PST-60 and PST-90 (64.5% and 37.2%, respectively) at the same electric field. Interestingly, PST-40 possesses higher figure of merit because of its lower loss tangent, suggesting the thin film to be a promising candidate for the microwave tunable devices.

4. Conclusion

$Pb_{0.6}Sr_{0.4}TiO_3$ thin films with different microstructures and dielectric responses deposited on LNO buffered silicon substrate was fabricated via the RF magnetron sputtering method at various RF powers ranging from 40 to 120 W. The correlation between the powers and the microstructure as well as dielectric response was systematically investigated. As indicated by X-ray diffraction patterns, with decreasing power, the crystal orientation of the thin films develops from random orientation to perfect (100)-orientation. Moreover, more homogeneous grain size distribution and denser microstructure were observed in the films prepared with lower RF powers. The capacitance–voltage analysis revealed that the films deposited at lower power show larger dielectric responses and larger tunability performances. Large dielectric constant and tunability of 947 and 80.88% (@400 kV/cm), respectively, were obtained under a power of 40 W, indicating this thin film to be a promising candidate for the frequency agile devices.

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