Original scientific paper

Informacije MIDEM
Journal of Microelectronics,
Electronic Components and Materials
Vol. 46, No. 3(2016), 136 – 141

Solution-derived $Ba_{0.5}Sr_{0.5}TiO_3$ thin-film capacitors in metal-insulator-metal configuration

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Abstract: The $Ba_{0.5}Sr_{0.5}TiO_3$ (BST 50/50) thin films with the thicknesses ~250 nm were deposited on polycrystalline alumina substrates by Chemical Solution Deposition. The films were prepared by the multi-step annealing process at 750 °C, 800 °C and 900 °C and the effect of the annealing temperature on the phase composition, microstructure and dielectric properties of the films was studied. All BST 50/50 films crystallize in a pure perovskite phase after heating in a rapid thermal annealing furnace. The microstructure of the film annealed at 750 °C is granular with ~30 nm sized grains. As the annealing temperature increases to 800 °C the granular microstructure remains and the average lateral grain size increases to ~70 nm, while the film annealed at 900 °C consists of predominantly columnar grains with the average lateral size ~100 nm. The kHz-range dielectric permittivity increases from 350 for the film annealed at 750 °C to 480 for the film annealed at 900 °C.

Keywords: $(Ba,Sr)TiO_3$; thin films; microstructure; dielectric properties

Tankoplastni kondenzatorji na osnovi $Ba_{0.5}Sr_{0.5}TiO_3$, pripravljenega s sintezo v raztopini, s konfiguracijo kovina - dielektrik - kovina

Izvleček: Tanke plasti $Ba_{0.5}Sr_{0.5}TiO_3$ (BST 50/50) z debelino ~250 nm smo pripravili na podlagah polikristaliničnega aluminijevega oksida s sintezo v raztopini. Vzorce smo pripravili z večstopenjskim segrevanjem pri temperaturah 750 °C, 800 °C in 900 °C in raziskovali vpliv temperature segrevanja na fazno sestavo, mikrostrukturo in dielektrične lastnosti plasti. Ugotovili smo, da vse plasti BST 50/50 kristalizirajo v čisti perovskitni fazi in da je mikrostruktura plasti, segretih pri temperaturi 750 °C finozrnata, s ~30 nm velikimi zrni. Z višjo temperaturo segrevanja, 800 °C, se je povprečna velikost zrn povečala na ~70 nm. Mikrostrukturo plasti, žganih pri 900 °C, sestavljajo pretežno stebričasta zrna s povprečno lateralno velikostjo ~100 nm. Dielektričnost plasti, izmerjena v kHz frekvenčnem območju, se je s povišanjem temperature segrevanja s 750 °C na 900 °C povečala s 350 na 480.

Ključne besede: $(Ba,Sr)TiO_3$; tanke plasti; mikrostruktura; dielektrične lastnosti

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1 Introduction

Barium strontium titanate $Ba_xSr_{1-x}TiO_3$, x=0-1 (BST) is a complex perovskite material, whose phase transition temperature (Curie temperature) from paraelectric to ferroelectric phase is tuned by the Ba/Sr ratio, from ~0 K for x=0 to ~400 K for x=1. Consequently also the dielectric properties of BST are tuned by the composition. In the paraelectric phase, yet close above the Curie temperature, the BST exhibits high dielectric permittivity and tunability, i.e. electric-field dependence of dielectric permittivity, but also low dielectric losses in GHz frequency range, which makes it suitable for the use in tunable microwave devices [1], [2].

In the case of solution-derived thin films different factors such as film thickness, grain size and shape [3–7], porosity [8], residual stress [6], [9], interaction with the electrodes [1], etc., strongly modify the response of the

