Ceramics International 30 (2004) 1525–1527

CERAMICS INTERNATIONAL

www.elsevier.com/locate/ceramint

Modified sol–gel processing for preparation of barium strontium titanate ceramic thin films

Xiaojing Yang*, Xi Yao, Liangying Zhang

Functional Materials Research Laboratory, Tongji University, Shanghai 200092, China

Received 4 December 2003; received in revised form 18 December 2003; accepted 22 December 2003

Available online 10 June 2004

Abstract

The $Ba_{0.7}Sr_{0.3}TiO_3$ (BST) thin films were prepared by sol–gel processing using barium acetate ($Ba(Ac)_2$), strontium acetate ($Sr(Ac)_2$) and titanium-tetrabutoxide as starting materials. Acetic acid and 2-methoxyethanol were selected as solvents, respectively. The single layer thickness of the films was about 200 nm determined by F20 filmetrics. The surface morphology of the film was observed using an atomic force microscope (AFM). X-ray diffraction (XRD) results show that the film exhibits a pure perovskite phase. The film has good dielectric properties. The dielectric constant and dielectric loss are 260 and 0.036 at 100 kHz, respectively.

Keywords: A. Sol–gel processes; C. Dielectric properties; $Ba_{0.7}Sr_{0.3}TiO_3$ film; Chelate

1. Introduction

Thin films of perovskite $Ba_xSr_{1-x}TiO_3$ system are promising candidates for microelectronic devices that can be integrated to semiconductor circuits. The lead-free solid solution $Ba_xSr_{1-x}TiO_3$ (BST) is a high permittivity dielectric material with low loss and is suitable for use in dynamic random access memory (DRAM) cells, tunable microwave devices, by-pass capacitors and infrared detectors [1,2]. In particular, the dielectric constant of films decreases when the thickness of the films is reduced [3,4]. Recently, there has been a great deal of interest in the application of ferroelectric thin films for tunable microwave devices, such as electrically tunable mixers, delay lines, filters, capacitors, oscillators, resonators and phase shifters [5,6]. The electrical properties such as dielectric constant, dielectric loss, and leakage current of BST thin films depend upon the deposition method, composition, dopant, electrode, microstructure, interfacial quality, and thickness of the films [7,8]. sol–gel method offers significant advantages over other film fabrication methods such as purity, homogeneity, stoichiometry control, the ability to coat large and complex area substrates and ease of processing. In the preparation of BST thin films, the sol–gel method has been extensively employed. In this paper, we report a BST single layer with the thickness of 200 nm prepared by sol–gel processing. The microstructure and electrical properties of the films are studied.

2. Experimental methods

In this experiment, barium acetate $Ba(CH_3COO)_2$ (purity $\geq$ 99%, Shanghai Chemical Reagent Co.) strontium acetate $Sr(CH_3COO)_2{\cdot}1/2H_2O$ (purity $\geq$ 99.5%, Shanghai Chemical Reagent Co.) and titanium butoxide $Ti(OC_4H_9)_4$ (purity $\geq$ 98%, Shanghai Chemical Reagent Co.) were used as starting materials. Glacial acetic acid and 2-methoxyethanol were selected as solvents, respectively. To completely eliminate the water associated with strontium acetate, 99.5% pure $Sr(CH_3COO)_2{\cdot}1/2H_2O$ was dried at about 70 °C for 24 h. The barium acetate and the strontium acetate were dissolved in a heated acetic acid with a ratio of 7:3. The solutions were then mixed and stirred. The titanium butoxide was added into the mixture with addition of moderate acetylacetone (AcAc), 2-methoxyethanol, 1,4-dioxane and adipic. The high boiling point of acetylacetone (AcAc) and 1,4-dioxane or adipic acid retain the atom mobility and significantly reduce the tendency to crack. pH value was adjusted using glacial acetic acid to remain in

* Corresponding author. Fax: +86-21-659-5179.
E-mail address: yangxiaojing@fmrl.ac.cn (X. Yang).

