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# Patterning of lead-zirconate-titanate thick-film structures by electrophoretic deposition from ethanol-based dispersions



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#### ABSTRACT

We studied the thickness uniformity and homogeneity of lead-zirconate-titanate thick films on goldcoated alumina substrates obtained by constant-current electrophoretic deposition from ethanol-based suspensions with different conductivities. Based on the geometry of the experimental set-up, a finiteelement model was constructed. The numerical analyses predicted a non-uniform current-density distribution on the electrodes, which was higher at the edges. We expected a thicker deposit at the edges, which was confirmed by measuring the cross-sectional profile of the as-deposited layer. The thickness non-uniformity was more pronounced for shorter deposition times and when performing the deposition from highly conductive suspensions. In the latter case the rate of deposition was decreased and the homogeneity of the deposits was increased, as evidenced by the scanning electron microscopy images. A homogeneous and uniform layer with a thickness of about 40  $\mu$ m was prepared from the ethanol-based suspension with a conductivity of 20  $\mu$ S/cm after 120 s.

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#### 1. Introduction

Electrophoretic deposition (EPD) relies on the mobility of charged particles dispersed in a liquid under an applied electric field and their deposition onto an oppositely charged electrode. It is a useful technique for preparing piezoelectric leadzirconate-titanate-based thick films [1–4], which can be used in multi-element transducers operating at frequencies over 30 MHz [5]. Such devices contain a number of aligned, rectangular, piezoelectric elements, each with a thickness of a few tens of µm and a width of less than 1 mm, with a distance between the elements of a few tens of micrometers [6]. However, the fabrication of such structures is challenging and currently limits the development of these transducers [7]. Various non-aqueous colloidal suspensions have been used for the processing of lead-zirconate-titanate thick films by EPD, however the structures possessed a non-uniform thickness and the material deposited between the two elements had an inferior lateral resolution [5,8]. The quality of the deposit depends on many parameters related to the properties of the suspension and to the deposition process reviewed comprehensively in [9–11].

When a suspension of charged particles is exposed to a DC electric field, the particles will move toward the oppositely charged

http://dx.doi.org/10.1016/j.jeurceramsoc.2015.08.033 0955-2219/© 2015 Elsevier Ltd. All rights reserved. electrodes with a velocity proportional to an electric field and an electrophoretic mobility. The electrophoretic mobility of a particles is proportional to the particle size and the zeta potential of the particles  $\xi$ , the dielectric permittivity of the solvent  $\epsilon$ , and the thickness of the double layer and is inversely proportional to the viscosity of the solvent  $\eta$  [12]. It was established that close to the electrode the double layer of the particles is distorted and the particles coagulate onto the electrode [10]. The particles located near or on the oppositely-charged electrode distort the local electric filed that consequently generates the electroosmotic flow. The flow directs liquid toward the particles and consequently the particles move away and/or along the electrode [13–15]. The electroosmotic flow velocity is proportional to the electric potential  $\Psi$ , the zeta potential of the particles  $\xi$  and the dielectric permittivity of the solvent  $\epsilon$  and is inversely proportional to the viscosity of the solvent  $\eta$ . Electroosmotic flow may lead to the particle aggregation and the formation of non-homogeneous deposits [14].

The electrical conductivity of the suspension is an important parameter that dictates the rate of the deposition and the morphology of the deposit. The presence of ions contributes to the electrical conductivity of the suspension, while the impact of charged particles to the conductivity is negligible. In alcohol-based solvents the ions originated mainly from additives for charging the particles [16,17]. Under constant-current deposition conditions, the increase in the suspension's conductivity decreases the magnitude of the applied potential, and consequently decreases the electrophoretic

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deposition rate [17]. High conductivity of the suspension favors the formation of uniform deposits as reported for acetylacetone-based suspension, since at low deposition rates the particles deposit at optimized positions and the rearrangement ability of the particles is higher [18]. Uniform deposits were formed from the ethanol-based suspensions with conductivities of  $20 \,\mu$ S/cm or higher, while non-uniform deposits were obtained from suspensions with conductivities lower than  $10 \,\mu$ S/cm [19,20]. On the other hand, a high conductivity of the suspension with its associated high ionic strength deteriorates the stability of the particles and frequently led to the formation of agglomerates. The resulting deposit is non-uniform with a low density. The presence of agglomerates also decreases the electrophoretic deposition rate since the agglomerates have a lower electrophoretic mobility than the individual particles [17].

