Inkjet Printing of High κ-Dielectric Ceramic/Polymer Composite Thick Films

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ABSTRACT

A novel and simple method for the preparation of high κ-dielectric thick films on flexible substrates via inkjet printing is presented. Therefore, a ceramic/polymer composite ink suitable for the inkjet printing process is developed. Barium strontium titanate is used as the high κ-ceramic filler and poly(methyl methacrylate) as the polymeric matrix. The preparation route for the developed composite ink as well as the requirements of the inkjet printing process to such inks are discussed. The ink shows no coffee stain effect and allows the fabrication of homogeneous dielectric thick films. Furthermore, the developed ink allows process temperatures below 125 °C, an important requirement for printing on flexible substrates. The fabrication of fully inkjet printed metal-insulator-metal capacitors on PET with promising dielectric properties is shown. The composite ink allows to obtain values for κ up to 12 times higher than for pure PMMA.

Keywords: inkjet printing, dielectric materials, capacitor, ceramic/polymer composite

1 INTRODUCTION

Inkjet printing is a promising technology for the selective deposition of functional materials for a wide range of applications, such as light emitting devices, electronic circuits or dielectric films [1–3]. This is due to the fact that inkjet printing is a digital technique and allows a cheap and flexible production of two- and three-dimensional structures directly from a digital model. There are several different inkjet technologies for the drop formation, but usually the piezoelectric drop-on-demand (DOD) technology is used for printing functional materials, especially ceramics [4]. With this technique drops of a fixed size and quantity of ink are obtained, as the drop ejection at the printhead nozzle is obtained through contraction of a piezoelectric element in response of an external voltage.

To deposit a functional material with DOD inkjet printing, the material has to be in the liquid phase, dispersed or dissolved in a solvent. When using inks containing solid particles, e.g. ceramics, the challenge is to fulfill the high requirements to the used inks of the inkjet printing process. Typically, those requirements can be divided into three categories; 1) the size of the solid particles and the stability of the ink, 2) the fluid properties of the ink and 3) the drying behavior on the substrate [5]. The first two categories regard the jettability of the ink and are usually relatively simple to fulfill. However, the control of the drying behavior is often a major challenge, regardless of the used solid component. Prtinable inks need to have a low viscosity and therefore tend to cause issues like inhomogeneous film thicknesses or bulged lines during drying. A common phenomenon is the coffee stain effect, which is observed for ceramic or metallic suspensions as well as for polymer solutions. This effect leads to ring-like structures with inhomogeneous film thickness and was first described by Deegan et al. [6]. Due to the complex process of drying, often a detailed ink development is necessary to achieve homogeneous solid thick films [7–9].

Considering current applications for inkjet printing in the area of printed electronics, it is surpising that to date either particle based inks or inks based on organic molecules are used. Especially in the field of dielectrics, there is always a compromise between the permittivity and the processability of a material. Ferroelectric ceramics like barium strontium titanate (BST) and barium titanate (BT) are widely used for dielectric applications. Those ceramics exhibit high values for the permittivity, but require a high temperature sintering step, which limits their field of application [10]. Therefore, organic polymers are used for the fabrication of printed flexible devices. In contrast to ferreoelectric ceramics, they are known for high mechanical flexibility and low temperature processability, but also for low permittivity [11]. This gap in the field of printed dielectric films is closed by our approach to utilise a ceramic/polymer composite ink for a one step fabrication of composite thick films via inkjet printing. In this study, we show the successful transfer of a developed BST/PMMA ink for printing on flexible substrates, like PET [12]. Besides the drying behavior of the composite ink, also fully printed MIM capacitors are fabricated and the dielectric properties of the composite thick films are characterized.

2 EXPERIMENTAL PROCEDURE

2.1 Materials

Barium strontium titanate (BST) powder with a stoichiometric composition of $Ba_{0.6}Sr_{0.4}TiO_3$ was synthesized in a modified sol-gel process [12]. Strontium acetate hemihydrate (0.281 mol) and barium acetate (0.422 mol were dissolved in acetic acid (30.0 mol) under nitrogen atmosphere. Afterwards titanium isopropoxide (0.703 mol) was added and the sol was diluted with water (181.8 mol). The sol was spray-dried (MM-HT-ex; Niro, Søborg, Denmark) and the metalorganic powder was calcined under purified dried air at 1100 °C for 1 h. The calcined BST powder was milled and dispersed in butyl diglycol (BDG) with the addition of DOLACOL D1001 as a dispersant using a laboratory stirred media mill (MiniCer; NETZSCH, Selb, Germany) with yttria stabilized zirconia-grinding media (d = 0.2 mm). The BET surface area increased from 4.7 m²/g after calcination up to 35.0 m²/g after milling (Gemini VII 2390, Micromeritics, Norcross, U.S.). The solid content of the obtained dispersion was 10 vol% BST. Particle size of the dispersion was determined using laser scattering (HORIBA LA950; Retsch Technology, Haan, Germany).

