

## Barium strontium titanate nanocrystalline thin films prepared by soft chemical method

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Available online 24 April 2007

### Abstract

Barium strontium titanate ( $\text{Ba}_{0.65}\text{Sr}_{0.35}\text{TiO}_3$ ) nanocrystalline thin films, which were produced by the soft chemical method, were crystallized at low temperature using a domestic microwave oven. A SiC susceptor were used to absorb the microwave energy and rapidly transfer the heat to the film. Low microwave power and short time have been used. The films obtained are crack-free, well-adhered, and fully crystallized. The microstructure displayed a polycrystalline nature with nanograin size. The metal-BST-metal structure of the thin films treated at 700 °C show good electric properties. The ferroelectric nature of the BST35 thin film was indicated by butterfly-shaped  $C-V$  curves. The capacitance–frequency curves reveal that the dielectric constant may reach a value up to 800 at 100 kHz. The dissipation factor was 0.01 at 100 kHz. The charge storage density as function of applied voltage graph showed that the charge storage densities are suitable for use in trench type 64 Mb ( $1-5 \mu\text{C}/\text{cm}^2$ ) and 265 Mb ( $2-11 \mu\text{C}/\text{cm}^2$ ) DRAMs.

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**Keywords:** BST; Films; Microwave processing; Dielectric properties; Capacitors

### 1. Introduction

Ferroelectric materials have been extensively studied in thin film form, mainly for application as multilayer ceramic capacitors (MLCCs) and dynamic random access memories (DRAM). Among the many types of ferroelectric materials, the barium strontium titanate (BST) has been the most intensively investigated because of its high dielectric constant, low dielectric loss and good thermal stability.<sup>1-4</sup> Moreover, the temperature range in which the ferroelectric behavior exists can be easily controlled by adjusting the barium-to-strontium ratio. However, the electrical properties of BST materials are closely linked to their microstructural feature and fabrication process.<sup>5-8</sup> Their manufacturing technology is known to have a strong effect on the structural and properties of ceramics and thin films: the size and shape of grains, the domain size and the atomic structure of grain boundaries.

In recent years, authors have been reported that the properties of nanostructures differ from that bulks due to small sizes and large surface-to-volume ratios.<sup>9,10</sup> So, aiming to obtain

better electrical properties, the study of the nanoscaled ferroelectric materials has attracted immense attention. Novel synthesis and heat treatment techniques have been developed. Among them, wet chemical method, which is usually inexpensive, can be conducted at low temperatures and still offers good compositional and structural control of the products, is particularly suitable for making nanostructured ferroelectric oxides. Recently, nano-powders and nanostructured thin films of BT have been fabricated by means of wet chemical methods in literature.<sup>11-15</sup>

However, a factor that has critical influence on the structure and property of the materials is the temperature of heat treatment. A higher temperature improve the crystallinity and electrical properties of the material but also lead to a higher level of processing inconvenience and more difficulties in the grain size control. Continuous effort has been seen in literature to developed techniques for making high quality nanostructures at lower temperatures.<sup>16,17</sup>

A new tool for high-temperature processing of materials, microwave energy, has been developed in recent years. Much attention has focused on this technology due to advantages it offers with microwave processing, including reduced processing costs, higher quality production, new materials and products, etc.<sup>18-20</sup>

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This work investigated microwave energy as a rapid thermal route for the crystallization of BST films, with the advantage of reducing the time and temperature of thermal treatments and aiming to avoid the grain growth.

## 2. Experimental

The BST films were prepared with a chemical solution, whose flow chart describing the  $\text{Ba}_{0.65}\text{Sr}_{0.35}\text{TiO}_3$  precursor solution and thin film processing is showed in Fig. 1. Titanium (IV) isopropoxide (AlfaAesar, 99.999% purity), barium carbonate (Aldrich, 99.999% purity), strontium carbonate (Aldrich, 99.9% purity), ethylene glycol (Labsynth, 99.5% purity) and citric acid (Merk, 99.9% purity) were used as raw materials. Aqueous solution of titanium citrate was prepared separately by dissolution of titanium (IV) isopropoxide in a citric acid solution heated at 60 °C under constant stirring. After total dissolution, ethylene glycol was added and the temperature was kept at 120 °C for 3 h. The Ti content was gravimetrically determined as  $\text{TiO}_2$ .

Stoichiometric amounts of  $\text{BaCO}_3$  as salt, and  $\text{SrCO}_3$  dissolved in water with  $\text{HNO}_3$  were added to this titanium citrate solution. Ammonium hydroxide ( $\text{NH}_4\text{OH}$ ) was added drop by drop into the constantly stirred solution until the pH reached 3–4. After the solution became homogeneous, ethylene glycol was added as a second solvent. The molar ratio metal/citric acid/ethylene glycol was chosen as 1/4/8. A polymeric resin was obtained by reaction of the metallic citrates with the ethylene glycol. The viscosity of the solution was adjusted by water evaporation until it reached 20 MPa s.

