

Orientation Control and Dielectric Properties of Sol-gel Deposited (Ba,Sr)TiO₃ Thin Films for Room-temperature Tunable Element Applications

Jiwei Zhai and Haydn Chen[†]

Department of Physics and Materials Science, City University of Hong Kong Kowloon, Hong Kong, P.R.C.
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ABSTRACT

The effects of the mole concentrations of precursor solution on the microstructure and dielectric properties of sol-gel deposited Ba_{0.85}Sr_{0.15}TiO₃(BST) thin films have been investigated. The films were of single perovskite phase with strong (100) preferred orientation when grown on LaNiO₃ buffered Pt/Ti/SiO₂/Si substrates using a diluted precursor solution. Variation of the precursor solution concentration resulted in a different microstructure and, in turn, affected the tunability of the sol-gel deposited films. It was observed that leakage currents increased asymmetrically for the negative and positive bias voltage with decreasing thickness. Overall results suggest that those BST films have acceptable properties for applications as room-temperature tunable elements.

Key words : BaSrTiO₃, Thin film, Tunability, Sol-gel deposition, Orientation

1. Introduction

Barium strontium titanate, Ba_xSr_{1-x}TiO₃(BST), is a solid solution compound that exhibits paraelectric or ferroelectric properties depending on the specific composition and temperature.¹⁾ The dielectric constant of BST can also be controlled electrically by applying a Direct Current(DC) electric field bias across it. Field dependent dielectric constant of BST may be exploited for Radio Frequency(RF) and microwave tunable filter applications. BST films have been fabricated with different Ba contents, or different ratios of BaTiO₃ to SrTiO₃, by various thin-film deposition techniques such as sputtering,²⁾ Metal-Organic Chemical Vapor Deposition(MOCVD),³⁾ Pulse Laser Ablation(PLD)⁴⁻⁷⁾ and sol-gel processing.⁸⁻¹⁰⁾ Compared with other deposition methods, the sol-gel process offers some advantages, such as the relatively low processing temperatures, composition homogeneity, precise control of composition, and large area deposition. However, most published works on sol-gel derived BST films have been concerned with film thickness greater than 400 nm.⁸⁻¹⁰⁾

In this paper, we report on the Ba_{0.85}Sr_{0.15}TiO₃ thin films deposited on LaNiO₃(LNO) as a buffer layer of the underlying Pt/Ti/SiO₂/Si substrates. The use of LNO buffer layer provides an excellent template facilitating the grain-on-grain growth so that highly oriented thin films with much improved properties are realized. Microstructure character-

ization and dielectric behavior of those highly <100> oriented BST thin films have been carried out to investigate the influence of different concentration of precursor solution.

2. Experimental Procedures

The BST thin films were prepared by sol-gel processing. The starting materials were barium acetate Ba(CH₃COO)₂, strontium acetate Sr(CH₃COO)₂, and titanium (IV) isopropoxide. Glacial acetic acid, 2-methoxyethanol, and ethylene glycol were used as the solvent and polymerizing agents, respectively. Barium acetate and strontium acetate were mixed in a ratio according to a predetermined number, and then dissolved into heated glacial acetic acid. This was followed by addition of titanium isopropoxide under constant stirring. The mixture was added with ethylene glycol as a stock solution. An exemplified composition used in this study was Ba_{0.85}Sr_{0.15}TiO₃. The spin-on solutions were prepared by diluting the stock solution with equi-volume amounts of glacial acetic acid and 2-methoxyethanol to obtain 0.1 M, 0.3 M, and 0.6 M in concentration.

The thin films were deposited on the highly oriented LaNiO₃ buffered Pt/Ti/SiO₂/Si substrates by spin coating of the dilute solution at 4000 rpm for 30 s. The thickness of LaNiO₃, Pt, Ti, and SiO₂ are 150 nm, 150 nm, 50 nm, and 150 nm, respectively. Before BST deposition, the LNO covered substrates were undergone a heat treatment at 800°C for 30 min. The wet films were dried in air at 500°C on a hot plate for 5 min before the final anneal at high temperature of 700°C for 30 min to crystallize the amorphous films. The desired film thickness was achieved by repeated spin coat-

[†]Corresponding author : Haydn Chen

E-mail : aphchen@cityu.edu.hk

Tel : +852-2788-7831 Fax : +852-2788-7830

ing-drying-annealing process. For this report the final thickness of the BST films are 210 nm, 280 nm, and 680 nm, for precursor solution of 0.1 M, 0.3 M, and 0.6 M concentration, respectively.