A 20 vol% solution of PMMA (weight-average molecular weight $M_w = 1.5 \times 10^4$ g·mol^{-1}) was prepared in butanone. The ink was obtained by mixing the prepared BST dispersion and the PMMA solution. The density was measured using a density meter with oscillating U-tube (DMA 4500 M; Anton Paar). The viscosities of the PMMA solution, BST dispersion, and ink were measured using a rheometer (MCR 300; Anton Paar, Graz, Austria) with a cone-plate measurement geometry (d_{cone} = 50 mm, α_{cone} = 2°). The surface tension was measured using a force tensiometer with the plate method (K100, Krüss, Hamburg, Germany).

2.2 Inkjet Printing

A single nozzle piezoelectric Drop-on-Demand inkjet printer (Autodrop Professional; Microdrop, Norderstedt, Germany) with 100 µm nozzle diameter was used. Printing parameters for a stable drop formation of the ink were U_{head} = 95 V as the driving voltage of the piezo actuator and t_{head} = 30 as pulse length at an ejection frequency of 500 Hz. The nozzle temperature was set to 25 °C. The substrate table was heated between 40 °C and 80 °C for drying. Inks were printed on Al_2O_3 substrates (Rubalit 710; CeramTec) as well as on Polyimide (Kapton® HN; DuPont) and PET (Melinex® ST506; DuPont).

Electrodes were printed using a commercial silver nano ink (Silverjet DGP 40LT-15C). Printing was done with a 100 µm printhead and U_{head} = 88 V and t_{head} = 15 µs. The nozzle was heated up to 25 °C. Electrodes were dried at 80 °C. Fully printed capacitor samples were thermal post-treated at 125 °C for 1 h in a lab oven.

2.3 Characterization

For characterization of the surface topography chromatic white light interferometry (MicroProf; Fries Research & Technology, Bergisch Gladbach, Germany) was used. Cross sections of the printed thick films were prepared using an ion beam slope cutter (Leica EM TIC 3X, Leica Microsystems, Germany) with triple ion beam. The microstructure of the thick film was investigated using SEM (Supra 55; Carl Zeiss, Oberkochen, Germany). The dielectric properties of the printed capacitors were determined using an impedance test instrument (IM6, Zahner, Kronach, Germany). The Impedance Z and phase angle φ were measured over a frequency range from 20 Hz to 100 kHz at 20 - 120 °C. Based on those results, the relative permittivity as well as the dielectric loss were calculated.

3 RESULTS AND DISCUSSION

The BST suspensions obtained by milling shows Newtonian flowing behavior with a viscosity of 13.6 mPa·s at 20 °C and γ' = 1000 s^{-1}. The particle size distribution after milling is shown in Figure 1. The small particle size results in a very good long term stability of the suspension.

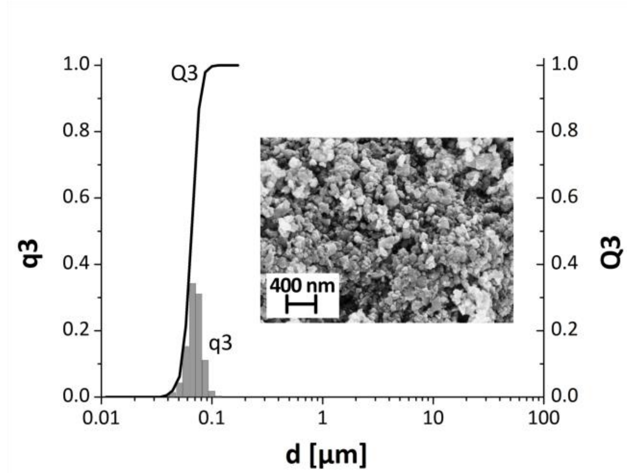

Figure 1: SLS particle size distribution of the dispersion and SEM image of the dried particles

The obtained BST/PMMA composite ink contains 13.4 vol% solid with a 50:50 ratio of BST and PMMA. The ink shows a good jettability with an Ohnesorge number of Oh = 0.20 [12]. In addition, the maximum particle size of d_{max} = 130 nm is more than 500 times smaller than the nozzle diameter of the used printhead (d_{nozzle} = 100 µm) and can easily be used with smaller printheads to achieve higher resolutions.

