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The influence of processing on the microstructure and the microwave properties of Co–F-codoped barium strontium titanate thick-films

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Abstract

The influence of processing on the microstructure and the dielectric properties of Co–F-codoped $Ba_{0.6}Sr_{0.4}TiO_3$ (BST) thick-films has been investigated. BST powders with different particle sizes were prepared and applied on alumina substrates by screen-printing. The resulting thick-films were sintered at different holding times and characterized with respect to their microstructure and microwave properties. The microstructure of the thick-films shows a clear dependency on sintering time and initial particle size. In addition to grain growth, the formation of a secondary phase is observed at the interface between substrate and BST with increasing sintering time. The dielectric characterization at microwave frequencies shows an increase of tunability with larger grain size while the dielectric loss is even lowered. This shows the strong influence of the microstructure on the material properties and the possibility of tailoring the material through specific processing.

Keywords: BST; Thick-film; Grain size; Porosity; Microwave properties

1. Introduction

Ferroelectric ceramics are promising candidates for passive tunable devices such as phase shifters, tunable matching networks, tunable filters and tunable antennas.[1–3] Currently most attention is given to the solid solution $Ba_xSr_{1-x}TiO_3$ (BST). This is due to the fact that the material shows low dielectric loss and a considerable field dependency of permittivity (i.e. tunability). In addition, the Curie temperature can be easily adapted to the application environment by changing the Ba to Sr ratio.

It is well documented that acceptor doping of the perovskite can be used to remarkably reduce the dielectric loss of BST at high frequencies.[4–8] However, this usually comes with a reduction of the material's tunability. Previous investigations showed that metal–fluorine-codoping of BST can lead to a decrease of the dielectric loss while holding the tunability on a level comparable to that of undoped BST thick-films.[9,10] The influence of acceptor–donor-doping of BST with metal and fluorine is not completely understood yet. While the codoping shows a significant influence on the properties of the material, the incorporation of fluorine has not yet been proved directly.[9,10]

Several metal elements act as acceptor dopants in BST when occupying the A- or B-site of the perovskite and having a lower oxidation state compared to the substituted ion. It is reported that Co is incorporated at the B-site of the perovskite structure with a oxidation state +3 under oxygen- or oxygen–nitrogen-atmosphere in $BaTiO_3$.[11,12] Assuming that this also holds for BST, a Co-doping leads to one oxygen vacancy per two incorporated Co-atoms in the perovskite structure. It is assumed that the fluorine occupies the oxygen vacancies caused by the acceptor-doping and thereby reduces the dielectric loss mechanisms. As doping not only affects the defect chemistry of the material but also its sintering behaviour, changes in the dielectric properties have to be considered with regard to the present microstructure.

It is obvious that the effective permittivity of a ferroelectric thick-film is decreased with increasing porosity. For grain sizes below 0.7 μm, $BaTiO_3$ shows a reduction of permittivity and a less discrete phase transition with decreasing grain size.[13,14] For $Ba_xSr_{1-x}TiO_3$ ($x = 0.3, 0.5, 0.7$) similar results are reported for a frequency of $f = 100\,kHz$.[15,16] So far, there are only few

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reports about microstructural influences on the dielectric properties of BST thick-films for frequencies above 1 GHz. It was shown experimentally and confirmed by simulation that permittivity as well as tunability of undoped $Ba_{0.6}Sr_{0.4}TiO_3$ could be increased slightly by shifting the median grain diameter from 0.34 to 0.38 μm.[17]

This article deals with the effect of grain size and porosity on tunability, dielectric loss and permittivity of screen-printed $Ba_{0.6}Sr_{0.4}TiO_3$ thick-films at microwave frequencies. The powder preparation process and the sintering of the thick-films were varied to achieve a larger range of grain sizes and different porosities. For the investigations a Co–F-codoping of the BST was chosen since previous investigations showed the lowest dielectric loss at lower GHz-frequencies for this composition when compared to other metal-fluorine codoped and undoped BST thick-films.[10]

2. Experimental

Co–F-codoped barium strontium titanate powders were synthesized through a modified sol–gel process. The nominal stoichiometric composition was chosen to $Ba_{0.6}Sr_{0.4}Ti_{0.99}Co_{0.01}O_{3-x}F_{0.09}$, where x ensures electric neutrality depending on the undetermined oxidation state of the components.