X-ray diffraction (XRD; SIEMENS D-500 powder diffractometer) was employed to identify the crystalline phase. The film thickness and the surface morphology were determined using a Field-Emission Scanning Electron Microscope (FESEM). For electrical measurements top gold electrodes of 200×200 μm² were deposited by DC-sputtering. The current-voltage (I-V) characteristics were measured using a HP 4140B. The Capacitance-Voltage (C-V) and Capacitance-Frequency (C-F) characteristics were measured using an Agilent 4284A LCR meter. The sample temperature was varied by using a hot stage during the electrical property measurements. All experimental data reported in this paper represent averages of at least three specimens.

3. Results and Discussion

Fig. 1 shows the XRD θ-2θ patterns for the BST thin films prepared with three different concentrations of the precursor solution after annealing at 700°C. It is evident that all films exhibit a single perovskite phase. When a dilute precursor solution with the concentrations of 0.1 M was used, films showed a strong <100> preferred orientation were shown. It is envisaged that for sufficiently dilute spin-on solution, the single-coated layer is very thin (e.g. ~8.5 nm for 0.1 M layer) and the condensation rate is low, therefore local grain-on-grain, or homoepitaxy, grown at the interface between the new coating layer and the former coated layer would occur, thus resulting in highly preferred orientation.¹¹ On the other hand, when the precursor solution concentration is higher, each spin-on layer becomes thicker (~30 nm for 0.3 M, ~110 nm for 0.6 M) because of the more abundant supply of molecules. Consequently, random nucleation would occur, giving rise to polycrystalline orientation.^{9,12}

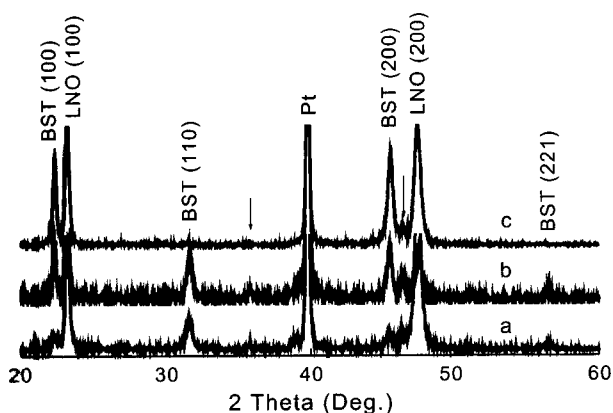


Fig. 1. XRD θ-2θ patterns of sol-gel deposited Ba_{0.85}Sr_{0.15}TiO₃ thin films prepared from (a) 0.6 M, (b) 0.3 M, and (c) 0.1 M precursor solution. All samples were undergone annealing at 700°C for 30 min. Arrows indicate the substrate peaks.

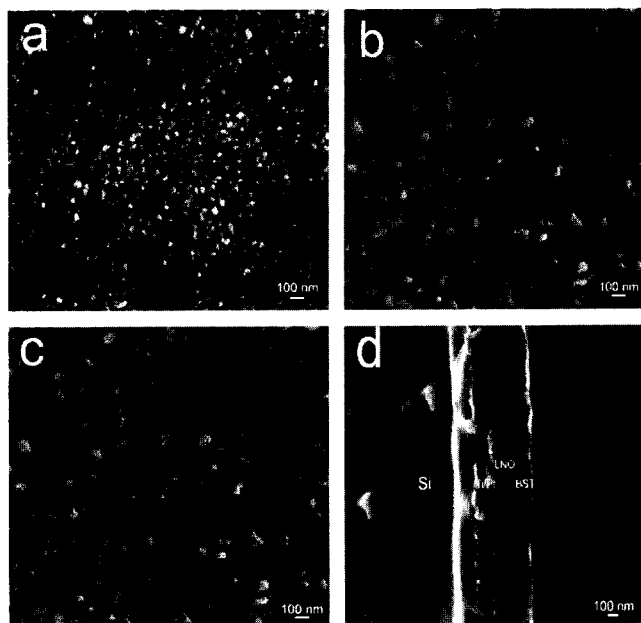


Fig. 2. FESEM micrographs of sol-gel deposited Ba_{0.85}Sr_{0.15}TiO₃ thin films prepared from (a) 0.6 M, (b) 0.3 M, and (c) 0.1 M precursor solution, and (d) the cross sectional morphology of (c). All samples were undergone annealing at 700°C for 30 min.

