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Systematic investigation of the annealing temperature and composition effects on the dielectric properties of sol–gel $Ba_xSr_{1-x}TiO_3$ thin films

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Abstract

In this work, $Ba_xSr_{1-x}TiO_3$ sol–gel thin films (x = 0.7, 0.5 and 0.3) deposited on Pt/Si substrate and post-annealed at different temperatures have been investigated. A systematic study of the structure, microstructure and dielectric properties has been achieved for each composition. To our knowledge, for the first time, a systematic effect of post-deposition annealing temperature and composition is reported. For each Ba/Sr ratio, higher annealing temperature leads to crystallinity improvement and to grain growth. A shift of the ferroelectric to paraelectric transition toward the bulk Curie temperature with the increase of the annealing temperature is shown. These results are correlated with the increase of the permittivity, tunability and dielectric losses measured on MIM capacitors at low frequency. Moreover, the high frequency results, between 800 MHz and 30 GHz, are in very good agreement with low frequency measurements, and show a huge tunability up to 80% under 600 kV/cm.

Keywords: Films; Grain size; Dielectric properties; $BaTiO_3$ and titanates; Capacitors

1. Introduction

Over the past few years, ferroelectric thin films have been widely considered for tunable microwave devices. A good lead free candidate is $Ba_xSr_{1-x}TiO_3$ (BST), showing a high permittivity, a good tunability, and low dielectric losses. It is well known that downsizing ceramic to thin film, these dielectric properties are affected.

BST thin films can be prepared by several techniques such as MOCVD, RF-magnetron sputtering, pulsed laser ablation and sol–gel processes.[1–4] Among these techniques, sol–gel deposition is of a great industrial interest, using simple equipment and fast process. In addition, it offers some advantages, such as good film homogeneity and stoichiometry and large area deposition.

The main goal for applications is to understand and control the effect of the composition and of process parameters on the properties. Many studies have been carried out concerning the Ba/Sr ratio effect, on the optical properties,[5–8] on nanomechanical characteristics,[9] on the electrical properties[10,11] or dielectric properties at low frequencies[12] and microwave frequencies.[13–15] The most influential process parameter common in many synthesis or deposition techniques is the temperature.[16–18] Wu et al. explored the effect of the annealing temperature for various compositions[19] on the dielectric properties but only at low frequency.

In this paper, a study of the structure, microstructure and of the dielectric properties at low and high frequencies of BST sol–gel thin films deposited by spin coating is presented, in which the effects of post-deposition annealing temperature and composition are investigated. To our knowledge, for the first time,

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a systematic behavior in terms of grain sizes, ferroelectric to paraelectric transitions and dielectric properties of three different $Ba_xSr_{1-x}TiO_3$ film compositions is reported, with $x = 0.7$ (BST70), $x = 0.5$ (BST50) and $x = 0.3$ (BST 30). Radio frequency measurements are also presented: a very high tunability at 10 GHz is reported.

2. Experimental procedure

The $Ba_xSr_{1-x}TiO_3$ precursor sols used in this study were purchased from Mitsubishi Material Corporation, Japan. Thin films of approximately the same thickness were prepared by spin coating using three different compositions with x equal to 0.7/0.5/0.3. The films were deposited on Pt/Si substrate. Each coated layer was pyrolyzed, and the process was repeated in order to obtain the desired thickness. Finally the whole films were post-annealed under oxygen at various temperatures from 600 °C to 800 °C. The phase formation and the film crystallinity were analyzed using a Panalytical X'pert MDP X-ray diffractometer in Bragg–Brentano geometry, with a 40 kV working voltage. The grain size and morphology were investigated by scanning electron microscopy (SEM) using a Nova NanoLab 600 microscope at 15 kV for the top view images, and a JEOL 6700 at 5 kV for the cross section image.

