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Dielectric Properties of (Ba,Sr)TiO_3 Thin Films for Applications in Electronics

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Abstract. Barium strontium titanate (BST) bulk ceramic was used as target for PLD thin film deposition. In order to avoid stoichiometry modification during the deposition, a more reactive oxidant ambient in the chamber was produced by using a radiofrequency discharge 13.56 MHz, 150 W. Thin films of stoichiometric BST was deposited on alumina substrate with the thickness between 400 and 500 nm heated at 650°C. An aditional anealing was made at 800°C for 6 hours. XRD and SEM were used for sample characterization. Capacity measurements at 100 kHz were performed versus temperature.

Keywords: Barium strontium titanate, film, PLD.

1. Introduction

Ferroelectrics are very attractive materials for a large field of applications. In informatics, they are used in DRAM memories [1, 2]. In the high frequency range, they have high applications potential, due to the nonlinear variation of their permittivity with the applied electric field. This property offer the opportunity to realize the electrically controlled of microwave devices [3, 4]. For this type of applications, materials are in the paraelectric phase in order to avoid high loss in microwave domain and thermal hysteresis.

The dielectric loss in ferroelectrics is not as small as that of common dielectric materials and the loss tangent ($\tan\delta$) is an important characteristic of the material, which should be taken into account in the device design. The temperature dependence of the dielectric permittivity over the operating temperature interval is another important issue: this is of particular concern in the vicinity of the ferroelectric transition temperature, where the material exhibits a strong tuneability, which depends strongly on the temperature.

Barium strontium titanate (BST) ceramics and films have recently received much attention for its high electric-field tunability and low dielectric loss [5–9]. These materials are very promising for practical applications such as phase shifters, delay lines, tunable filters, steerable antennas. To be used in these devices, a BST system must possess the following characteristics: high dielectric constant, high tuneability, low dissipation factor and low temperature dependence.

2. Methods

2.1. BST Target Preparation and Characterization

$Ba_{1-x}Sr_xTiO_3$ ceramic compounds with the molar formula $Ba_{0.5}Sr_{0.5}TiO_3$ (BST) were prepared by standard solid-state reaction. $SrCO_3$, $BaCO_3$, and TiO_2 oxide powders of higher purity than 99.9% were used as starting materials. The BST samples were doped with 1.0 mol. % MgO and 0,5 mol. % MnO_2 in order to improve the granular growth and to control the porous structure [10]. Mixing was carried out for 2 hours in an agate bottle containing agate balls. The mixing-milling media were distilled water. The mixtures were calcinated at T = 1 100°C for 2 hours, crushed, mixed with polyvinyl alcohol (PVA) and then pressed in a cylindrical mold to yield cylindrical pellets. The samples BST were sintered for 2 hours in air at temperatures between 1 220 ÷ 1 320°C.

Structural and morphological analysis was performed on BST samples by using X-ray diffraction (XRD) and Scanning Electron Microscopy (SEM). The values of the dielectric constant ε_r and of losses at microwave frequencies were measured by using the Hakki-Coleman dielectric resonator method [11].

The doped BST ceramic sintered at 1 285°C with good quality from the point of view of morphology, structure and dielectric properties ($\varepsilon_r \sim 1\ 100$ and $\tan\delta \sim 2 \times 10^{-3}$) [12] were selected as target for film deposition.

2.2. Film Deposition

Thin films of BST on platinum coated alumina and sapphire were performed by pulsed laser deposition-PLD and radiofrequency assisted pulsed laser deposition, RF-PLD. The RF-PLD system consists in a clasical PLD system added with a radiofrequency plasma beam source, which is made up by a double-chamber discharge system supplied by a CESAR 1310 RF power generator of 13.56 MHz, and 1 kW maximum power. The discharge is generated in the active chamber in flowing oxygen between two parallel electrodes: it expands into the ablation chamber due to the pressure

gradient as a plasma beam through an aperture performed in the bottom electrode, which acts as a nozzle. This type of system was needed in order to improve the surface roughness and to avoid oxygen vacancies inside the film.