Fig. 2 shows FESEM images of the sol-gel deposited Ba_{0.85}Sr_{0.15}TiO₃ thin films from (a) 0.6 M, (b) 0.3 M and (c) 0.1 M precursor solution, and (d) the cross sectional morphology of (c); all films have subjected to a final anneal at 700°C. BST thin films prepared with 0.6 M solution have the grain sizes about 30–50 nm, whereas larger grain sizes of about 100–150 nm were found in the other two cases. Presumably the highly oriented grains in the LNO buffer layer could serve as a template for the subsequently deposited crystalline BST film. Fig. 2(b) and 2(c) also show that the regions of voids are filled with aggregates of smaller grains (<50 nm). After a post-deposition annealing at higher temperature (>800°C), the grain size has increased to ~400 nm, similar to the case previously reported by Chang *et al.*⁷

The difference in the leakage current characteristics is shown in Fig. 3. There is one order of magnitude difference between films prepared with 0.1 M concentration and those with the other two cases, which is due to the enhanced ionic polarization and improved crystallinity with larger grain size and <100> preferred orientation. The films with larger grain sizes and more aligned grain configurations have overall shorter conduction paths along the grain boundaries, which causes an increase in the leakage current. The leakage current characteristics are noticeably different in the positive and negative voltage region. This asymmetry of the J-V characteristic is due to the non-identical top and bottom electrode work functions at the two interfaces, consistent with previous reports.^{13,14} It is generally known that the Schottky barriers at the top Au/BST electrode and the bottom BST/LNO interfaces control the leakage current of

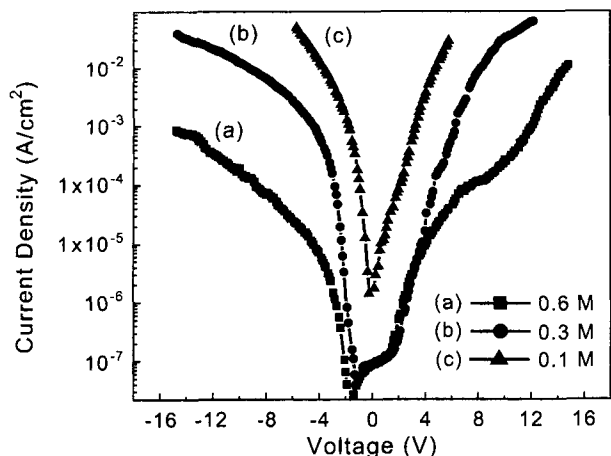


Fig. 3. J-V characteristics of sol-gel deposited $Ba_{0.85}Sr_{0.15}TiO_3$ thin films prepared from (a) 0.6 M, (b) 0.3 M, and (c) 0.1 M precursor solution. All samples were undergone annealing at 700°C for 30 min.

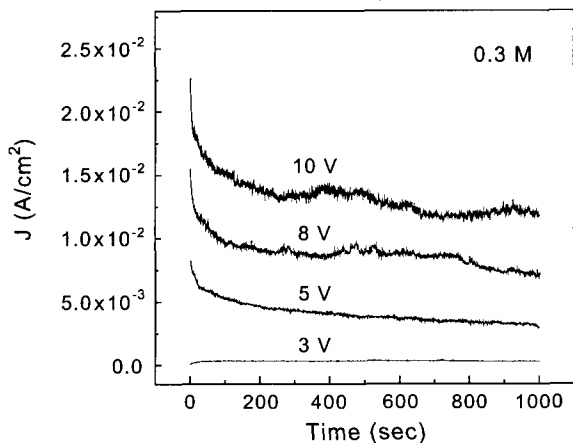


Fig. 4. Current-time characteristics of the $Ba_{0.85}Sr_{0.15}TiO_3$ thin films prepared from 0.3 M precursor solution measured at various DC bias voltages.

