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Comparison of barium titanate thin films prepared by inkjet printing and spin coating

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Abstract

In this paper, barium titanate films were prepared by different deposition techniques (spin coating, office Epson inkjet printer and commercial Dimatix inkjet printer). As inkjet technique requires special rheological properties of inks the first part of the study deals with the preparation of inks, whereas the second part examines and compares structural characteristics of the deposited films. Inks were synthesized by sol-gel method and parameters such as viscosity, particle size and surface tension were measured. Deposited films were examined by optical and scanning electron microscopy, XRD analysis and Raman spectroscopy. The findings consider advantages and disadvantages of the particular deposition techniques.

Keywords: *$BaTiO_3$, thin films, sol-gel, inkjet, spin coating*

I. Introduction

In past few decades thin films have attracted great attention especially in the field of microelectronics. Compared to bulk materials, thin films can provide many advantages such as higher integration density, operational speed, low cost of production and less power consumption [1,2]. Due to this fact, a number of thin film deposition techniques were developed. Some of these techniques, such as spin and dip coating, are very simple and cheap, but lack possibility of obtaining complex forms [3,4]. On the other hand, there are techniques with excellent performances in obtaining complex forms such as lithography, but their setup is often very complicated and expensive [5]. Inkjet printing is a relatively novel technique in thin film technology, and has been used successfully to build ceramic objects of submillimeter-scaled components and multimaterial devices [6]. It is based on computer-controlled droplet-deposition on previously prepared substrate surface, and offers opportunity for low cost direct fabrication of complex forms. However, for a successful printing, appropriate rheological properties of inks are required, because when a droplet is expelled, energy goes into viscous flow, surface tension of the drop and kinetic energy [7–10]. Thus, optimal viscosity, surface tension and particle size are usually prescribed by the producer of inkjet printing devices.

Barium titanate is one of the most important ferroelectric materials for many applications in microelectronic, especially for ceramic capacitor production [11]. In last few years many authors have investigated printed pure or doped barium titanate films [4,12–14]. The simplest way to prepare printable barium titanate inks is by utilizing sol-gel synthesis, where manipulation over rheological parameters is relatively easy. In this study sol-gel derived barium titanate thin films deposited by spin coating and two different inkjet printing techniques were investigated. The main goal was to investigate the advantages of inkjet printing in comparison to widely used spin coating technique.

II. Experimental

Barium titanate sols (Table 1) were prepared by using barium carbonate ($BaCO_3$, Merck) and tetrabutylorthotitanate ($Ti(C_4H_9)_4$, Fluka) as precursors. In order to prepare barium titanate sol of desired concentration, a certain amount of barium carbonate was dissolved in glacial acetic acid glacial (CH_3COOH, Lach:ner), at 70 °C. After that, the solution was cooled down to room

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Table 1. Notation of investigated samples

Sample notation	Concentration of $BaTiO_3$ [mol/dm^3]	Amount of glycerine [vol.%]
B2.5	0.25	0
B2.5G5	0.25	5
B2.5G10	0.25	10
B2.5G20	0.25	20

