Available online at www.sciencedirect.com

ScienceDirect

Ceramics International 41 (2015) S520–S525

CERAMICS INTERNATIONAL

www.elsevier.com/locate/ceramint

Influence of deposition temperature on microstructure and electrical properties of modified (Ba, Sr)TiO_3 ferroelectric thin films

Dongxu Yan[a,b], Lizhu Luo[b], Yongbin Zhang[b], Zhihang Peng[a], Hong Liu[a], Dingquan Xiao[a], Tianwei Liu[b], Xinchun Lai[b], Jianguo Zhu[a,*]

[a]*College of Materials Science and Engineering, Sichuan University, Chengdu 610064, China*
[b]*Science and Technology on Surface Physics and Chemistry Laboratory, Mianyang 621907, China*

Received 26 October 2014; accepted 10 March 2015
Available online 31 March 2015

Abstract

Modified $Ba_{0.67}Sr_{0.33}TiO_3$ (BST) thin films were deposited on Pt/Ti/SiO_2/Si substrates using RF magnetron sputtering. By optimizing the deposition temperature (T_d), the dielectric and ferroelectric properties of BST films were improved. The onset of crystallization of the BST films was observed at about 600 °C, beyond which there was an increase in grain size with further increasing T_d up to 700 °C. The better crystallized film deposited at 700 °C with a thickness of 670 nm shows a polycrystalline and dense structure, a dielectric constant (ε_r)=953.40 (at 100 kHz), and a remanent polarization ($2P_r$)=23.87 μC/cm^2. The dielectric tunability at 1 MHz increases as T_d increases, and reaches the highest value of 55.40% for an applied field of 770 kV/cm at the highest T_d of 700 °C. X-ray diffraction (XRD), scanning electron microscopy (SEM) and electric performance analysis also indicate that the deposition temperature during growth strongly affects the microstructure of BST films. This in turn influences the dielectric, ferroelectric and tunable behavior of BST films.

Keywords: BST; Ferroelectric films; Deposition temperature; Tunability

1. Introduction

Barium strontium titanate ($Ba_{1-x}Sr_xTiO_3$) is a solid solution ferroelectric material [1] exhibiting a large dielectric constant change with an applied dc electric field. The dc electric-field dependent dielectric constant can be employed to develop tunable microwave devices [2–5], such as tunable varactors [6,7], filters [8], resonators [9], and phase shifters [10]. $Ba_{1-x}Sr_xTiO_3$ is currently a material of choice for microwave applications due to its low loss [11] and composition dependent Curie temperature(T_c) [1], which ranges from −163 to 120 °C for $x=0$ to $x=1$ respectively. To realize better tunability, its composition (Ba/Sr ratio) has to be chosen such that the T_c is just at around room temperature (the operating temperature), which is more favorable for practical device application. We have recently reported a detailed study [12,13] on the effect of Mn/Y codoping and sintering temperature on the microstructure and electrical properties of bulk $Ba_{0.67}Sr_{0.33}TiO_3$ ceramics. We also have obtained modified bulk $Ba_{0.67}Sr_{0.33}TiO_3$, which processes a low dielectric loss (tan δ < 0.0073 at 1 kHz) and good dispersion characteristics.

However, bulk BST shows several drawbacks: its dielectric constant is too high, which inevitably leads to a very complicated impedance matching circuit [14]; its size is not suitable for integrated devices; very high processing temperature is necessary in order to obtain good crystallinity. Therefore, great emphasis in this research field has been placed on thin film BST.

Thin film BST offers advantages over bulk BST for tunable microwave applications. Large electric fields (0–400 kV/cm) can be achieved in thin film BST (∼224 nm) using low voltages [15]. It is well known that the electric properties of thin film BST is sensitive to its microstructure and crystallinity which are determined by deposition conditions [16] such as

*Corresponding author. Tel.: +86 028 85412415; fax: +86 028 85416050.
E-mail addresses: joyner68@sina.com, nic0400@scu.edu.cn (J. Zhu).

http://dx.doi.org/10.1016/j.ceramint.2015.03.158
0272-8842/

deposition temperature and O_2/Ar ratio. Due to the enormous technological importance in micro-electric applications, it is indispensable to study the interdependence of the electric properties of thin film BST as a function of sputtering conditions. Therefore, optimizing deposition conditions present an intriguing opportunity to develop thin film BST for tunable microwave applications with stringent demands focused on high tunability, while still maintaining a low dielectric loss. In this work, our focus is to study the effect of deposition temperature on the crystallinity, dielectric and ferroelectric properties of the modified $Ba_{0.67}Sr_{0.33}TiO_3$ [13] by RF magnetron sputtering on Pt/Ti/SiO2/Si substrates, and correlate these to observed tunability behavior.

