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Processing and dielectric characterization of $Ba_{0.3}Sr_{0.7}TiO_3$ thin films on alumina substrates

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Abstract

$Ba_{0.3}Sr_{0.7}TiO_3$ (BST) thin films were prepared from the sols based on alkaline earth acetates and titanium propoxide in 2-methoxyethanol–acetic acid solvents and deposited on polished alumina substrates by spin coating. The perovskite phase crystallizes upon heating at/above 700 °C. By increasing the annealing temperature from 700 to 900 °C the grain size increases from 40 to 80 nm, due to the increased driving force for crystallization. The annealing time has got only a minor influence on grain size as a consequence of constrained conditions of the film. The dielectric permittivity and tunability ($\varepsilon_{0\,V}/\varepsilon_{200\,V}$) of BST films, measured at 1 MHz, strongly depend on the grain size, exhibiting the values of 345 and 1.47, and 722 and 1.93 for the films with 40 and 80 nm-sized grains, respectively.

Keywords: Films; Grain size; Dielectric properties; Functional applications; $(Ba,Sr)TiO_3$

1. Introduction

Ferroelectric thin films have been intensively studied for possible applications in tunable microwave devices because of their high dielectric permittivity, low dielectric losses and high tunability, that is the non-linear dependence of the permittivity on the applied electric field.[1,2] Ferroelectric domains lead to high dielectric losses, therefore materials for tunable applications are generally used in the paraelectric state, where the losses are low, while the permittivity is still large.

$(Ba,Sr)TiO_3$ solid solution is among the most promising candidates for tunable devices. Its Curie temperature strongly depends upon the Ba/Sr ratio[3] and the compositions, which are in the paraelectric phase at room temperature, exhibit high permittivity and low losses at microwave frequencies.[2]

Thin film microstructure critically influences the dielectric properties. For films, prepared by chemical solution deposition (CSD) the microstructure can be tailored by the chemistry of the sol and by the processing conditions, mainly by the temperatures of the individual heat treatment steps—drying, pyrolysis and annealing. Hoffmann and Waser showed that in $BaTiO_3$ and $SrTiO_3$ thin films on platinized silicon substrates, the microstructure can be tailored from granular to columnar by adjusting the sol concentration and heating regime. The columnar $BaTiO_3$ films annealed at 750 °C exhibit higher permittivity than the granular films.[4] Kageyama et al. observed that the grain size of $Ba_{0.6}Sr_{0.4}TiO_3$ films on sapphire increases with increasing film thickness in the range 90–1050 nm; the permittivity is almost constant and the tunability increases with the film thickness.[5] Ihlefeld et al. prepared $BaTiO_3$ films on Cu foils. They found that with increasing annealing temperature and consequently increasing the grain size, the permittivity of the films increases, reaching the values close to those of bulk material.[6] A similar relationship between annealing temperature, the microstructure and the dielectric properties has been reported for $(Ba,Sr)TiO_3$ thin films on platinized silicon[7] and platinized alumina substrates,[8] namely with increasing the annealing temperature the grain size increases and the dielectric properties are improved.

The aim of the present work was to prepare $Ba_{0.3}Sr_{0.7}TiO_3$ (BST) thin film capacitors on alumina substrates and to study the effect of the annealing conditions on the microstructure development and consequently on the dielectric properties. The composition with Ba/Sr ratio of 30/70 with the Curie temper-

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ature of about −100 °C,[3] was selected because it is suitable for electrical beam steering in a wide temperature range, for example on-board mobile platforms such as airplanes.

2. Experimental

$Ba_{0.3}Sr_{0.7}TiO_3$ thin films were deposited on polished alumina substrates (99.6%, 25.4 mm × 25.4 mm × 0.26 mm or 10 mm × 10 mm × 0.26 mm, Coorstek). The BST sols were prepared from alkaline earth acetates ($Ba(CH_3COO)_2$, 99.0–102.0%, $Sr(CH_3COO)_2 \times 0.5{\cdot}H_2O$, reagent grade, JM Alfa) and Ti propoxide ($Ti(OC_3H_7)_4$, JM Alfa). The acetates were dried before use. Metal content of the starting compounds was determined gravimetrically. Ti-propoxide was diluted by 2-methoxyethanol (99.3%, Aldrich) and the acetates were dissolved in acetic acid (100%, JM Alfa). The two solutions were mixed for 2 h at 60 °C. The concentration of the sol was adjusted to 0.25 or 0.4 M.