0272-8842/$30.00 © 2004 Elsevier Ltd and Techna Group S.r.l. All rights reserved.
doi:10.1016/j.ceramint.2003.12.122

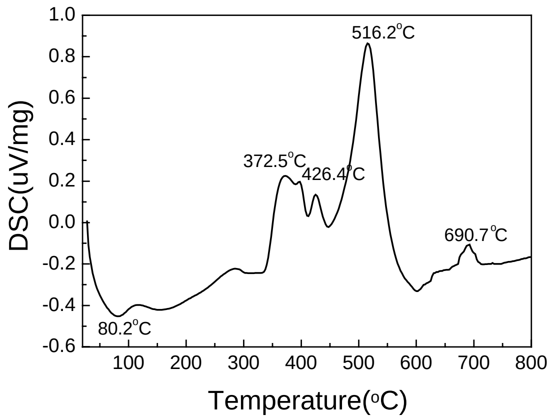

Fig. 1. DSC curve of $Ba_{0.7}Sr_{0.3}TiO_3$ xero-gel precursor.

the range of 2–4. The solutions were refluxed in a reflux condenser at a temperature of about 50 °C for 3 h to obtain clear solution. The resultant solution was filtered to form a clear yellow solution. And the solution was stored in sealed bottles for several months without precipitation. The precursor solution was coated on the Pt/Ti/SiO_2/Si substrates. Spin coating was performed using a spinner rotated at a rate of 3000 rpm for 20 s. The as-deposited BST thin films were heated by a three-step heating procedure: first heated at a low temperature of 200 °C for 30 min to dry the gel, then pyrolyzed at 400 °C in air for 60 min and crystallized at about 700 °C in air for 60 min. DSC and TG (DSC/TG NETZSCH STA449C) analyses were carried out in air with a heating rate of 10 °C/min. A F20 filmetrics was used to measure the thickness of the thin film. X-ray diffraction (XRD) profiles were obtained using a D8 advance diffractometer with Cu Kα radiation. To determine the phase formation, the crystallinity, and the orientation of the films, the surface morphology of the film was analyzed by atomic force microscope (AFM). Dielectric measurements were carried out using the metal–insulator–metal (MIM) capacitor configuration. Au top electrode (1 mm diameter) was deposited on the film by direct current sputtering. Dielectric constant–voltage, dielectric constant, and loss were measured using an HP4284 impedance analyzer.

3. Results and discussion

The result of the differential thermal analysis of the $Ba_{0.7}Sr_{0.3}TiO_3$ gel is shown in Fig. 1. It can be seen from Fig. 1 that there is an endothermic peaks at 80.2 °C there are four exothermic peaks at 372.5, 426.4, 516.2 and 690.7 °C, respectively. The endothermic peak at 80.2 °C in DSC curve mostly results from the rapid volatilization of water. The exothermic peaks at 372.5 and 426.4 °C are related to the pyrolysis of organic compound (to produce CO_2 and H_2O). The exothermic peak at 516.2 °C results from the formation of Ti–O–Ti–O$\cdots$[TiO_2]. The end exothermic peak at 690.7 °C is associated with the formation of BST.

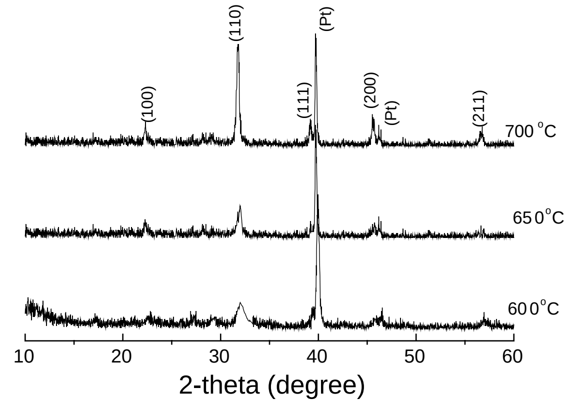

Fig. 2. X-ray diffraction pattern of BST thin film annealed at different temperatures.