The films were deposited onto Pt/Ti/ $\text{SiO}_2$ /Si substrates by spinning the deposition solution at 4000 rev./min for 30 s. After deposition, the films were treated in a conventional furnace at 400 °C for 2 h to eliminate any remaining organic material. Then,

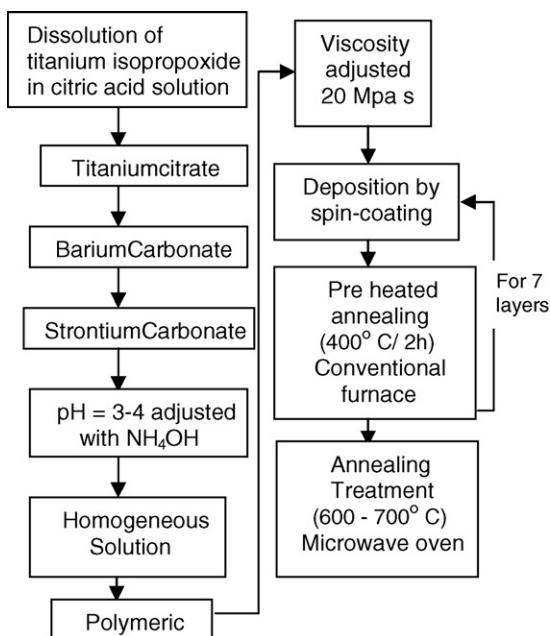


Fig. 1. Flow-chart illustrating the procedure for the preparation of  $\text{Ba}_{0.65}\text{Sr}_{0.35}\text{TiO}_3$  precursor solutions and thin films.

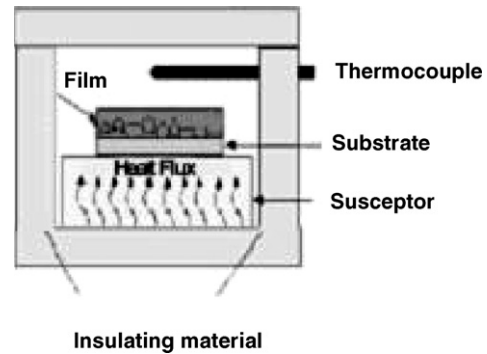


Fig. 2. Schematic arrangement for the film crystallization inside the microwave oven.

the films were crystallized at 600, 650 and 700 °C for 15 min in a domestic microwave oven using a SiC susceptor, which absorbs the microwave energy and rapidly transfers the heat to the film. No post annealing treatment was performed after crystallization. The desired thickness was obtained by several cycles of deposition and annealing treatment.

The schematic arrangement for the film crystallization inside the microwave oven was published by Zanetti et al.<sup>17</sup> and is showed in Fig. 2. Briefly, the film was placed over the SiC susceptor, which was coupled to a thermal insulator. The temperature was measured with a K-type thermocouple placed 4 mm above the film, and the oven's heating rate was 100 °C/min. The film was cooled at the rate allowed by the susceptor and the insulating material. A thermocouple thermometer (FLUKE, 54 II) was used to determine the heating profile in each case.

After crystallization, the films were characterized by X-ray diffraction using a BraggBretano diffractometer (Siemens D-5000) and  $\text{Cu K}\alpha$  radiation to monitor the phase evolution. Atomic force microscopy (AFM) (Digital, NanoScope 3A) was used to examine the films' surface morphology and microstructure.

For the electrical measurements, Au upper electrodes, each with a nominal area of  $7.07 \times 10^{-4} \text{ cm}^2$ , were sputter deposited through a shadow mask. Before taking the electrical measurements, the Au/BST/Pt was annealed at 200 °C for 30 min to improve the electrode/film contact. The capacitance–voltage ( $C$ – $V$ ) properties were characterized using an impedance analyzer (Model 4194A, Hewlett Packard), with the capacitance value measured using a small ac signal of 10 mV at 100 kHz. The dielectric constant and dissipation factor were measured as a function of frequency using a frequency range of 100 Hz to 10 MHz. All the measurements were taken at room temperature.

## 3. Results and discussion

Fig. 3 shows the XRD patterns for the films treated at 600, 650 and 700 °C in the microwave oven. As can be seen, even at 600 °C the film displayed a well-crystallized perovskite phase. No significant changes were observed as the temperature rose to 700 °C. The films were polycrystalline without preferential orientation, and no secondary phase was detected.