For the synthesis barium acetate (0.42 mol), strontium acetate hemihydrate (0.28 mol) and trifluoracetetic acid (21.0 mmol) were dissolved in acetetic acid (29.9 mol) and stirred over night in a chemical reactor under nitrogen atmosphere. Titanium-(IV)-isopropoxide (0.70 mol) was added and a clear sol formed. Cobalt acetate tetrahydrate (7.0 mmol) was dissolved in water (181.3 mol, specific conductance $\sigma < 10^{-9}$ S/m) and added to the reactor. The diluted sol was filtered (mesh width: 1 μm) and spray-dried. The obtained metal–organic precursor was calcinated in alumina crucibles in a tube furnace at 900 °C for 1 h.

One part of the powder was milled using an attritor, a second and a third part using a planetary ball mill. The milled powders were dispersed in terpineol using a dispersant (Hypermer KD1) and a binder (ethyl cellulose) to obtain suitable screen-printing pastes. One paste was created using the attriton-milled powder. A second and a third paste were created using the planetary-ball-milled powder and a mixture of both types of powders, respectively. In the latter case, a ratio of 30:70 was chosen for the proportion of attriton-milled powder to planetary-ball-milled one. The pastes were dispersed in two steps by using a dissolver and a three roll mill for each paste. All pastes were printed on polycrystalline alumina substrates (Rubalit® 710, CeramTec). After drying at 50 °C for 24 h the specimen were cold isostatically densified at 400 MPa for 3 min to avoid cracking during sintering. Eventually the thick-films were sintered at 1200 °C for 1 h, 10 h and 24 h, respectively. The thermal treatment in the tube furnace (calcination and sintering) was done under dried purified air (molecular sieve and silica gel) with heating rates and cooling rates of 5 K/min. A schematic plan of powder, paste and thick-film preparation is shown in Fig. 1.

The stoichiometry of the metal elements in the powders was measured using X-ray fluorescence spectroscopy (SRS 303AS, Bruker-AXS). Titration after pyrohydrolysis (at the laboratory of H.C. Starck GmbH, Goslar, Germany) was used to determine the amount of fluorine present in the powders. Additionally small amounts of screen-printing pastes were calcinated under sintering conditions and analyzed in regard to their fluorine content, too.

The specific surface area of the powders was determined by single point BET measurement (FlowSorb II 2300, Micromeritics). Assuming homogeneous monodisperse spherical particles with neglectable contact area, the BET diameter d_{BET} was calculated and used as an estimation for the primary particle size of the powders. With the measured specific surface area A_{BET} and the theoretical density ρ it can be calculated after

$$d_{\mathrm{BET}} = \frac{6}{\rho A_{\mathrm{BET}}}. \qquad (1)$$

The size of primary particles and aggregates was determined by laser diffraction (Horiba LA950, Retsch Technology) in isopropyl alcohol ($n_{\mathrm{IPA}} = 1.378$),[18] assuming the complex refractive index of BST: $n_{\mathrm{BST}} = 2.4 - 0.1i$.

The phase content of powders and sintered thick-films was examined by X-ray diffraction (D5000, Siemens, Cu-radiation: $K_{\alpha 1}$ and $K_{\alpha 2}$). Scanning electron microscopy (Supra 55, Zeiss) was used to investigate the microstructure of the powders and the thick-films. Grain size distribution and thick-film height were determined by image analysis (analySIS pro, Olympus Soft Imaging Solutions) of several SEM pictures. The porosity P was calculated through the measured height h and weight m of the thick-films, the lateral dimensions of the print layout (square, $x = 47.5$ mm) and the theoretical density after

$$P = 1 - \frac{m}{\rho h x^2}. \qquad (2)$$

The microwave properties of the thick-films were determined by measuring the scattering parameters (S-parameters) of coplanar waveguides (CPW) applied on the top surface of the sintered films. On each specimen multiple waveguides were realized through a lithography step on a evaporated Cr/Au seed layer followed by a galvanic growth of Au. After the galvanization to a thickness of at least 1.5 μm the photoresist and the remaining seed layer were removed through etching. The S-parameters were determined by temperature controlled ($T = 23$ °C) on-wafer measurements using a vector network analyzer in a frequency range of 0.1–40 GHz at tuning voltages U between 0 and 100 V (step size 10 V). The bias field E was calculated with tuning voltage and gap width s of the CPWs after $E = U/s$.

The relative effective permittivity $\varepsilon_{\mathrm{r,eff}}$ and dissipation factor $\tan\delta$ of the thick-films were extracted from the measured S-parameters by conformal mapping model based method. This method allows the extraction of the values for each measuring point taking into account the geometry and the properties of the substrate and the waveguides.[19,20] The CPW geometry used allows to extract reliable dielectric properties in the frequency range 5–40 GHz.