Fig. 2 shows the XRD patterns of the films post-annealed at different temperatures. It can be seen from Fig. 2 that partially crystallized films were obtained after annealing at 650 °C, and as the annealing temperature increased, the peak

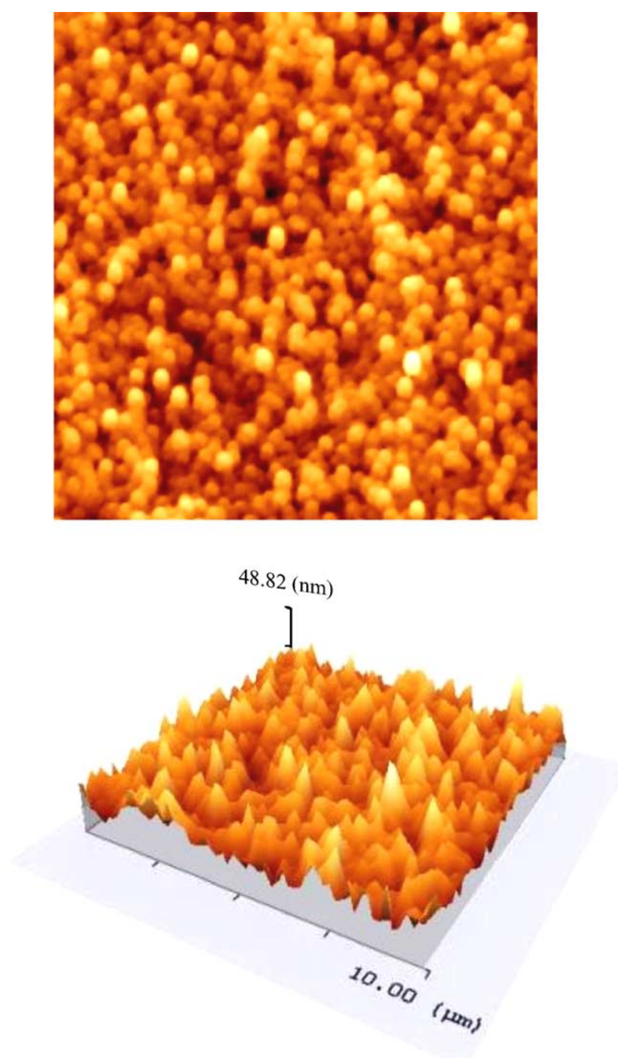

Fig. 3. AFM images of the surface of the $Ba_{0.7}Sr_{0.3}TiO_3$ thin film annealed at 700 °C.

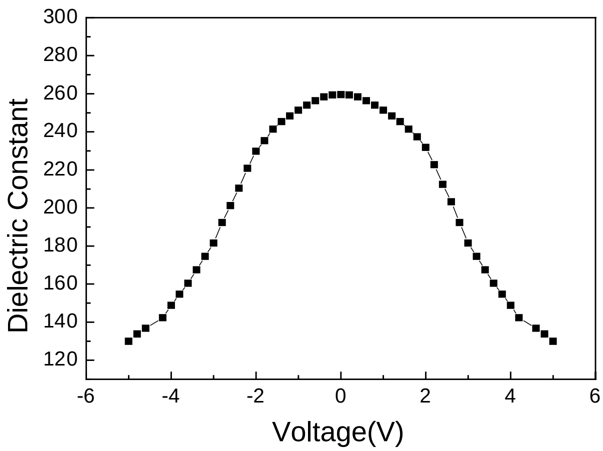

Fig. 4. Dielectric constant–voltage characteristics of the $Ba_{0.7}Sr_{0.3}TiO_3$ thin film at frequency of 100 kHz.

intensity increased. As the annealing temperature increased from 650 °C to 700 °C, all major peaks in its X-ray diffraction patterns are corresponding to the cubic perovskite. This is consistent with the result of DSC analysis see Fig. 1.

Thickness of the films are found to be 200 nm determined by F20 filmetrics. And the refractive index for the BST annealed at 700 °C is about 2.26, which approaches the refractive index (2.3) of microcrystalline BST films [9–11].

Fig. 3 shows the AFM images of the surface morphology of a $Ba_{0.7}Sr_{0.3}TiO_3$ thin film synthesized by sol–gel method and annealed at 700 °C. The film was fully crystallized, dense and crack-free. The $Ba_{0.7}Sr_{0.3}TiO_3$ thin film has a well microstructure.