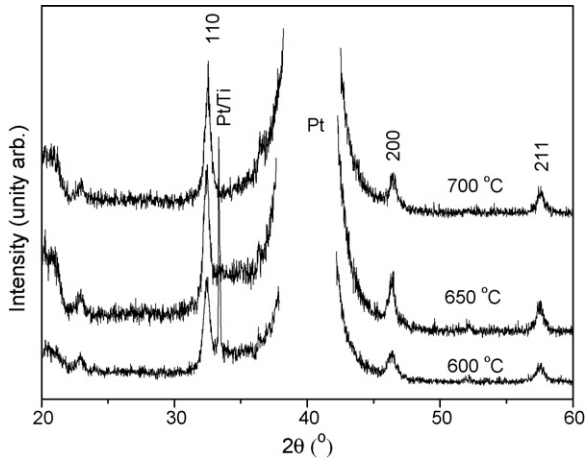


Fig. 3. XRD patterns for the films crystallized at different temperatures in a domestic microwave oven.

In Fig. 4, it was showed the microstructures, observed by AFM, of the films treated for 15 min in the microwave oven at 650 and 700 °C. The films showed a nanograin size structure even when treated at 700 °C. However, as the temperature increased to 700 °C, the grain size range increase from 16 to 35 nm to 60–80 nm and the surface roughness increased from 5.0 to 8.1 nm.

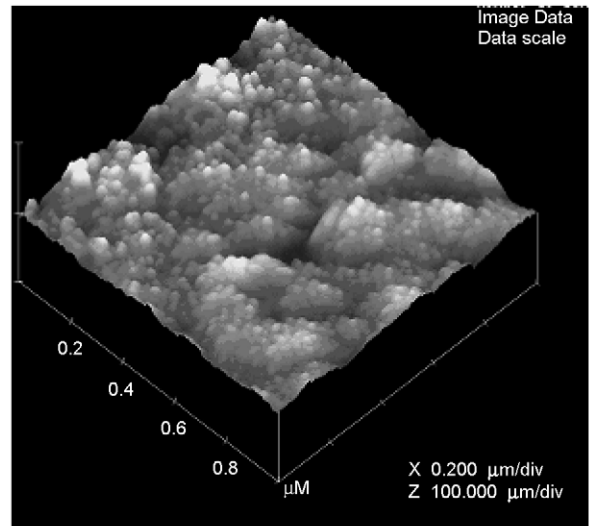
The dielectric and ferroelectric behavior of the Ba<sub>0.65</sub>Sr<sub>0.35</sub>TiO<sub>3</sub> thin films was measured in the metal-BST-metal configuration with the films sandwiched between the bottom platinum and top gold electrodes. The measurements of the dielectric constant and dissipation factor as function of the frequency are showed in Fig. 5. The dielectric constant and dissipation factor values, measured at 100 kHz in the film treated at 700 °C were, respectively, 699 and 0.018. These values were higher than that reported until now in the literature. Considerable dispersion can be observed in the frequency range (from 100 Hz to 10 kHz), which may be attributed to space charges at the film/electrode interface. The high dielectric loss at low frequency in this film confirmed the presence of space charges at the electrode/film interfaces.

The bias voltage dependence of the capacitance was studied in BST thin film. The capacitance–voltage (*C–V*) measurements of the films treated at 700 °C displayed a butterfly-like curve (Fig. 6) characteristic of a ferroelectric material.

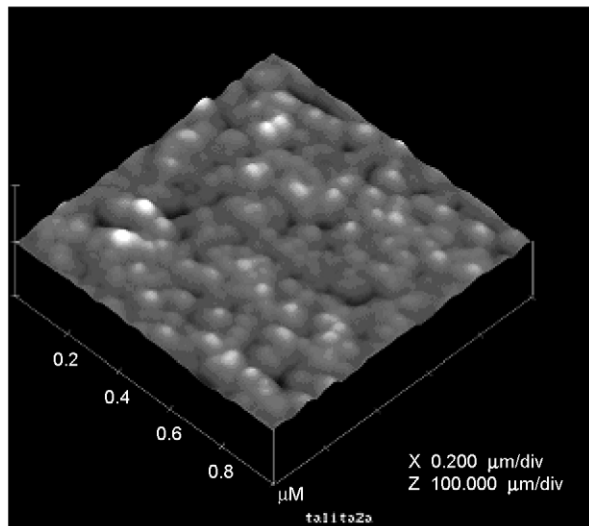
Dielectric material for DRAM applications should have a high charge storage density and a low leakage current density. The charge storage density *Q<sub>c</sub>* of Ba<sub>0.65</sub>Sr<sub>0.35</sub>TiO<sub>3</sub> thin film was estimated from the *C–V* characteristics in Fig. 6, using the relationship

$$Q_c = \epsilon_0 \epsilon_r E,$$

where *E* is the applied electric field,  $\epsilon_0$  the vacuum permittivity, and  $\epsilon_r$  is the dielectric constant of the Ba<sub>0.65</sub>Sr<sub>0.35</sub>TiO<sub>3</sub> film. The charge storage density as a function of applied voltage is shown in Fig. 7. For this relatively great thickness, the charge storage densities are suitable for use in trench type 64 Mb (1–5  $\mu\text{C}/\text{cm}^2$ ) and 256 Mb (2–11  $\mu\text{C}/\text{cm}^2$ ) DRAMs.