In contrast to dielectric ceramic inks, the composite formulation needs no high temperature sintering to be dimensionally stable after drying. Hence, the fabrication of dielectric thick films on flexible substrates can be realised. Therefore, the drying behavior on different commercial available polymer substrates was studied. Figure 2 displays the topography and the corresponding cross sectional profiles of printed drop structures with different size (n = number of droplets per structure), dried at 60 °C. The drying behavior on Al_2O_3-substrates showed an ideal drying temperature of 60 °C [12], which was confirmed for printing on flexible substrates. The cross sectional profiles of the drops on PET show very homogeneous structures with steep edges. In contrast, the ink forms spherical structures on Kapton.

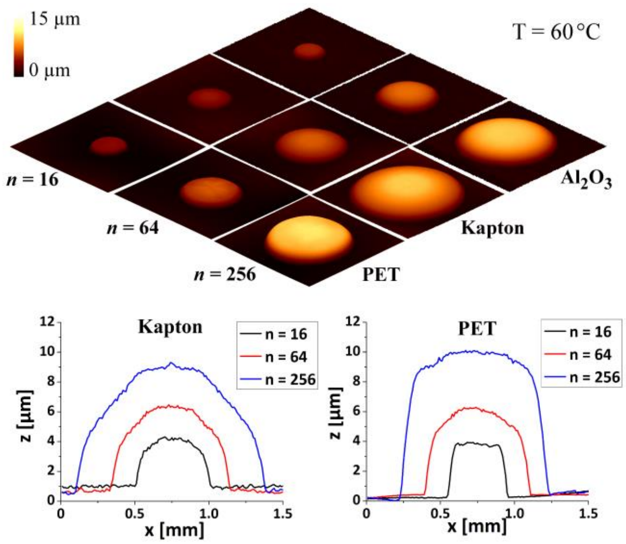

Figure 2: Top: Topography of printed drop structures on different substrates, dried at 60 °C [12]; Bottom: Cross sectional profiles of the drop structures on Kapton and PET

Nevertheless, it needs to be noted that the approach of a BST/PMMA composite ink results in dense structures on all tested substrates without any further adjustment of the ink composition. No inhomogeneities, such as the coffee stain effect, were observed. This is due to the fact of the fast evaporation of butanone after deposition along with the interactions between the polymer chains.

For the fabrication of fully inkjet printed MIM capacitors, the PET substrate was selected. The bottom and top electrodes were printed using a commercial silver ink optimized for plastic films (Silverjet DGP 40LT-15C). The topography of a printed capacitor is shown in Figure 3. The effective capacitor area is 2 x 2 mm², but the composite layer was larger to prevent boundary effects. The dielectric BST/PMMA thick film was printed as a single layer with a droplet spacing of 70 µm. It can be stated, that printing a single layer leads to a higher homogeneity of the thick film compared to printing two layers and hence the composite layer could possibly be printed smaller [12].

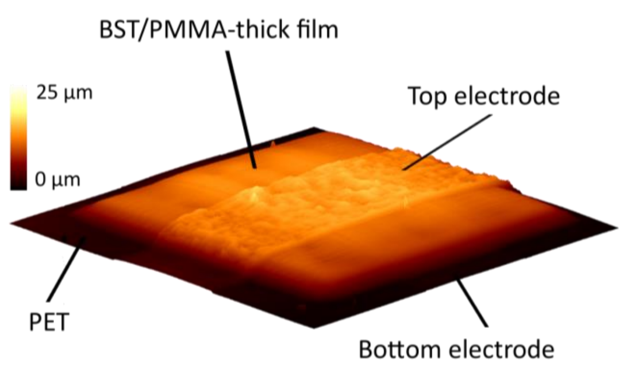

Figure 3: Topography of a fully inkjet printed MIM capacitor on PET

For the bottom electrode a single Ag layer was sufficient, whereas three were needed for the top electrode. Only a single temperature treatment step was carried out after finishing the top electrodes. The obtained specific conductivities were 12 % (~13 µΩ/cm) for the bottom and 3 % (~55 µΩ/cm) for the top electrodes concerning the bulk material .

A cross sectional image of a fully printed capacitor is displayed in Figure 4. The use of a triple ion beam (TIB) system allows to maintain the characteristic microstructure of the composite layer.