The films were prepared by two-step annealing, where the first step was to deposit the 0.25 M sol on the alumina substrate, dry at 200 °C for 2 min, pyrolyze at 350 °C for 2 min and anneal at 700 °C for 15 min in air. In the next step, the 0.4 M sol was deposited on the substrate, dried at 200 °C for 2 min and pyrolyzed at 350 °C for 2 min. The procedure was repeated five times. The film was then annealed at 700–900 °C for 15–60 min in air. In all cases the samples were quickly pushed into the heated tube-furnace. The final film thickness measured by Rank Taylor Hobson profilometer was between 300 and 400 nm.

The phase composition of the thin films was determined by X-ray diffraction (XRD) using a Cu Kα radiation source in a θ–2θ geometry. The microstructure was analyzed by field emission scanning electron microscopy (FE-SEM, Supra 35 VP, Carl Zeiss). The grain size was calculated by the lineal intercept method by counting 100–150 grains.

For dielectric measurements, air-gapped capacitors (0.750 mm × 1.5 mm) were patterned by lift-off photolithography and Cr/Au electrodes were deposited by magnetron sputtering. The gap width for the BST capacitors was 8.5 ± 1 μm.

The room temperature low-frequency dielectric measurements were performed with a computer controlled measurement set-up consisting of a Keithley 237 Source Measure Unit and a HP 4192A Impedance Analyzer. Capacitance–voltage characteristics were recorded using the following dc voltage cycle: 0 V → +200 V → 0 V → −200 V → 0 V.

3. Results

BST thin films on alumina crystallize in randomly oriented perovskite phase after annealing at 700 °C. By increasing the annealing temperature to 900 °C, we observe that the width of the perovskite peaks (FWHM) decreases and that the relative intensity of the peaks increases indicating improved crystallinity (Fig. 1).

The SEM micrograph of the fracture surface of the film annealed at 700 °C for 60 min reveals 40 nm sized equiaxed grains (Fig. 2). Similar granular cross-section microstructure

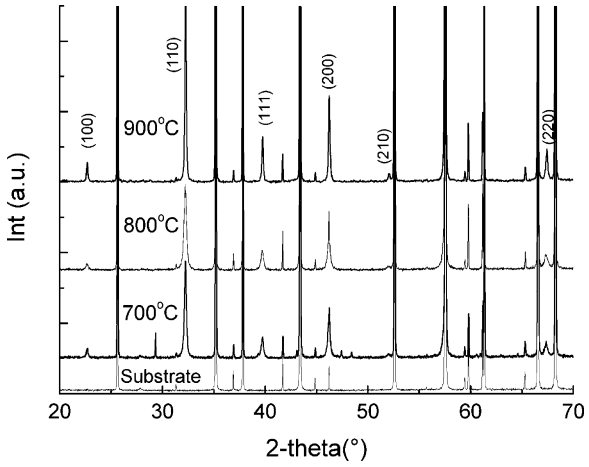

Fig. 1. XRD patterns of $Ba_{0.3}Sr_{0.7}TiO_3$ thin films on alumina annealed at 700–900 °C for 60 min. The main reflections of the perovskite phase are indexed. The XRD pattern of the alumina substrate is added for reference.

was observed in all investigated BST films. The granular microstructure is in agreement with the mechanism of nucleation of the perovskite phase within the bulk of the film proposed by Hoffmann and Waser for $BaTiO_3$ and $(Ba,Sr)TiO_3$ thin films on Pt/Si substrates.[4] Granular microstructure was also observed for $(Ba,Sr)TiO_3$ thin films grown on platinized alumina,[8] Pt/Si[4,9] and sapphire.[5]

In order to obtain insight into the influence of annealing conditions on the microstructure development of BST thin films we compared surface microstructures of the films annealed at 700 and 900 °C (Fig. 3). The films annealed at 700 °C for 15 and 60 min consist of about 40–45 nm sized grains, respectively. The grain size remains almost the same after increasing the annealing time even to 300 min (micrograph not shown here).

By increasing the annealing temperature to 900 °C the microstructure noticeably coarsens. The average grain size in the BST films, annealed for 15 and 60 min, is 60 and 80 nm, respectively. There is some interganular porosity in all analyzed samples, but it is difficult to quantify its content.

We explain the strongly promoted grain growth with the increased annealing temperature by the mechanism of thin film crystallization. When the amorphous film with some remaining

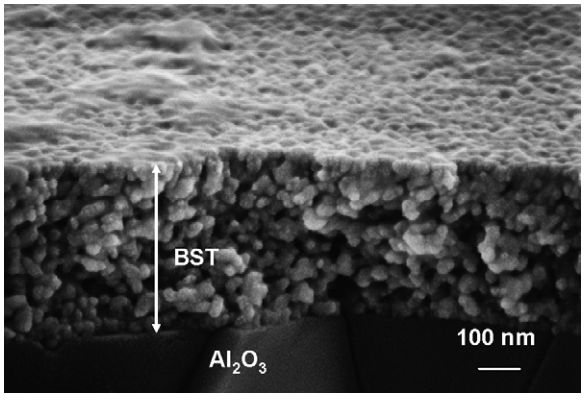

Fig. 2. FE-SEM micrograph of the fracture surface of $Ba_{0.3}Sr_{0.7}TiO_3$ film on alumina prepared by two-step annealing at 700 °C for 60 min.