(a)



(b)

Fig. 4. AFM images of Ba<sub>0.65</sub>Sr<sub>0.35</sub>TiO<sub>3</sub> films on the Pt/Ti/SiO<sub>2</sub>/Si substrate at different temperatures.

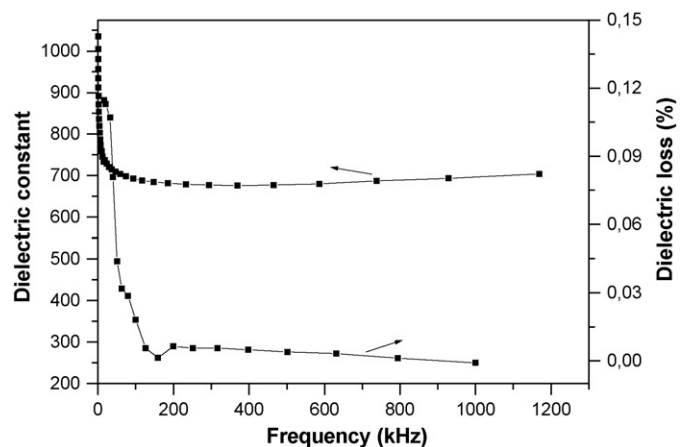


Fig. 5. Dielectric constant and dissipation factor of Ba<sub>0.65</sub>Sr<sub>0.35</sub>TiO<sub>3</sub> thin film as a function of frequency.

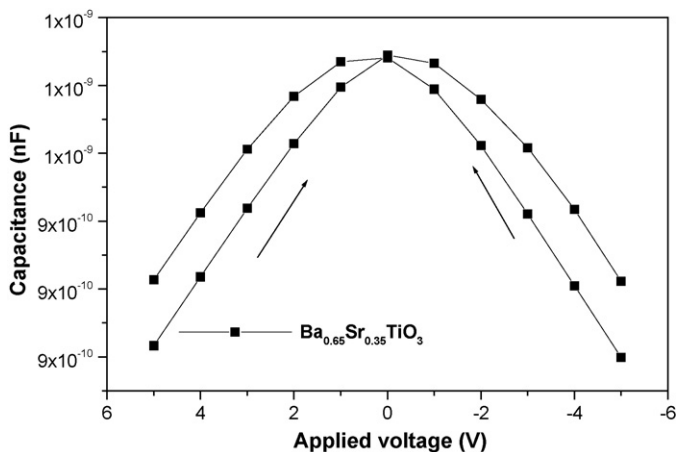


Fig. 6. C–V curves of thin films at the frequency of 100 kHz.

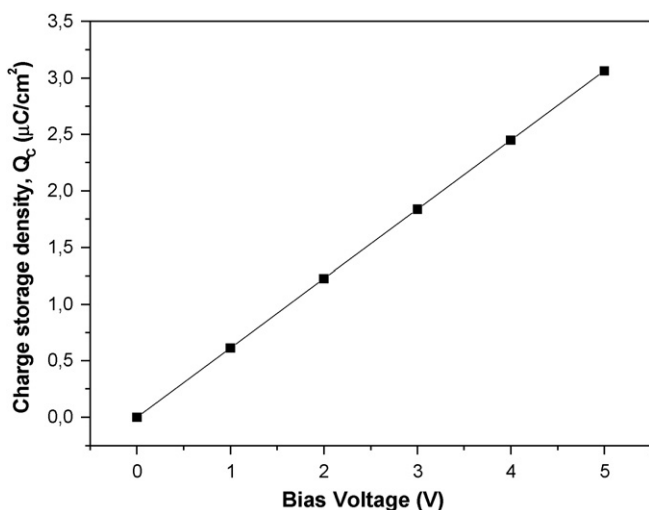


Fig. 7. Charge storage density as a function of applied voltage.

#### 4. Conclusions

BST nanocrystalline thin films were prepared by soft chemical method and crystallized in a short time and lower temperature of heat treatment using a microwave oven. By using these techniques, it is possible to obtain dense and homogeneous films with low investment, short time and good electrical properties.

The dielectric constant and dielectric loss values are similar to the values in the literature, for films heat treatment at least three times less using the microwave oven.

The films prepared are suitable for use in trench type 64 Mb (1–5  $\mu\text{C}/\text{cm}^2$ ) and 256 Mb (2–11  $\mu\text{C}/\text{cm}^2$ ) DRAMs.

#### Acknowledgements

The authors gratefully acknowledge the financial support of the Brazilian financing agencies FAPESP and CNPq.

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