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Microstructure and microwave properties of inkjet printed barium strontium titanate thick-films for tunable microwave devices

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Abstract

Barium strontium titanate (BST) is a promising material for passive tunable microwave devices such as phase shifters, tunable filters or tunable matching networks. This publication covers the preparation of BST thick-films for microwave applications through inkjet printing. A $Ba_{0.6}Sr_{0.4}TiO_3$ ink was prepared, printed on alumina substrates and sintered at temperatures between 1100 °C and 1200 °C. The microstructure of the thick-films reveals the evolution of grain growth and porosity with increasing sintering temperature. Furthermore, a reaction with the substrate was observed for $T \geq 1175$ °C. A maximum tunability of 36% was observed at temperatures right below the onset of the substrate reactions. This process conditions were used for the preparation of a loaded line phase shifter, which successfully shows the capability of the inkjet printing process for future microwave device fabrication.

Keywords: Inkjet printing; BST; Thick-films; Microstructure; 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 barium strontium titanate $Ba_xSr_{1-x}TiO_3$ (BST). This is due to the fact that the material shows low dielectric loss and a considerable field-dependent permittivity, i.e. tunability. During the last years several successful implementations of passive tunable microwave devices on screen printed BST thick-films were reported[2,4–6].

Currently, there is also a large interest in using inkjet printing for the manufacturing of low-cost electronic components. Especially the high flexibility of the process gives significant advantages over conventional manufacturing processes. The main feature of the inkjet printing process is that it is contact- and maskless. Hence, it allows a preparation directly from a digital model. Furthermore, the simultaneous use of multiple printheads enables a fast production of graded components and multilayer structures[7,8]. Due to the flexibility, it is beneficial to use the inkjet printing process for a future microwave device preparation.

The main challenge of the process is that the low viscosity of the inks and the interaction with the substrate often lead to problems during printing and drying, causing bulged lines or an inhomogeneous film thickness. Microwave components have demanding requirements on thick-film homogeneity and size. A good control of the ink and the process parameters is necessary to achieve this[7,9]. Furthermore, the process has strict limitations to the particle size of the inks, which is usually in the sub-micron range. A coarse-grained microstructure usually yields better microwave properties for BST[10,11], while smaller particle sizes are desired to comply with the printhead limitations. Therefore, investigations have to be carried out to examine if

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Table 1
Ink composition (DOL = DOLACOL 1001, EC = ethyl cellulose, IPA = isopropyl alcohol, BDG = butyl diglycol).

	Volume fraction/%				
	BST	DOL	EC	IPA	BDG
BST ink	4.93	1.06	1.05	48.68	44.27

the inkjet printed films can reach the quality of the conventional screen printed films for microwave device fabrication.

There are only few publications that deal with inkjet printing of tunable dielectrics and none of them report a dielectric characterization above 1 GHz. Ding et al.[12] studied the rheology and gelation behavior of BST sols for inkjet printing. Kaydanova et al.[13,14] printed a BST sol and achieved a tunability of 30% at $E = 9$ Vμm and $f = 1$ MHz in the ceramic thin-films. Sakai et al.[15–17] printed BST and BST–$MgTiO_3$ composite suspensions and characterized the thick-films up to 10 MHz.

This article deals with microstructure-property relations in inkjet printed $Ba_{0.6}Sr_{0.4}TiO_3$ thick-films at microwave frequencies. In an earlier publication we reported on the development of a BST ink composition which is suitable for the preparation homogeneous thick-films[18]. However, only the ink preparation, ink properties and the drying behavior have been studied. Based on these previous results an undoped BST ink was prepared, printed on alumina substrates and sintered between 1100 °C and 1200 °C. The thick-films were characterized with respect to their microstructure and microwave properties to investigate the suitability for tunable microwave devices. Eventually, a tunable phase shifter was prepared on inkjet printed lines to prove the capability of the inkjet printing process for the fabrication of tunable microwave components.