So as to study the dielectric properties at low frequencies of our films, metal–insulator–metal (MIM) structures were formed by depositing top electrodes by RF-magnetron sputtering at room temperature through a shadow mask. These 100 nm thick top electrodes were circular with a diameter of 600 μm. The capacitance–voltage (*C*–*V*) characteristic of MIM capacitors were investigated at room temperature using a Süss Microtec PM5 probe system and a Hewlett Packard 4194A Impedance/Gain Phase Analyzer. The *C*–*V* curves were measured at 100 kHz and 0.1 V AC signal, and the dielectric permittivity was then calculated using capacitance, and the dimensional parameters: the thickness *d* obtained from cross section SEM images, and top electrode areas *A* measured with an optical microscope. The capacitance–temperature (*C*–*T*) characteristics were carried out in a home built measurement cell. The samples were mounted inside a furnace, in a vacuum chamber equipped with a cryogenic cooler. The furnace temperature was regulated with a Eurotherm device and a platinum resistance temperature sensor fixed on the furnace. A second Pt sensor was fixed in the substrate holder to give the sample temperature. The measurements were performed under helium atmosphere providing a good thermal contact. This system can afford a large temperature control range from −200 °C to 150 °C. Capacitance–frequency (*C*–*F*) characteristics were measured with a Wayne Kerr 6500B Impedance Analyzer each 15 s during the sample temperature ramp up rate (0.5 K/min) thereby giving *C*–*T* curves at many frequencies.

The RF properties were investigated on Parallel Plate Capacitors (PPC) shown in Fig. 1. A design consisting of two imbricate gold circle patches as signal and ground electrodes is patterned over BST layer. Two PPCs have been fabricated of dimensions given by:

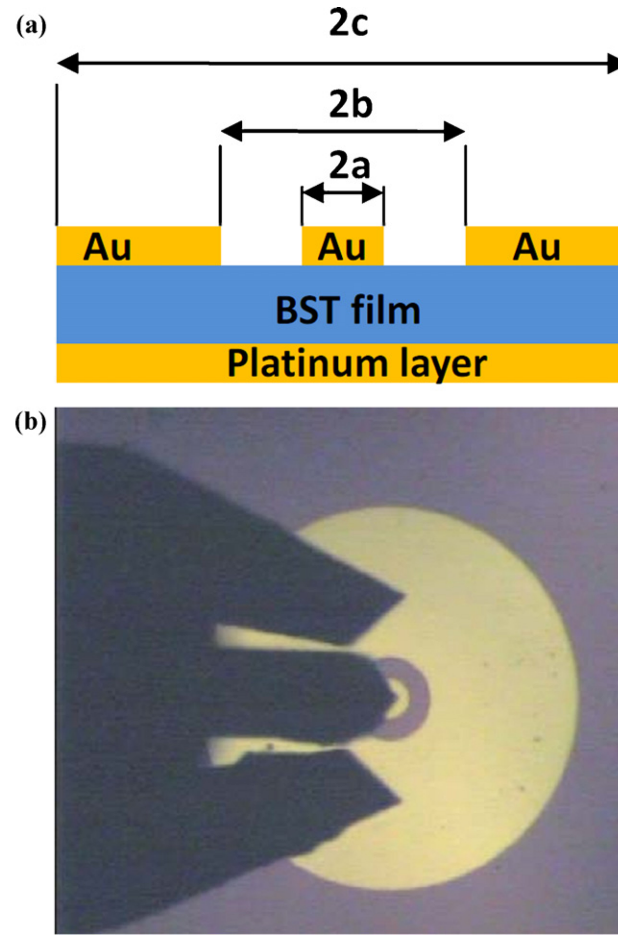

Fig. 1. (a) Layout of the fabricated MIM capacitors for the RF measurements and (b) microscopic top view picture of the structure.

$$\text{Capacitor 1 (Denoted by } C_a) : a_a = 20\,\mu\text{m}, \quad b_a = 60\,\mu\text{m}, \quad c_a = 280\,\mu\text{m}.$$

$$\text{Capacitor 2 (Denoted by } C_b) : a_a = 30\,\mu\text{m}, \quad b_a = 60\,\mu\text{m}, \quad c_a = 280\,\mu\text{m}.$$

These dimensions take into account the RF probes pitch (150 μm) needed to be satisfied for the measurement process (Fig. 1(b)). One port reflection measurements of the parallel plate varactors at frequency ranges from 800 MHz to 30 GHz are carried out by using the Anritsu 37397C vector network analyzer (VNA) and Picoprobes with 150 μm GSG coplanar pitch. The bias voltage is supplied via the internal bias tee of the VNA that allows biasing up to 40 V, while SOLT calibration is used. This method was first proposed by Ma et al.[20] One of the advantages of this test structure is its minimized parasitic R and L, in addition to its easy fabrication.

A simplified model of this PPC may be given as shown in Fig. 2.