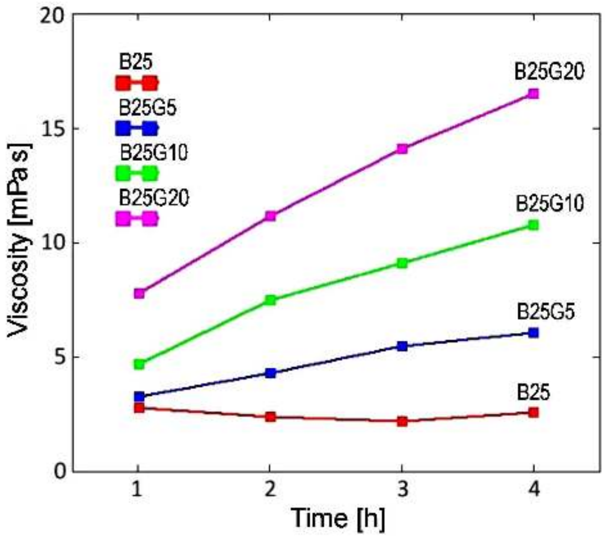


Figure 1. Viscosity over time for sols of different compositions

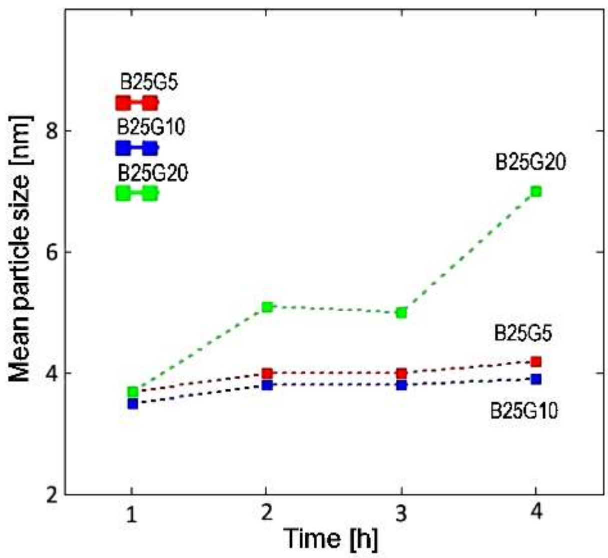


Figure 2. Mean particle size over time

temperature. Subsequently different amounts of glycerine ($C_3H_8O_3$, Zorka Šabac) were added in the system to regulate viscosity which is followed by addition of stoichiometric amount of tetrabutylorthotitanate. During the whole preparation procedure a magnetic stirrer agitated the mixture.

The prepared sols were deposited on previously cleaned silicon substrates in three different ways by: i) inkjet deposition materials printer DMP-3000 (Dimatix), ii) an office inkjet printer Epson XP-202 and iii) spin coating. Each deposited film was finally thermally treated at different temperature up to 800 °C for 30 min.

In order to examine printability of the sols, particle size distribution, viscosity and surface tension were measured. Particle size distribution was determined by dynamic light scattering using Malvern Zetasizer Nano device. Viscosity measurement was done with rotational viscosimeter Thermo HAAKE RheoStress 600. Surface tension was measured by Du Nouy method using Sigma 703D, KSV tensiometer. Regularity of edges, uniformity of films and the existence of cracks were examined by optical microscopy. Further morphological analysis of the films was investigated by scanning electron microscopy (SEM) using JEOL JSM-6460LV microscope and atomic force microscopy, AFM using DI CPII, Veeco. Structural characterization of the obtained films was done by X-ray diffraction (XRD) analysis and Raman spectroscopy. Crystallinity and phase composition were investigated by XRD analysis using Rigaku MiniFlex600 diffractometer. The presence of tetragonal barium titanate phase was examined by Raman spectroscopy using Thermo Fisher Scientific DXR™ Raman Microscope.

III. Results and discussion

3.1. Characterization of sols

The preliminary deposition results confirmed that the films prepared from concentrated $BaTiO_3$ sols have higher tendency to crack due to their larger thickness [15]. This was the reason why in this study the sols with concentration of 0.25 M were investigated. In the first part of this research it was essential to achieve control over particle size, viscosity and surface tension values, as inkjet deposition technique is very sensitive to sol rheology. These parameters vary with chemical composition and time and their optimal values are characteristic of every inkjet device. Thus, for the inkjet deposition material printer DMP3000 (Dimatix) the optimal values of viscosity, surface tension and particle size are 10–12 mPa·s, 25–55 mN/m and <200 nm, respectively. On the other hand, office inkjet printer Epson XP-202 normally uses inks with viscosities around 5 mPa·s.

Figure 1 shows steady increase in viscosity over time for the sols containing glycerine. Viscosity of the pure barium titanate B25 sol remains almost constant over time, whereas continuous increase of viscosity is obvious for the sols containing glycerine (Fig. 1). The increase in viscosity over time is even greater for the sols with a higher proportion of glycerine, i.e. for more vis-