First, with the help of RF-PLD system, a platinum bottom electrode was deposited on sapphire and alumina substrates in radiofrequency argon plasma discharge at 100 W. Next step was to deposit BST on platinum coated sapphire and alumina in radiofrequency oxygen plasma discharge at 100 W. The beam of a Nd:YAG solid-state laser with wavelength 265 nm, pulse length 5 ns and the repetition rate 10 Hz, was focused through a spherical lens on BST ceramic target at 45° incidence. In order to achieve a uniform ablation, the target was simultaneously rotated and translated.

The substrates were heated to the deposition temperature with a ramp of 20°C/min and then after deposition, cooled with 10°C/min, at 150°C for Pt/sapphire thin films and 650°–720°C for BST/Pt/sapphire thin films. The substrates used were placed at a distance of 4–5 cm from the target. The vacuum system allows obtaining a base pressure of about 10^{-6}–10^{-5} mbar before deposition.

The deposited ZST films were annealed *ex situ* for 2 h in a conventional thermal oven, at the 800°C for 6 hours, for crystallization of the deposited layer.

2.3. Film characterization

The characterization of BST thin films was carried out by X-ray diffraction, Scanning Electron Microscopy (SEM) and dielectric measurements.

The structure of BST thin films was investigated by X-ray diffraction (XRD) using a TUR-M62 diffractometer (Cu Ka = 0.1541 nm). The layers morphology was analyzed via Scanning Electron Microscopy (SEM), with a Hitachi S2600 N microscope. The electrical measurements were performed using an Agilent LCR meter. The capacitance-voltage (C-V) characteristics of BST films were recorded using a computer controlled Keithley multimeter at 100 kHz in the temperature range –237 ÷ +27°C. The temperature control was made by using a Cryostat Janis CCS - 400EB.

3. Results

The X-ray diffraction patterns of the BST thin films, deposited on sapphire (BST 1) and alumina (BST 2) substrates, are shown in Fig. 1. The temperature substrate was of 650°C for both BST 1 and BST 2 samples. In addition, the BST 1 sample was post-annealed at 800°C for 6 hours.

The X-ray diffraction patterns of the BST thin films show narrow peaks, proving a good crystallization of the films. After the thermal treatment, a better crystallization degree and a decrease of the amorphous component contribution were obtained. Some peaks, related to the alumina substrate and Pt, are visible on the X-ray diagrams.

The crystallite mean dimension ($\overline{D}$) was calculated from the formula:

$$\overline{D}\ (nm) = k\lambda(nm)/\beta\cos\theta, \tag{1}$$

where β is half of the linewidth (rads), θ is the Bragg angle and k a constant depending

on the crystallites shape. In a spherical coordinate system, $k = 1.0747$ for crystalline plans with Miller indices (hkl) greater than (110). For BST 1 and BST 2 the crystallite mean dimension are given in Table 1.

The lattice constants of thin film samples were determined and compared with the values of the BST target. They correspond fairly very well to the values of $Ba_{0.5}Sr_{0.5}TiO_3$ [10] and are also presented in Table 1.

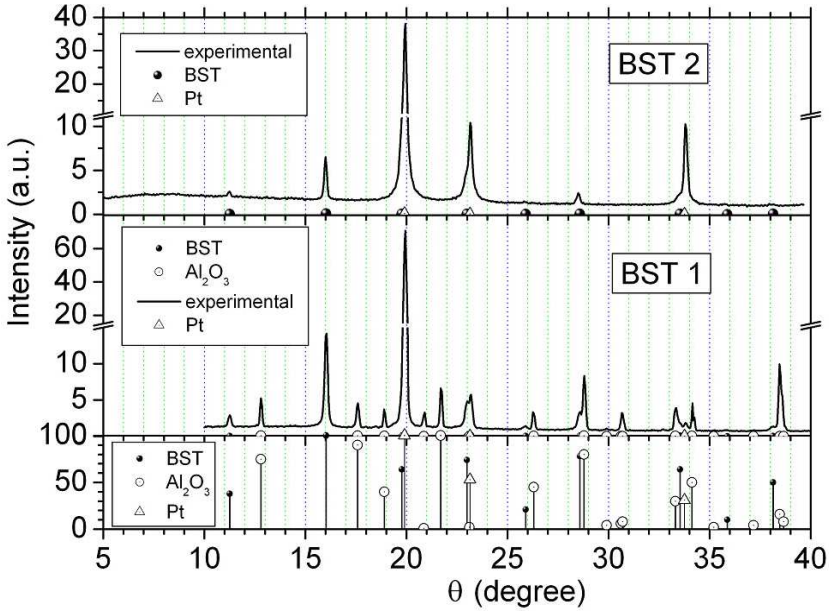

Fig. 1. XRD patterns of BST thin films deposited at 650°C on sapphire (BST 1) and alumina (BST 2).