films and therefore their effect should be considered. For example Sinnamon et al. [10] prepared BST 50/50 thin films with the thicknesses in the range from 15 nm to 1.5 µm by pulsed laser deposition on $SrRuO_3$/MgO substrates. The authors showed that as the film thickness increased from 15 nm to 1.5 µm the respective average lateral grain size increased from 80 nm to 460 nm. Consequently, the dielectric permittivity, measured at 10 kHz, strongly increased from around 50 for the thinnest to 650 for the thickest film. Aygün et al. [7] studied the influence of the annealing process, i.e. one-, two- or multi-step, on the microstructure of ~550-nm-thick $BaTiO_3$ thin films deposited by spin-coating on copper foils. When the films were prepared by one-step annealing, where multiple deposits were annealed only once at 900 °C, the films consisted of a granular microstructure with ~100 nm large grains and fine pores between the grains. The films prepared by the multi-step annealing, where each of many deposits was annealed separately at 900 °C, consisted of a dense and columnar microstructure with the average lateral grain size ~185 nm. The authors found that the change of the granular to the columnar microstructure and a reduced level of porosity strongly influenced the kHz-range dielectric permittivity (measured at room temperature) of the films; the dielectric permittivity increased from ~1500 for the $BaTiO_3$ film with the granular microstructure to above 3000 for the film with the columnar microstructure.

In this work we focused on the preparation of $Ba_{0.5}Sr_{0.5}TiO_3$ (BST 50/50) thin-film capacitors in a metal-insulator-metal configuration on platinized alumina substrates. We studied the influence of the annealing temperature on the phase composition, microstructure and dielectric properties of the films, measured in the kHz range and at room temperature.

2 Materials and methods

The BST 50/50 coating solution was synthesized from the earth-alkaline acetates ($Ba(CH_3COO)_2$, 99.999 %, Alfa Aesar, $Sr(CH_3COO)_2$, 99.81 %, Alfa Aesar) and Ti-butoxide ($Ti(OC_4H_8)_4$, 99.61 %, Fluka). The acetates were dried before use and then dissolved in acetic acid (100 %, Merck) and Ti-butoxide was diluted by the 2-methoxyethanol ($CH_3OCH_2CH_2OH$, 99.3+ %, Sigma Aldrich). The two solutions were mixed for 2 hours at room temperature and the concentration of the solution was adjusted to 0.25 M.

Prior deposition of the films the platinum with the thickness of ~100 nm was RF-sputtered on polished alumina substrates (99.6 %, 3.95 g/cm^3, 25.4 mm x 25.4 mm x 0.26 mm, Coorstek). The BST 50/50 solution was then deposited on the substrates by spin-coating, followed by drying at 200 °C for 2 min and pyrolysis at 350 °C for 2 min. After each deposition-drying-pyrolysis step the films were heated in a rapid thermal annealing furnace (LPT, TM100-BT) at temperatures between 750 °C and 900 °C with the heating rate of 15 K/s. The time of annealing of the first deposit was 15 min, intermediate deposits were annealed for 5 min and the final deposit for 60 min. The deposition-drying-pyrolysis-annealing steps (multi-step annealing) were repeated seven times to reach the final thickness of ~250 nm.

The phase composition of all BST 50/50 thin films was determined by PANalytical X'Pert PRO MPD X-ray diffractometer (XRD) with CuKα1 radiation. The XRD patterns were recorded in a 2θ region from 10 ° to 50 ° with the step of 0.017 ° and the exposure time of 100 s.

The surface and cross-section microstructures of the films were analyzed with a field-emission scanning electron microscope (FE-SEM, JSM-7600F, JEOL). The average lateral grain sizes of the BST 50/50 films were determined by the linear-intercept method based on the FE-SEM surface micrographs.

For investigation of dielectric properties in the kHz frequency range Cr/Au top electrodes with a diameter of 0.4 mm were deposited by magnetron sputtering (5 Pa, Milano, Italy). Capacitance-voltage characteristics, measured at 100 kHz, were recorded with the following DC biasing scheme: 0 V → + 5 V → 0 V→ - 5 V → 0 V.

3 Results and discussion

3.1 Phase composition

The XRD patterns of BST 50/50 films annealed at 750 °C and 900 °C are shown in Figure 1. The platinized alumina substrate is added as a reference. Since the intensities of the substrate are much higher than the intensities of the perovskite BST 50/50 phase, the peaks belonging to the substrate were reduced and are denoted by *. According to the XRD analysis all films (not shown here for the film annealed at 800 °C) crystallize in a randomly oriented perovskite phase. With increasing annealing temperature the intensities of the perovskite diffraction peaks increase and the full width at half maximum decreases, indicating improved crystallinity of the films and larger crystallite sizes.