The dielectric and pyroelectric behavior of $Ba_{0.7}Sr_{0.3}TiO_3$ thin film annealed at 700 °C were measured in a metal–BST–metal configuration with the film sandwiched between the bottom platinum and top Au electrodes. The dielectric constant and dielectric loss for $Ba_{0.7}Sr_{0.3}TiO_3$ thin film at a frequency of 100 kHz were 260 and 0.036, respectively. Fig. 4 shows the dielectric constant–voltage characteristic of the $Ba_{0.7}Sr_{0.3}TiO_3$ thin film at room temperature. Dielectric constant of the thin film was calculated from the capacitance measured at 100 kHz with bias voltage. The dielectric constant was measured while a dc field was -5 V $\rightarrow$ 0 V $\rightarrow$ 5 V. The dielectric constant decreased rapidly from 260 to 130 as the voltage increased from 0 to 5 V.

4. Conclusions

Well crystallized single layer BST film with the thickness of about 200 nm was successfully fabricated by sol–gel technique. From XRD studies, it was confirmed that pre-fired films were amorphous and well-crystallized films were obtained after annealing at 700 °C for 1 h. The phase formation and structure of the deposited films were also confirmed by using an atomic force microscopy (AFM). The dielectric constant and dielectric loss of the single layer of BST films are 260 and 0.036 at 100 kHz, respectively.

Acknowledgements

This work was supported by the Ministry of Sciences and Technology of China though 973-project under grant 2002CB613304, Shanghai Nano Fundamental Committee under contract No. 0152NM038 and the university key studies project of Shanghai.

References

[1] S. Ezhilvalavan, T.-Y. Tseng, Review progress in the developments of (Ba, Sr)TiO_3 (BST) thin films for gigabit era DRAMs, Mater. Chem. Phys. 65 (2000) 227–248.

[2] V.A. Vasiljev, K.A. Vorotilov, Sol–gel derived barium–strontium titanate films, J. Sol–Gel Sci. Technol. 13 (1998) 877–883.

[3] M. Nayak, T.-Y. Tseng, Dielectric tunability of barium strontium titanate film prepared by a sol–gel method, Thin Solid Films 408 (2002) 194–199.

[4] S.U. Adikary, H.L.W. Chan, Compositionally graded $Ba_xSr_{1-x}TiO_3$ thin films for tunable microwave applications, Mater. Chem. Phys. 79 (2003) 157–160.

[5] H.Z. Jin, J. Zhu, P. Ehrhart, F. Fitsilis, C.L. Jia, S. Regnery, K. Urban, R. Waser, An interfacial defect layer observed at (Ba, Sr)TiO_3/Pt interface, Thin Solid Films 429 (2003) 282–285.

[6] M.W. Cole, P.C. Joshi, M.H. Ervin, M.C. Wood, R.L. Pfeffer, The influence of Mg doping on the materials properties of $Ba_{1-x}Sr_xTiO_3$ thin films for tunable device applications, Thin Solid Films 374 (2000) 34–41.

[7] T. Zhang, H. Gu, J. Liu, Structural and optical properties of BST thin films prepared by the sol–gel process, Microelectron. Eng. 66 (2003) 860–864.

[8] Y. Ding, C. Jin, Z. Meng, Investigation on the amorphous–crystalline transition and microstructure of sol–gel derived $(Ba_{1-x}Sr_x)TiO_3$ thin films, Pergamon Mater. Res. Bull. 35 (2000) 1187–1193.

[9] N. Ichinose, T. Ogiwara, Preparation and rapid thermal annealing effect of (Ba, Sr)TiO_3 thin films, Jpn. J. Appl. Phys. 33 (1994) 293–297.

[10] M. Yoshida, H. Yamaguchi, T. Sakuma, Y. Miyasaka, Chemical vapor deposition of (Ba, Sr)TiO_3, J. Electrochem. Soc. 142 (1995) 244–248.

[11] T.S. Kim, M.H. Oh, C.H. Kim, Influences of indium tin oxide layer on the properties of rf magnetron-sputtered (Ba, Sr)TiO_3 thin films on indium tin oxide-coated glass substrate, Jpn. J. Appl. Phys. 32 (1993) 2837–2841.