Table 1. Unit cell parameters and crystallite mean dimension of BST films

Sample	Unit cell constant a_0 [nm]	Unit cell volume V_0 [$\times 10^{-3}$ nm^3]	Crystallite mean dimension $\overline{D}$[nm]
BST 1	0.396	62.09	52
BST 2	0.395	61.63	61

The SEM analysis revealed BST films with rough surface due to the randomly oriented grain morphology as resulting from Fig. 2. The SEM image is for the BST film surface annealed at 800°C at 6 hours. It can be seen submicronic grains, randomly oriented due to the film deposition on the alumina polycrystalline substrate. The majority of grains exhibit spherical shape with sizes in the range of $0.1 \div 0.2$ μm. Few larger cubic well faceted grains with dimension $0.3 \div 0.5$ μm are also present.

Next, copper was evaporated on BST thin film PLD deposited on alumina and a metallic interdigital structure was realized by photolithography. At room temperature, the measured capacitance for this BST interdigital structure was 45.7 pF. In order to focus on the BST effects, the measured values will be normalized in the

following to 30.2 pF, which is the capacitance of the same interdigital structure on alumina, in the absence of BST.

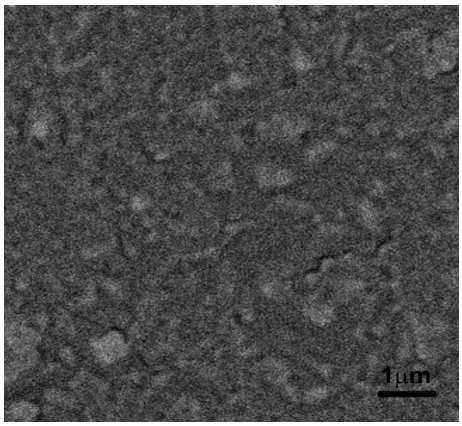

Fig. 2. SEM image of the BST 2 film deposited at 650°C on alumina substrate, annealed at 800°C for 6 hours.

The capacitance of the BST interdigital capacitor was investigated in the temperature range –237°C ÷ +27°C for a frequency of 100 kHz. The maximum value of capacitance due to the BST is 15.5 pF, as can be seen from Fig. 3. Such capacitance variation with the temperature is characteristic for a ferroelectric thin film. The transition temperature of the BST film was measured at –72°C .

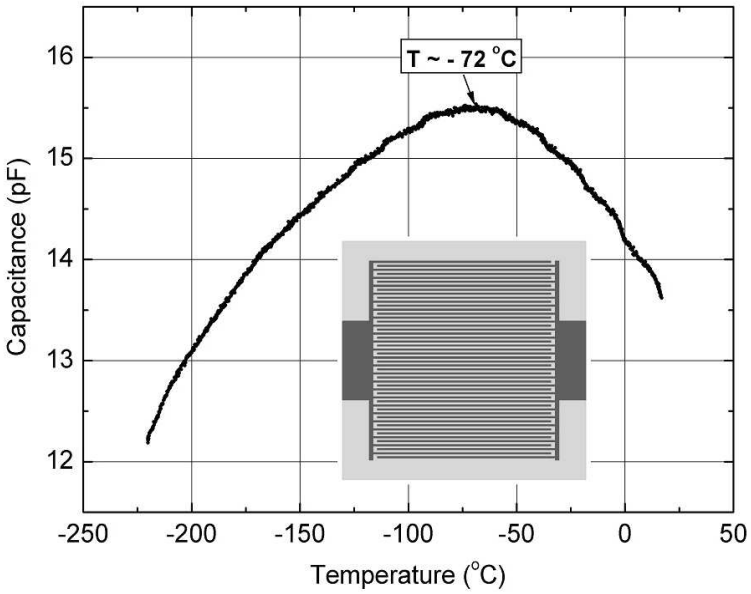

Fig. 3. Capacitance of BST 2 film versus temperature.