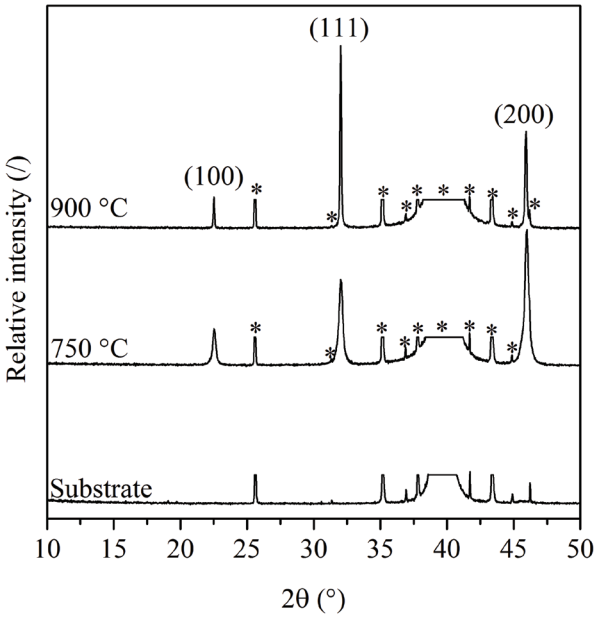

Figure 1: XRD patterns of the BST 50/50 films prepared on platinized alumina substrate at 750 °C and 900 °C. The peaks corresponding to the perovskite phase are denoted with the Miller indices [11]. The pattern of the substrate is also shown as a reference. * - reduced peaks of the substrate.

3.2 Microstructure

The FE-SEM cross-section and plan-view micrographs of BST 50/50 films annealed at temperatures between 750 °C and 900 °C are presented in Figures 2 and 3. The thickness of the film annealed at 750 °C, determined from the cross-section micrograph, is 260 nm and decreases to 210 nm as the annealing temperature increases to 900 °C. The decrease of the film thickness with increasing annealing temperature, shown also in Figure 4, indicates densification of the films.

The film annealed at 750 °C consists of equiaxed grains with the average lateral size of approximately 30 nm. The surface micrograph presented in Figure 3 shows that the microstructure of the film is uniform with some fine pores between the grains. A similar granular microstructure with the grains of a few tens of nm has been commonly observed in the case of the solution-derived $BaTiO_3$, $SrTiO_3$ and BST thin films prepared by one- or two-step annealing processes and forms via predominantly homogenous nucleation mechanism [5], [12], [13].

With increasing the annealing temperature to 800 °C the average lateral grain size increases to approximately 70 nm and the porosity and pore size decrease, as is observed from the surface microstructure of the film in Figure 3. With further increase of the annealing temperature to 900 °C the average lateral grain size increases to almost 100 nm, the microstructure is uniform, dense and predominantly columnar with the grains that extend though the whole film thickness, as is shown in Figure 2. The dependence of the grain size on the annealing temperature is shown also in Figure 4; evidently the microstructure is coarsening in parallel with the enhanced densification, evidenced as the decrease of the film thickness. The dense microstructure of the film annealed at 900 °C is related to the multi-step heat treatment where each deposit is annealed after drying and pyrolysis, which was also reported for solution-derived $BaTiO_3$, $SrTiO_3$ and BST thin films prepared by the multi-step annealing process by different research groups [5], [7], [14], [15].

