

## Inkjet Printing of Thin Dielectric Films Based on BaTiO<sub>3</sub>

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BaTiO<sub>3</sub> thin films have been prepared by inkjet depositing of ceramic inks based on barium titanate nanopowder. Formulated inks had good sedimentation stability. The most significant stabilization of the pigment was observed for samples formulated on ethyl and n-butyl alcohols. All prepared inks had dilatant flow with a pronounced minimum viscosity of Newtonian flow. The printing operation was performed using thermal drop-on-demand inkjet printer. Printed films had dense structure and considerable adhesion to the substrate surface. Optical profilometry of the three layer film showed thickness about 400 nm. Due to strong adhesion printed coatings have not separated from the substrate surface. Special method of forming an intermediate polymer film on the substrate surface has been used to separate printed patterns. Aggressively dissolving of an intermediate polymer film has been observed during printing on this intermediate layer. After printing of each subsequent layer substrate thickness has been reduced on average 200 nm and took place rising of surface roughness. However, printed layer has been removed from the substrate surface.

**Keywords:** Inkjet printing, Ceramic inks, Thin film, Barium Titanate, Nanopowder, Rheology Characteristics, Non-Newtonian flow, Dilatancy, Viscosity, Roughness, Adhesion.

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### 1. INTRODUCTION

The present tendency to a portability of electronic devices is need to significantly decreasing in of capacitors dimensions with a simultaneous increasing of specific capacity. It is known that the capacitance of a ceramic capacitor may be raised through the thickness decreasing of dielectric layers and increasing of their number. Effective reduction of the film thickness can be carried out only with using nanosize materials. In recent years, inkjet printing has gained much attention as a new promising technique for obtaining of thin functional coatings. Proper selection optimal characteristics of printing material are very important for manufacturing thin films. Developing of functional materials with required properties is the most urgent problem of inkjet printing. Thus, investigation influence of ink properties, such as content of BaTiO<sub>3</sub>, rheology and viscosity, on characteristics of printing material is very essential.

### 2. MATERIALS AND METHODS

BaTiO<sub>3</sub> nanopowder with a mean particle size of 20 nm has been used as green material for the preparation of ceramic inks by the mechanical mixing method. The amount of solid phase has been estimated 5 wt.%.

The ink for this application has been produced by two steps. At first, barium titanate nanopowder has been milled one hour with liquid dispersant in planetary-type mill to obtain adsorbed layer on the surface of particles and then solution of the rest components has been added and milled hour again. Agate balls with 5 mm in diameter were used for pulverizing the soft agglomerated particles into primary particles. Inkjet inks have been formulated in the medium of ethyl alcohol and n-butanol. Ceramic

pigment has been dispersed in the number of polyatomic alcohols and their derivatives. Polyethylene glycol with relative molecular mass 6000 has been added as wetting agent. Formulated inks have been characterized by rheological viscosity analysis.

The multilayer structures have been fabricated through printing several layers of functional inks on a polymer substrate. The printing operation was performed using a Cannon PIXMA IP2700 printer. This printer used thermal drop-on-demand inkjet technology. Films thickness and roughness parameters have been identified by optical profilometry.

### 3. RESULTS AND DISCUSSION

#### 3.1 Dispersion of Ceramic Inks

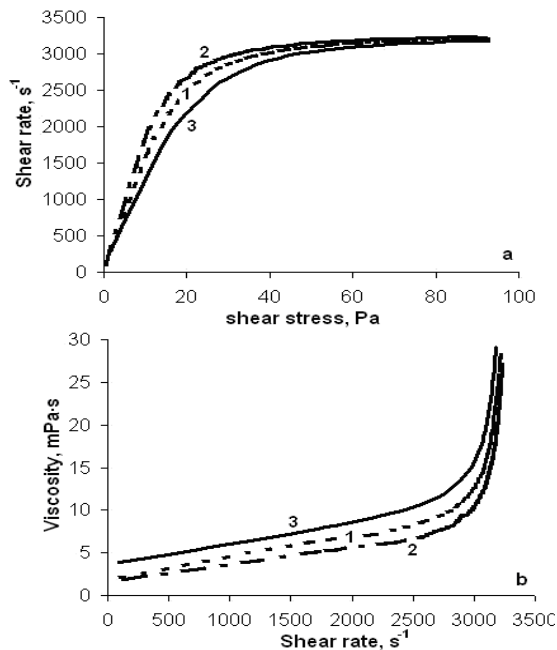
Selection of the liquid ink vehicle was performed in order to a good affinity with the solvent nanopowder BaTiO<sub>3</sub>. Most effective modification of nanosized BaTiO<sub>3</sub> has been occurred in a ethanol solution. Formulated inks had good sedimentation stability during 30 days. The most significant stabilization of the pigment was observed for formulated on n-butyl alcohol samples. Such type inks have a lower surface tension and evaporation rate of a volatile solvent with a slight increasing of viscosity. As a consequence, ink has a higher spreading coefficient.

#### 3.2 Inks Rheology Characteristics

Flow behavior matching which response commercial inks was the main criterion for selection ink composition. Commercially available sample had dilatant flow with a pronounced minimum viscosity of Newtonian flow (Fig. 1, curve 1). This character of flow is observed in weakly dilatant systems and is characterized by a

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large region of Newtonian flow. For formulated functional inks, both for ethanol and n-butanol (Fig. 1, curves 2 and 3), behavior with duplicated character of the flow have been observed. Described rheological relationships corresponded for compositions with the uniform amount of the dispersant and pigment weight content equal to 5 wt. %.