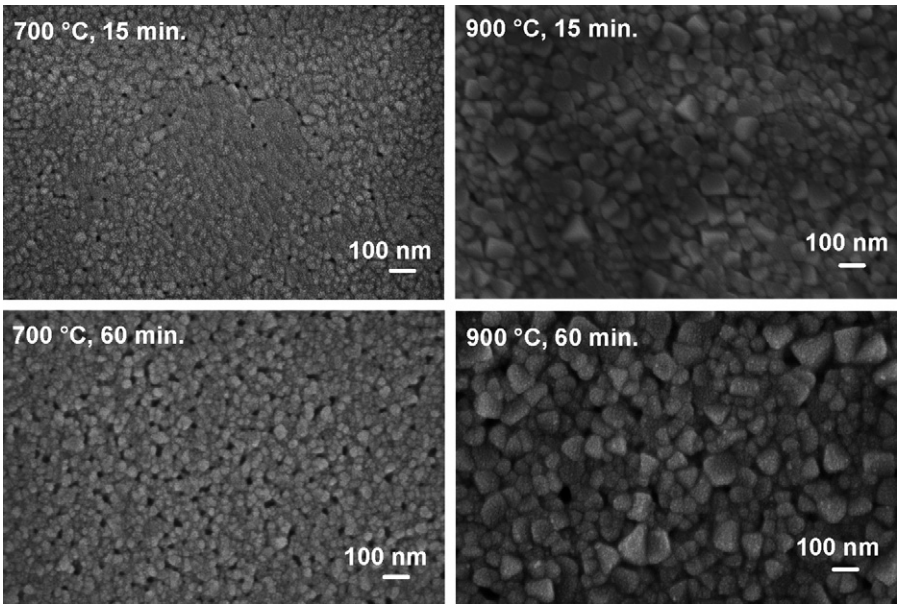

Fig. 3. FE-SEM micrographs of the surface microstructures of the $Ba_{0.3}Sr_{0.7}TiO_3$ films annealed at 700 and at 900 °C for 15 and 60 min.

$$C_{\text{exp}} = \varepsilon_0 w \left[\frac{2}{\pi} \ln\left(\frac{4l}{s}\right) + \frac{\varepsilon_{\text{substrate}} - 1}{\pi} \ln\left(16\frac{h_{\text{substrate}} + h_{\text{film}}}{\pi s}\right) + \frac{\varepsilon_{\text{film}} - \varepsilon_{\text{substrate}}}{(s/h_{\text{film}}) + ((4/\pi) \ln 2)} \right] \quad (2)$$

organic residues is inserted into the hot furnace, the crystallization of the perovskite phase occurs only after the decomposition of the residues is complete, similarly as observed by Hasenkox et al.[10] for $BaTiO_3$ and $SrTiO_3$ thin films prepared from acetate-alkoxide based sols. By increasing the annealing temperature the driving force for crystallization and also for grain growth increases.

The annealing time has only a minor effect on the grain size as expected for the case of a ceramic film constrained by a rigid substrate.[11]

Koutsaroff et al. report that the grain size of $Ba_{0.7}Sr_{0.3}TiO_3$ thin films on platinized alumina, annealed at 685 and 785 °C, increases from 43 to 55 nm, based on the calculation of the X-ray peak broadening.[8]

The capacitance–voltage response of the BST thin films annealed at 700 and 900 °C for 60 min measured at 1 MHz is shown in Fig. 4. From the comparison of the two *C–V* curves it is evident that both the *C* (0 V) and the tunability of capacitance are strongly enhanced with the increased annealing temperature and consequently with the larger grain size of the BST films.