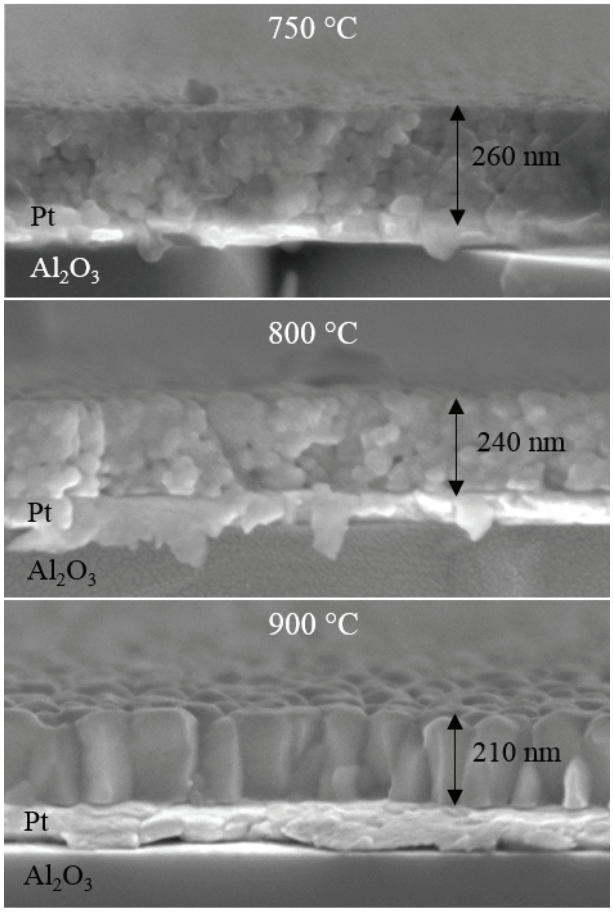

Figure 2: The FE-SEM cross-section micrographs of the BST 50/50 films annealed at temperatures between 750 °C and 900 °C.

3.3 Dielectric properties

Dielectric permittivity and losses of the BST 50/50 thin films annealed at temperatures between 750 °C and 900 °C are plotted in Figure 5. The dielectric permittivity and losses of the BST 50/50 film annealed at 750 °C are 350 and 0.037, measured at 100 kHz and room tem-

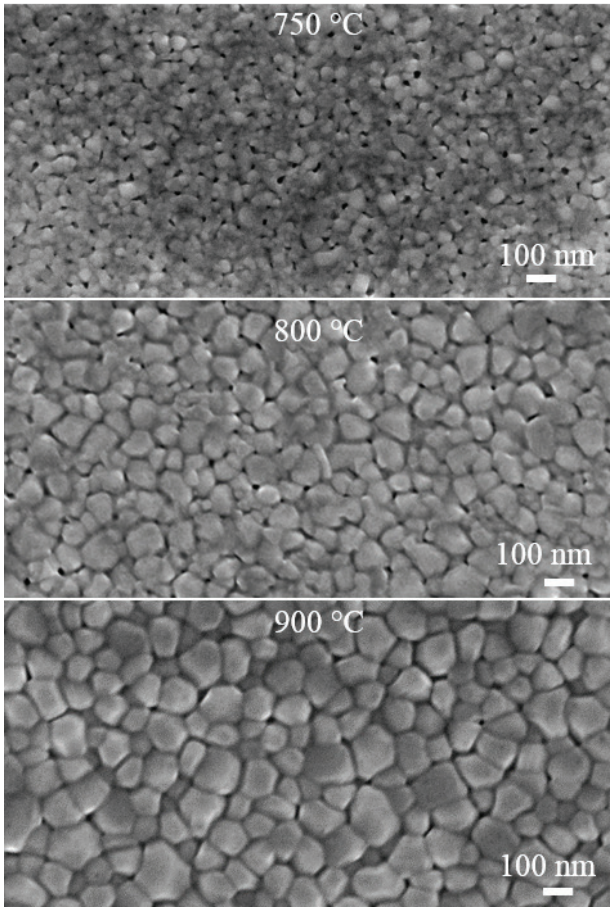

Figure 3: The FE-SEM surface micrographs of the BST 50/50 films annealed at temperatures between 750 °C and 900 °C.

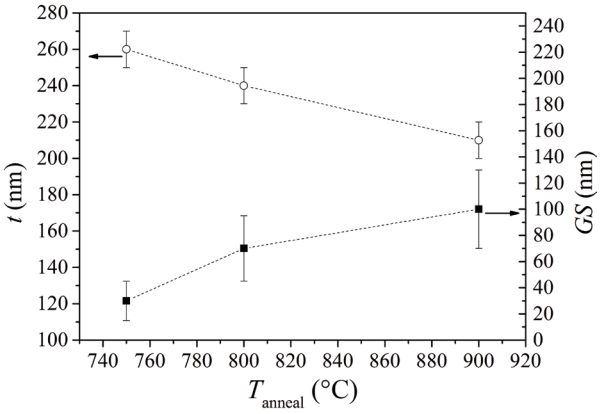

Figure 4: The dependence of the film thickness *t* and grain size *GS* on the annealing temperature T_{anneal} of the BST 50/50 thin films.

perature. With increasing the annealing temperature to 900 °C the dielectric permittivity increases to 480 and the losses remain similar, around 0.042. We connect the increase of the dielectric permittivity of the BST 50/50 films with increasing annealing temperature to the change of the granular and porous to the columnar and dense microstructure of the films, which is consistent with observations from the literature [5], [7], [15].