2. Experimental procedure

A $Ba_{0.6}Sr_{0.4}TiO_3$ powder was synthesized in a modified sol–gel process, as described by Zhou et al.[19]. The process uses a solution of Ba- and Sr-acetates and Ti-isopropoxide that is spray dried and subsequently calcined for 1 h at 1100 °C. An inkjet printing ink was prepared using a stirred media mill (MiniCer, NETZSCH-Feinmahltechnik, Germany). Butyl diglycol (Merck, Germany) was used as solvent and DOLACOL D1001 (Zschimmer & Schwarz, Germany) as dispersant. The ink was prepared with 40 wt.% BST powder and 1.6 wt.% dispersant in the solvent. After milling and dispersing, the ink was diluted to a solid content of $\phi = 5$ vol.% under addition of isopropyl alcohol (Merck, Germany) as a fast drying agent and ethyl cellulose (Sigma–Aldrich, USA) as a rheology affecting additive[18]. The final ink composition is shown in Table 1.

The particle size d_{50} of the ink was determined by image analysis of scanning electron micrographs (Supra 55, Zeiss, Germany) of the dried ink (8500 particles counted)[18]. The viscosity η was measured using a rheometer (MCR 300, Anton Paar, Austria) with cone-plate measurement geometry ($d_{cone} = 50$ mm, $\alpha_{cone} = 2°$). The density ρ of the ink was determined with a density meter (DMA 4500 M, Anton Paar, Austria) and the surface tension γ was measured with the pendant drop method (OCA 20, DataPhysics, Germany). Printability of the ink was verified by calculating the Ohnesorge-Number

$$Oh = \frac{\eta}{\sqrt{\gamma \rho a}} \qquad (1)$$

with the nozzle diameter $a = 100$ μm and verifying the condition $0.1 < Oh < 1$[8].

A single nozzle piezoelectric drop-on-demand inkjet printer (Autodrop Professional, Microdrop, Germany) was used to print the ink on high-purity polycrystalline alumina substrates (Rubalit 710, CeramTec, Germany; 99.6% Al_2O_3[20]). The printing was performed using a temperature controlled printhead with 100 μm nozzle diameter. The printing frequency was $f = 500$ Hz and the substrates were heated to 50 °C for drying. The preparation of the lines for the material characterization was done by printing one layer of BST with a substrate table velocity of $v = 15$ mm/s. This results in a drop spacing of $p = v/f = 30$ μm. The lines for the phase shifter were prepared by printing two layers with a substrate table velocity of $v = 20$ mm/s, which leads to a drop spacing of $p = 40$ μm for each layer.

After drying the specimens were sintered for 1 h in a tube furnace under dried purified air (molecular sieve and silica gel) with heating rates and cooling rates of 5 K/min. The sintering temperature was varied between 1100 °C and 1200 °C. The phase content of powders and sintered thick-films was examined by X-ray diffraction (D5000, Siemens; Cu-radiation: $K_{\alpha1}$ and $K_{\alpha2}$). Cross sections of the films were prepared by ion beam milling (Leica EM TIC 3X, Leica Microsystems, Germany). Scanning electron microscopy (Supra 55, Zeiss, Germany) was used to investigate the microstructure of the sintered thick-films. The grain size and porosity of the thick-films was determined by image analysis[10]. For grain size determination SEM top view micrographs were used. The porosity was measured using the cross sections.

The microwave properties of the thick-films were determined by measuring the scattering parameters (*S*-parameters) of coplanar waveguides (CPW) which were photo lithographically patterned on top of inkjet printed films after sintering. On each specimen multiple waveguides were patterned on an 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 0.1–20 GHz at tuning voltages V between 0 and 150 V. The bias field E was calculated with tuning voltage V and gap width $s = 15$ μm of the CPWs according to $E = V/s$.

The relative effective permittivity ε_r and dissipation factor $\tan\delta$ of the thick-films were extracted making use of the conformal mapping model of a CPW. 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[21,22]. The CPW geometry was chosen in accordance to the required frequency range of $f = 5$–20 GHz. The relative