The dielectric permittivity of BST thin films was calculated by applying the partial capacitance method (PCM).[12] According to the PCM, the equivalent electrical circuit of the analyzed planar capacitor consists of three capacitors connected in parallel:

$$C_{\text{exp}} = C_{\text{air}} + C_{\text{film}} + C_{\text{subs}} \quad (1)$$

where C_{exp} is the experimentally measured capacitance, and C_{air}, C_{film} and C_{subs} are the capacitances of the air, film and substrate, respectively. Further, the capacitance C_{exp} is given by:

where h_{film} and $h_{\text{substrate}}$ are the thickness of the film and of the substrate, respectively; $\varepsilon_{\text{film}}$ and $\varepsilon_{\text{substrate}}$ the dielectric permittivity of the film and of the substrate, respectively, $\varepsilon_{\text{substrate}} = 9.8$ and s, w and l terms are the gap width, the electrode width and the length of the planar capacitor. The dielectric permittivity of the film can be calculated from Eq. (2). The values of permittivity and tunability expressed as $n_\varepsilon = \varepsilon_{0\,\text{V}}/\varepsilon_{200\,\text{V}}$ are collected in Table 1.

The dielectric permittivity of BST thin films annealed at 700 and 900 °C is 345 and 722, respectively, in agreement with the trend observed in $BaTiO_3$ thin films, namely that the films with larger grain sizes exhibit higher values of permittivity.[6,13] It is also possible that the permittivity of BST films increases as a consequence of the enhanced homogeneity of the BST solid

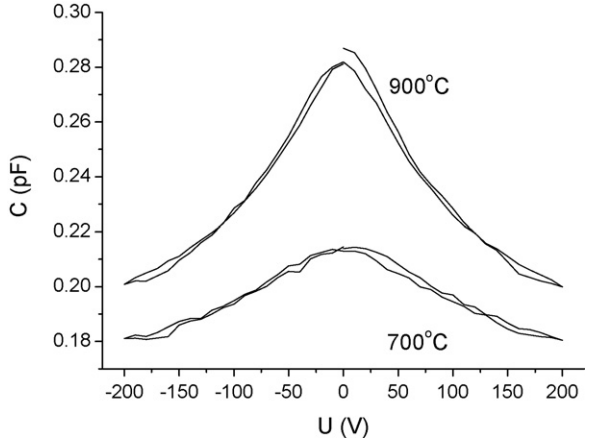

Fig. 4. Voltage dependence of the capacitance measured at 1 MHz for the $Ba_{0.3}Sr_{0.7}TiO_3$ films prepared by annealing at 700 and 900 °C for 60 min.

Table 1
Dielectric permittivity and tunability (n_ε) at the applied voltage of 200 V for $Ba_{0.3}Sr_{0.7}TiO_3$ films on alumina, annealed at 700 and 900 °C for 60 min

T (°C)	h (nm)	s (μm)	ε	n_ε
700	395 ± 10	8.5 ± 1	345 ± 35	1.49
900	292 ± 20	8.5 ± 1	722 ± 50	1.93

The measurements were performed at 1 MHz and at room temperature. The thickness (h) and gap width (s) of the samples are included.

solution achieved by annealing at an elevated temperature. The permittivity reported for $Ba_{0.3}Sr_{0.7}TiO_3$ thin film, deposited on Pt/Si by rf-sputtering at 750 °C is 190.[14] The permittivity of the $Ba_{0.3}Sr_{0.7}TiO_3$ film annealed at 900 °C is comparable to the value 625 reported for sputtered $Ba_{0.4}Sr_{0.6}TiO_3$ thin films on Cu foils annealed at 900 °C,[15] and 580–620 reported for $Ba_{0.6}Sr_{0.4}TiO_3$ films of different thickness on sapphire by metalloorganic deposition and annealed at 900 °C.[5]

The tunability of the BST films increases from 1.49 to 1.93 for films annealed at 700 and 900 °C, respectively. The enhanced tunability corresponds to the increase of grain size. Kageyama et al. observed that with increasing the thickness and correspondingly the grain size of $Ba_{0.6}Sr_{0.4}TiO_3$ thin film planar capcitors on sapphire, the tunability expressed as $(C_0 - C_V)/(C_0 \times 100)$ increases from 30% to about 47%.[5]

4. Summary

$Ba_{0.3}Sr_{0.7}TiO_3$ thin films were prepared from alkaline earth acetates and titanium *n*-propoxide in acetic acid/2-methoxyethanol solvents. The films crystallize in randomly oriented perovskite phase upon annealing at 700 °C. We observe a strong impact of the annealing temperature on the grain size of the films: by increasing the temperature from 700 to 900 °C the grain size increases from 40 to 80 nm. The annealing time has got only a minor influence on the grain size as expected for the constrained conditions.

The values of permittivity and tunability $n_\varepsilon = \varepsilon_{0\,V}/\varepsilon_{200\,V}$ of the films annealed at 700 and 900 °C, measured at room temperature and at 1 MHz, are 345 and 722, and 1.49 and 1.93, respectively. The results clearly show that with increasing grain size of the dielectric permittivity and tunability of $Ba_{0.3}Sr_{0.7}TiO_3$ films on alumina are enhanced.

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