1 – commercial inks; 2 – ceramic ink based on ethanol; 3 – ink based on n-butanol

**Fig. 1** – Flow curves (a) and viscosity dependence on shear rate (b) of different inkjet inks

The rheological properties of ceramic inks are influenced by the solid content. It was seen from Fig.2 that the viscosity of the ink has been sharp decreased with adding solid fraction. Further rising of solid content led to linear increase in viscosity value.

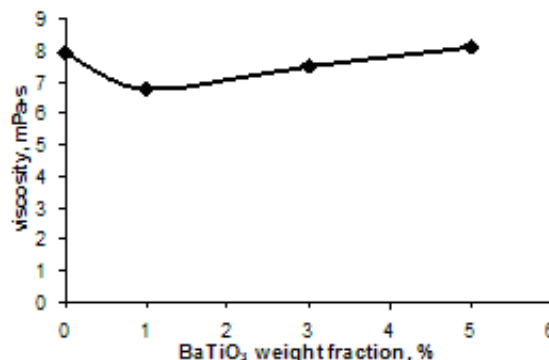
### 3.3 Characterization of the Inkjet printed films

Printed of the ethanol-based ink have been resulted in deposition of film with dense structure and considerable adhesion to the substrate surface. Optical profilometry of the three layer film showed thickness about 400 nm (Fig 3). However, obtained films have significant roughness. Rise of the roughness of the deposited film can be explained by the rough surface of the substrate.

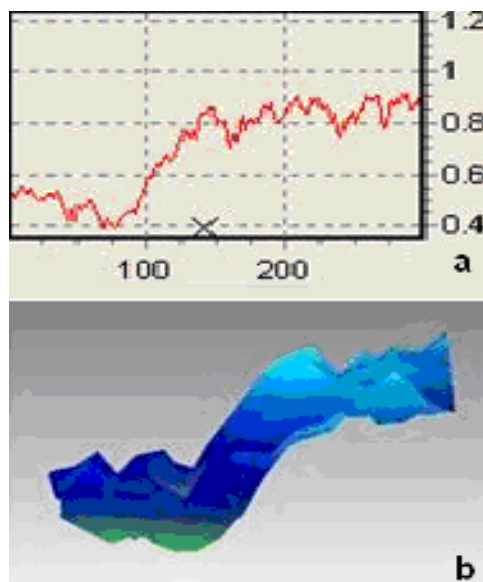
Printed coatings had not separated from the surface of polymer matrix due to strong adhesion. Special method of forming an intermediate polymer film on the substrate surface has been used to separate printed patterns. Casted film had a thickness of about 2  $\mu m$  and negligible roughness (Fig. 4 a).

Aggressively dissolving of an intermediate polymer film has been observed during printing n-butanol-based inks on this intermediate layer. After printing of each subsequent layer substrate thickness has been reduced

on average 200 nm (Fig. 4 b-d). The roughness of the first layer and the initial substrate has been comparable and third film had the value of an order of magnitude higher. However, printed layer has been removed from the substrate surface.



**Fig. 2** – Influence of mass fraction of barium titanate on viscosity of ceramic ink



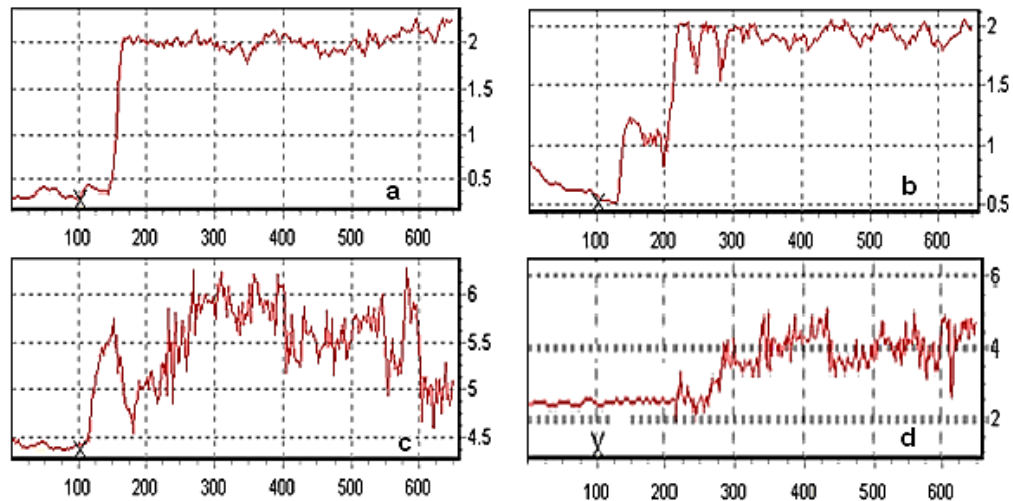
**Fig. 3** – Surface profiles of deposited multilayer film (thickness 400 nm): a – 2D surface profile; b – 3D surface profile

## 4. CONCLUSIONS

In the low-viscosity systems maximum amount of the stabilized solid phase is 5 wt. %. Pigment inks are stable to sedimentation for at least 30 days.

Fabricated multilayer ceramic layers had a dense structure and thickness of about 400 nm. Surface roughness of the printed structures was significant for both types of inks.

Prepared films exhibit significant adhesion to the substrate surface. Printed material can be separated only by applying to the substrate surface of the intermediate polymer film.



a – intermediate polymer film; b – one layer; c – two layers; d – three layers

Fig. 4 – 2D surface profiles of printed BaTiO<sub>3</sub> films

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