Au/BST/LNO capacitor configuration. Therefore, unless these potential barriers are identical, asymmetric J-V characteristics are expected.

The J-T characteristics, i.e., current density versus time, of the some BST films were also tested at room temperature. Fig. 4 shows some of those results. Under the various applied DC biases, the film displayed a typical dielectric relaxation in the initial time regime, which sustained for about 1000 s without resistance degradation or breakdown.

Fig. 5 shows the tuning of the capacitance as a function of applied DC voltage for BST thin films, measured at 22°C and 1 MHz. The loss tangent measurements as a function of bias voltage gave curves of similar shape to the tuning curves. The loss tangent characteristics are different in the positive and negative voltage region, especially for the 0.1 M and 0.3 M solution deposited thin films. The asymmetry in the $\tan\delta$ -V characteristic is also due to the non-identical top and bottom electrode work functions at the two interfaces. This phenomenon implies that the interfaces cast a larger

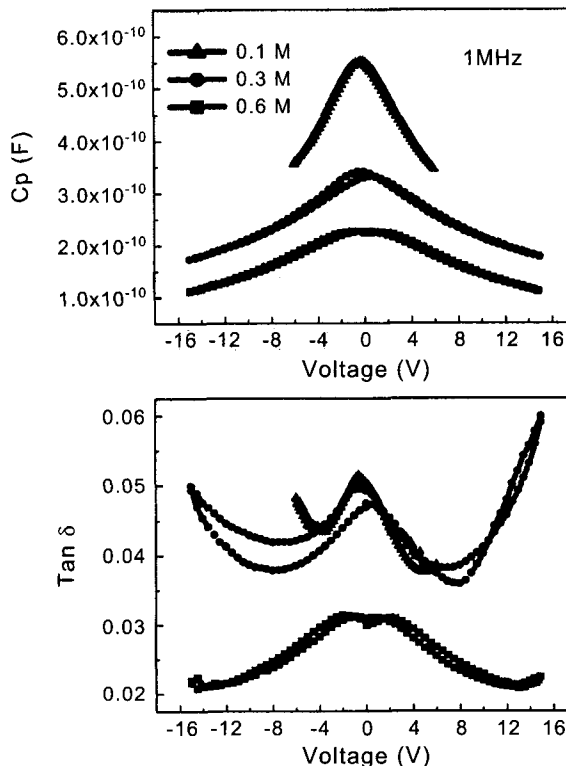


Fig. 5. Variation of the capacitance with applied DC electric field for the $Ba_{0.85}Sr_{0.15}TiO_3$ thin films prepared from 0.6 M, 0.3 M, and 0.1 M precursor solution (measurement temperature was 22°C). All samples were undergone annealing at 700°C for 30 min.

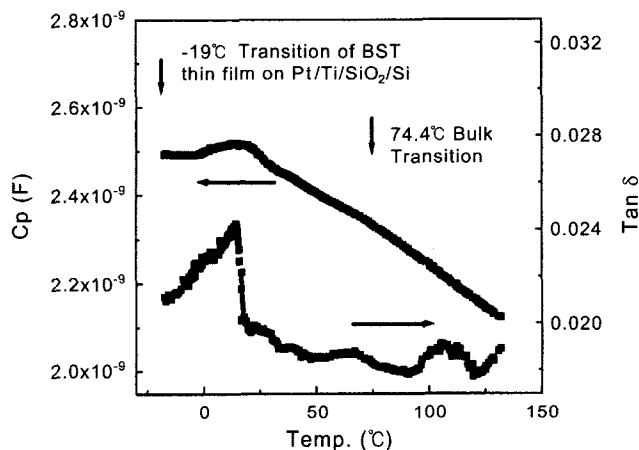


Fig. 6. The capacitance of BST thin film (0.1 M solution deposited) as a function of temperature (measurement frequency was 10 kHz).

effect on the asymmetry. From Fig. 5, we obtained the amount of room temperature tuning as 49%, 24%, and 27% for 0.6 M, 0.3 M, and 0.1 M solution deposited thin films at 1 MHz, respectively, but with lower applied DC voltage. The 30% tuning can be achieved with a DC bias of 4 voltages for the 0.1 M solution deposited thin films.