The uniformity of the deposits in term of their thickness is closely related to the uniformity of the electric field between the two electrodes. It was shown that in the case of carbon nanotubes dispersed in isopropanol and deposited at constant voltage onto glass substrate, the electric field depends on the inter-electrode distance and the lateral dimensions of the electrode [21]. When the inter-electrode distance was comparable or smaller than the lateral dimensions of the electrode, the electric field along the depositing electrode was relatively uniform, but it was stronger at its edges. The presence of edges in the patterned planar strip electrodes had a significant effect on the particle deposition, which was studied theoretically using a finite-element analysis (FEA) by Pascall et al. [22]. The developed model related to the Al and CuO particles dispersed in a mixture of ethanol and water illustrated that the electric field was enhanced stronger at the edges of the electrode, which resulted in deposits with thicker edges for short deposition times. However, at longer times the center of the deposits grew faster than the edges, which resulted in a more uniform thickness of the deposit. They also showed that the deposit grew not only vertically but also laterally. These predictions were experimentally confirmed in [23], which proved that the Al/CuO deposit obtained from ethanol/water-based suspension on patterned stripelectrodes was concave-shaped after 5 s and become uniform after 55 s of deposition. Bernardo et al. [8] showed that the lateral resolution of the deposits on patterned 1-mm-wide strips depends on the inter-electrode distance and the shape of the counter electrode. The lateral resolution was higher when a square-patterned planar counter electrode was used and increased with the increasing inter-electrode distance.

In this article we studied the processing of niobium-doped leadzirconate-titanate thick films from an ethanol-based suspensions using electrophoretic deposition under constant-current conditions. Based on a simple finite-element (FE) model built according to the experimental set-up we predict the influence of the effective electrical conductivity of the suspension on the electrical potential distribution and on the current density in the system in the initial stage of the deposition process. The aim of this study was to experimentally examine the effect of the electrical conductivity of the suspension on the deposition mass, homogeneity and thicknessuniformity of the deposit at a various deposition times and based on the obtained results envisage the optimal conditions for processing the piezoelectric elements with define geometry and homogeneous microstructure.

#### 2. Experimental

 $Pb_{0.99}(Zr_{0.53}Ti_{0.47})_{0.98}Nb_{0.02}O_3$  (denoted PZTNb) powders were synthesized from PbO (99.9%, Aldrich, Germany), ZrO<sub>2</sub> (99.1%, Tosoh, Japan), TiO<sub>2</sub> (99.8%, Alfa Aesar, Germany) and Nb<sub>2</sub>O<sub>5</sub> (99.9%, Sigma Aldrich, Germany) by solid-state synthesis. The

homogenised powder mixture was fired at 1100 °C. Details are given in [20]. The PbO powder was milled in an attrition mill for 4 h in order to decrease its particle size. The PZTNb and PbO powders had volume particle sizes  $d_{(v,50)}$  of 0.26 µm and 2.19 µm, respectively. The particle size distribution and the morphology of the powders are described elsewhere [3].

The PZTNb and PbO suspensions were prepared following an experimental procedure adapted from those described elsewhere [20]. First, a polyacrilic acid (PAA, 50 wt.% in H<sub>2</sub>O, electronic grade, molar mass 2000, Alfa Aesar, Germany) was mixed with nbutylamine (BA, Alfa Aesar, Germany) at a constant PAA/BA molar ratio of 1:2.5. This mixture was diluted in absolute ethanol (Carlo Erba, Italy) adjusting the PAA concentration to different values in order to obtain suspensions with different conductivities. These solutions were used for the dispersion of the corresponding amount of PZTNb or PbO particles to obtain a constant PAA concentration of 100 µmol per gram of ceramic powder. In this way, the solids loads in the suspensions with PAA concentrations of 5.8, 7.3, and 10.3 mM were 0.7, 0.9, and 1.2 vol.%, respectively. The PbO suspension with a solids load of 1 vol.% was added to the PZTNb suspensions in such a way that the final suspensions contained 98 mol% of PZTNb and 2 mol% of PbO. Polyvinyl butyral (PVB, Aldrich, molar mass 50,000-80,000) was added as a binder to all the prepared suspensions at a concentration of 3 wt.% with respect to the solids load. The PZTNb/PbO suspensions with PAA concentrations of 5.8, 7.3, and 10.3 mM that were used for the electrophoretic deposition are denoted as SP1, SP2, and SP3, respectively.

A custom-built electrophoretic deposition set-up consisted of a glass chamber with a diameter of 45 mm and two vertically aligned electrodes, separated by a distance of 25 mm (Fig. 1). The electrodes were two identical  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> square plates (99.9%, Kyocera, Japan) with thicknesses of 0.64 mm and lengths of 12.7 mm. A gold paste (8884-G, ESL, USA) was screen-printed onto one side of the alumina plate and fired at 900 °C for 10 min. The 10  $\mu$ m-thick Au electrode with dimensions of 8 mm × 8 mm on the alumina plate were used as both the working and counter electrodes.

The electrodes were immersed in 40 ml of suspension. The deposition process was performed at a constant-current density of  $1.56 \text{ mA/cm}^2$ , provided by a source meter (Keithley 2400, USA). The experiments were conducted at  $22 \pm 1$  °C without any mechanical stirring for a specified amount of time ranging from 30 to 300 s. During the deposition process the voltage was recorded by the source



Fig. 1. Schematic of the electrophoretic deposition set-up. Note the dimensions are not in proportion.

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