The voltage / electric-field dependence of the permittivity and dielectric losses of BST 50/50 film, which was annealed at 750 °C, measured at 100 kHz and 300 K, is presented in Figure 6. The tunability, expressed as the ratio of the permittivity at 0 V and 5 V, is 1.3 (23 %).

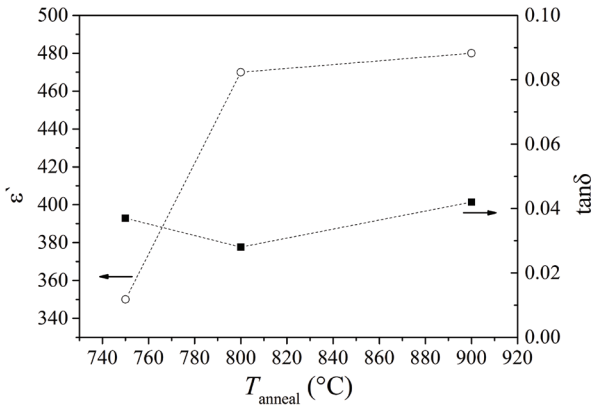

Figure 5: Dielectric permittivity ε` and dielectric losses tanσ of BST 50/50 thin films annealed at temperatures (T_{anneal}) between 750 °C and 900 °C. The dielectric properties were measured at 100 kHz and at room temperature.

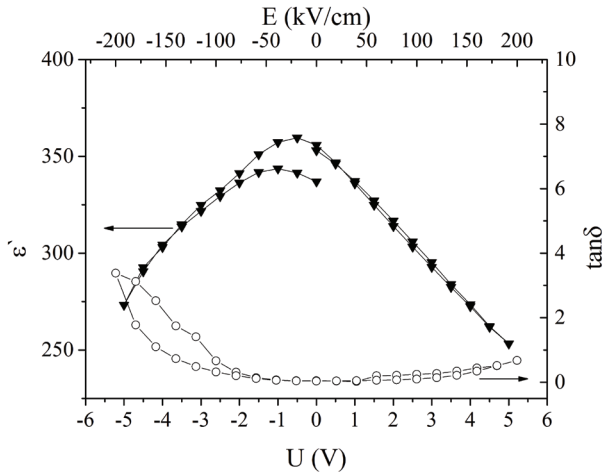

Figure 6: The voltage (and field) dependence of the dielectric permittivity and losses for the BST 50/50 film annealed at 750 °C, measured at 100 kHz and room temperature.

A hysteresis is observed in both curves (see Figure 6) as well as an increase of the dielectric losses as the electric field exceeds -80 kV/cm. The origin for the hysteresis in the films in the paraelectric phase could be related to the presence of polar-nano regions [16] or to the pres-

ence of oxygen vacancies and space charges at the interface between the film and the substrate and/or at the grain boundaries [17]. However, explaining this phenomenon by a specific mechanism would require a further study.

4 Conclusions

The effect of the annealing temperature on the phase composition, microstructure and dielectric properties of solution-derived BST 50/50 films prepared on platinized alumina substrates was studied. According to the XRD analysis all films crystallized in a pure perovskite phase after rapid annealing at temperatures between 750 °C and 900 °C. The FE-SEM analysis revealed that the film prepared at 750 °C was 260 nm thick and that the thickness decreased to 210 nm with increasing annealing temperature to 900 °C, indicating improved densification. The film annealed at 750 °C consisted of approximately 30-nm-sized equiaxed grains. The surface microstructure was uniform and some fine pores were observed between the grains. As the annealing temperature increased to 800 °C the grains were around 70 nm in size and the porosity and pore size decreased. When the BST 50/50 film was annealed at higher temperature, i.e. 900 °C, it consisted of columnar grains with average lateral grain size around 100 nm. The dielectric permittivity of the film annealed at 750 °C was 350 and it increased to 480 with increasing annealing temperature to 900 °C, which we relate to the change of the grain size and shape and reduced level of porosity.

5 Acknowledgments

This work was supported by the Slovenian Research Agency (P2-0105, PR-05026 and J2-5482).

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Arrived: 31. 08. 2016
Accepted: 22. 09. 2016