2. Experimental procedure

Modified BST ceramic target was prepared using citrate–nitrate combustion derived powder [12,13], following the composition of $Ba_{0.67}Sr_{0.33}TiO_3$ co-doped with 0.5 mol% for Mn and 1.0 mol% for Y dopants. The dense ceramic target possesses pure polycrystalline perovskite structure (Fig. 1), and its relative density reaches to 92.5% of the theoretical value. BST films were grown onto Pt (200 nm)/Ti(50 nm)/SiO_2(500 nm)/Si substrates by off-axis RF magnetron sputtering from the BST target under an Ar/O_2 (4:1) gas mixture at 2 Pa. The deposition temperature varied from 550 to 700 °C and the RF power during BST deposition was held constant. Prior to deposition, the substrates were ultrasonically cleaned with acetone, ethanol, and de-ionized water, and the target was pre-sputtered in the chamber for 3 h to remove any surface contamination. Details of the processing conditions are given in Table 1.

Patterned Au top electrodes were deposited through a shadow mask onto the BST films at 50 °C, using DC magnetron sputtering. The crystal structures of BST films were assessed by glancing angle X-ray diffraction (GXRD). A JSM5900 field-emission scanning microscope (FESEM) was utilized to assess the cross-sectional and plan-view film microstructures. The chemical composition and bonding were determined by X-ray photoelectron spectroscope (XPS: PerkinElmer PHI5600) instrument equipped with Al Kα radiation. Dielectric and tunable properties were measured by using a precision impedance analyzer (HP 4294A). The polarization electric-field (*P–E*) hysteresis loops were measured by using a Radiant Precision Ferroelectric Measurement System (RT2000 Tester, USA).

3. Results and discussion

GXRD was utilized to assess the crystallinity of the BST films and to determine whether or not the films possess a single phase structure. Fig. 2 displays the diffraction patterns of the BST films deposited on Pt/Ti/SiO_2/Si substrates. The absence of BST peaks in the patterns for the BST film deposited at 550 °C indicates that the films are amorphous in nature. Minimally crystallized BST film was obtained at a deposition temperature of 600 °C with no clear evidence of secondary phase formation. As deposition temperature increases, the peak intensity of BST increases and the FWHM of (110) peak decreases, indicating enhanced crystallinity and an increase in grain size. Based on the X-ray characterization results, 700 °C was determined to be the optimum deposition temperature, at which the film possesses a cubic and non-textured polycrystalline structure.

Fig. 3 displays the surface and cross-sectional morphologies of the BST films deposited at different temperatures. Qualitatively, the surface morphologies are in good accordance with

Table 1
Sputtering conditions for the modified BST deposition.

Target	Modified $Ba_{0.67}Sr_{0.33}TiO_3$
Deposition temperature	550–700 °C
Deposition pressure	2 Pa
O_2/(Ar + O_2) flow ratio	25%
RF sputtering power	50 W
Target-substrate distance	60 mm

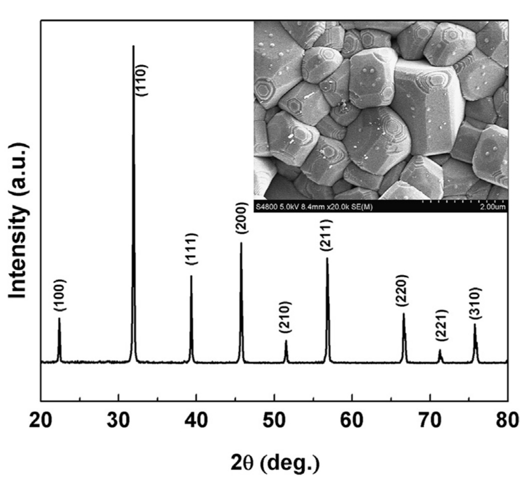

Fig. 1. XRD pattern and surface morphology (Insert) of modified BST ceramic target.

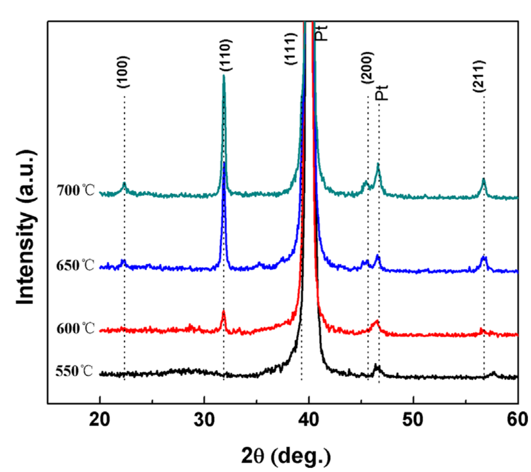

Fig. 2. XRD patterns of the modified BST thin films deposited at different temperatures.