The capacitance of BST thin films (0.1 M solution deposited) as a function of temperature is shown in Fig. 6. The

temperature corresponding to the peak capacitance of the film (15°C) is higher than the corresponding BST thin films (-19°C) deposited by the same sol-gel processing but on Pt/Ti/SiO₂/Si substrates; they are all lower, however, than the corresponding bulk Curie temperatures (74.4°C).¹⁰⁾ A possible explanation for these T_{\max} shifts could be the presence of the strain accumulated within the BST films.^{15,16)} Film strain may be originated from several sources including the deposition process, lattice mismatch, and thermal expansion mismatch.

The Curie temperature of BST film shown in Fig. 6 is near room temperature; the ferroelectric transition is broad over some temperature range. As a result, room temperature P-E curves still display a slim hysteresis loop as demonstrated in Fig. 7 for films prepared from three precursor solution concentrations. On the other hand, because of increased

leakage for films prepared with 0.3 M and 0.1 M solution it is not uncommon to these P-E curves in Fig. 7(b) and 7(c) that are not fully saturated. Consequently the seemingly hysteresis effect could be the manifestation of leakage loss.

4. Conclusions

The sol-gel derived Ba_{0.85}Sr_{0.15}TiO₃ thin films were prepared with 0.6 M, 0.3 M, and 0.1 M concentrations of spin-on precursor solution. These films show single perovskite phase. For films grown on LaNiO₃ buffered Pt/Ti/SiO₂/Si substrates using 0.1 M precursor solution a strong texture with highly (100) preferred orientation were obtained. Thin BST films (<210 nm) show Curie transition below the room temperature; a 30% tuning is attainable with only the application of 4 DC voltages. The leakage currents of thin films increase asymmetrically for the negative and positive biased voltage with decreasing thickness. This asymmetry is due to the non-identical top (Au metal electrode) and bottom electrode (LaNiO₃ oxide electrode) work functions at the two interfaces.

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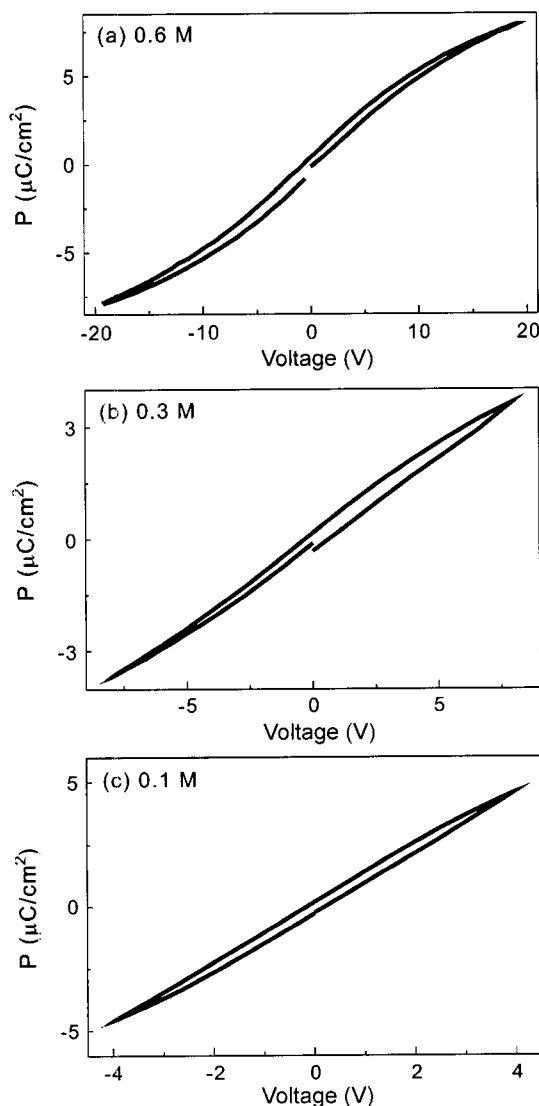


Fig. 7. Room temperature P-E curves of sol-gel deposited Ba_{0.85}Sr_{0.15}TiO₃ thin films prepared from (a) 0.6 M, (b) 0.3 M, and (c) 0.1 M precursor solution. All samples were undergone annealing at 700°C for 30 min.

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