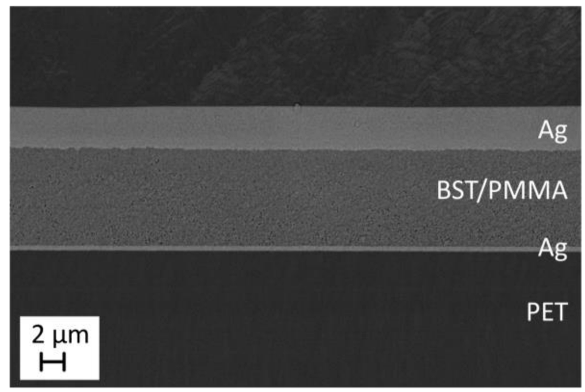

Figure 4: TIB-SEM cross sectional image of a fully inkjet printed MIM capacitor

The PET substrate has a very smooth surface, resulting in a smooth and thin bottom electrode. The different functional layers are well seperated and no dissolving of previously printed layers was observed. Especially, the intrusion of silver particles into the dielectric and resulting short circuits are prevented. The 50:50 composite layer shows almost no porosity, an important factor for obtaining high values for the dielectric constant. Furthermore, a uniform distribution of BST and PMMA is observed, without signs of a seperation of the two solids. PMMA interacts with the oxidic surface of the BST. This results in a high homogeneity in the composite ink, that is maintained during drying. The top electrode needed to be printed with 3 layers. Due to a fast solvent absorption of the composite layer beneath, no continuous film was obtained with less layers.

The dielectric properties of fully printed capacitors were characterized. Figure 5 shows the measured values for κ and tan δ at a frequency of f = 100 kHz and at different temperatures.

The dielectric constant slightly decreases with increasing temperature. This is due to the fact that the Curie temperature for the used $Ba_{0.6}Sr_{0.4}TiO_3$ is $T_C \approx$ -2 °C. Reaching the glass temperature of PMMA ($T_g \approx$ 105 °C) results in a slgihtly increase of κ again. With a calculated value of $\kappa = 35 \pm 1$ at 20 °C a significant increase compared to pure PMMA (~3) was achieved [13].

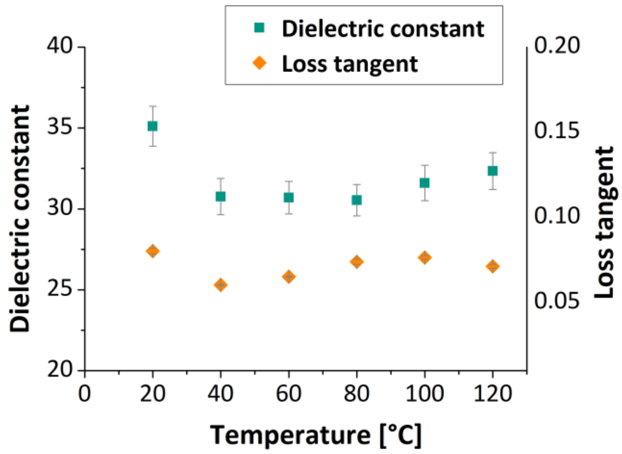

Figure 5: Temperature dependence of the dielectric properties of 50:50 BST/PMMA composite thick films at $f = 100$ kHz

The results are in good agreement to theoretical and experimental data reported in literature for BST/PMMA composites [14].
Compared to reported approaches of infiltrating a printed ceramic layer with polymer resins to obtain flexible dielectric thick films with increased dielectric constant, our approach of directly printing the ceramic/polymer composite ink offers several improvements [15,16]. The fabrication is simple can be done in a single printing step, the composition of the composite can be accurately controlled and at the same time inreased values for κ are achieved. By using different solutions of BST and PMMA, the ink composition can be adjusted as well as the ratio between BST and PMMA varied.

Several possibilities for a further increase of the dielectric constant, such as the ceramic particle size, will be studied in future investigations.

4 CONCLUSION

High κ-dielectric materials for printed applications have received increasing interests in recent years. Therefore, it is surprising that to date either low κ poylmer or high κ ceramic inks are reported. This gap is closed by our novel approach of developing ceramic/polymer composite inks. Such inks allow a highly promising combination of the single material properties as well as the fabrication of dielectric thick films on flexible substrates in a single process step. The reported BST/PMMA ink enables the preparation of very homogeneous composite thick films with low porosity. In addition, smooth topographies are maintained, well suited for the fabrication of fully printed multi-layer components. The dielectric properties of fully printed MIM capacitors on PET were characterized. A dielectric constant of $\kappa = 35 \pm 1$ at 20 °C and $f = 100$ kHz was obtained, which is up to 12 times higher than for pure PMMA (~3).

The investigation shows that using ceramic/polymer composite inks is a very promising approach to obtain dielectric thick films with increased dielectric constant compared to pure polymeric films, while at the same time allowing the use of flexible polymer substrates. Such inks are suitable for different inkjet printing systems and expand the already high flexibility of this technologie.

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