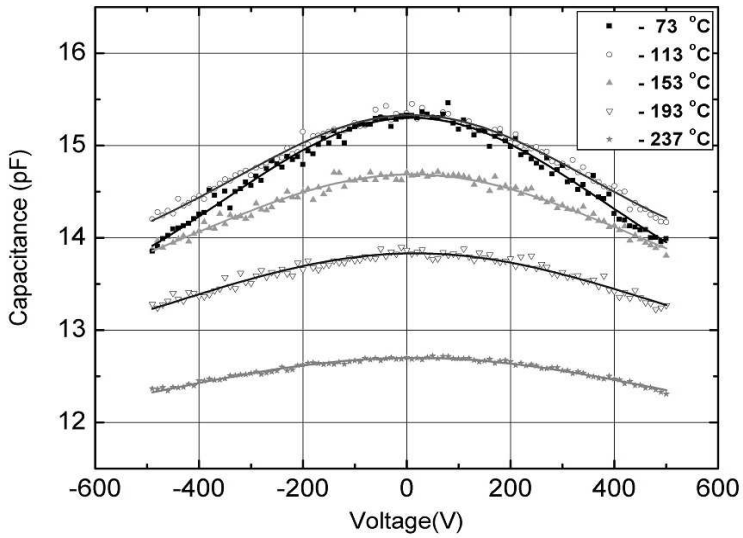

Fig. 4. Capacitance versus voltage of BST 2 film in ferroelectric state.

Tuneability measurements for the structure were performed in the same interval of temperatures: –237°C ÷ +27°C. A DC bias of 500 V was applied to the interdigital structure. The measurements of capacitance variation with the DC bias applied voltage are shown in Fig. 4 and Fig. 5 for 9 values of temperatures.

For the interdigital structure the maximum tuneability for the BST thin film on alumina substrate was obtained in the –113°C ÷ –53°C temperature interval.

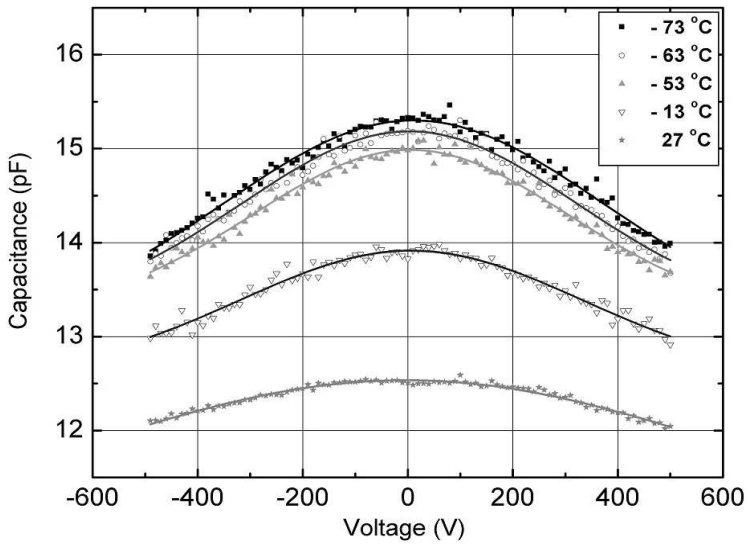

Fig. 5. Capacitance versus voltage of BST 2 film in paraelectric state.

4. Conclusions

BST thin films on alumina and sapphire substrates were obtained by PLD.

Capacitance variation with the temperature indicate a diffuse ferroelectric- paraelectric phase transition with $T_c = -72°C$ for the BST thin film.

Tunability measurements performed on a large temperature interval indicated the maximum tuneability in the range of $-113°C \div -53°C$ for the metal / ferroelectric / metal (MFM) interdigital structure.

The low dimensions of crystallites with a lot of defects per unit volume, could be a possible explanation for the diffuse phase transition and the low tuning of capacitance.

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