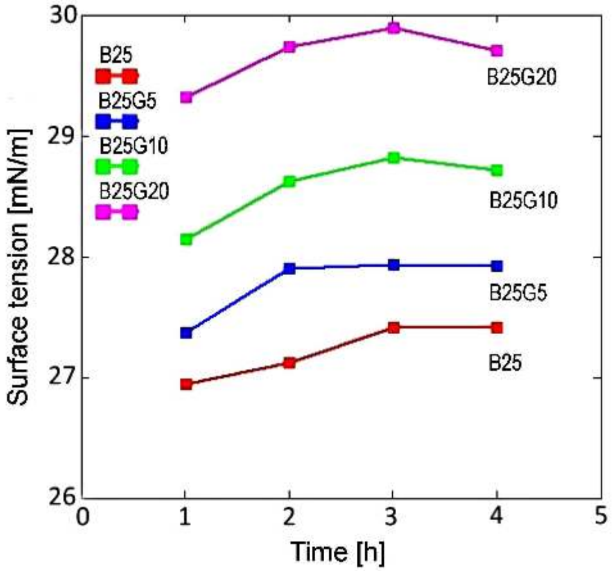


Figure 3. Surface tension values over time

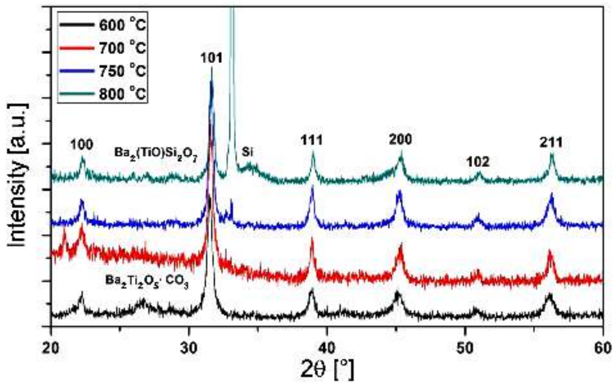


Figure 4. XRD patterns of $BaTiO_3$ films sintered at different temperatures

cous sols. This trend in viscosity values can be attributed to the increasing number of particles over time.

Determination of mean particle size by dynamic light scattering is shown in Fig. 2. Measurements show that particles having size in range from 3 to 7 nm are present in the sols that contain glycerine. Particle size does not vary significantly over time and remain small enough to be printed through nozzles in relevant time frame. During first 4 hours after synthesis no particles could be observed in system without glycerine. This supports the fact that number of particles affects viscosity and correlates with the results of viscosity measurements of the sample B25.

Surface tension measurements are shown in Fig. 3. All measured values are in the optimal range required for printing and spin coating. There is a steady increase in surface tension over time and also with the increasing content of glycerine, what was expected as surface tension of the acetic acid and glycerine were 27 and 64 mN/m, respectively.

According to the obtained results sols of appropriate rheological properties were chosen for inkjet printing. Thus, the pure barium titanium sol (B25) was used for printing on the Epson office inkjet printer, whereas this sol was not appropriate for the inkjet deposition material printer DMP3000 (Dimatix) due to its low viscosity. Although, the recommended viscosity for the Dimatix inkjet printer is 10–12 mPa·s, preliminary experiments confirmed possibility of printing sols with lower viscosity. This was the reason why the sol with addition of 10 vol.% of glycerin (B25G10) was used for inkjet printing with Dimatix device.

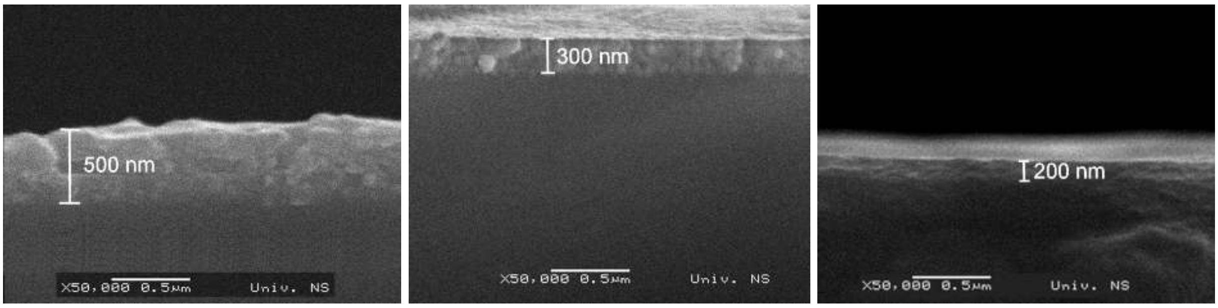
3.2. Characterization of films

In order to examine crystalline structure formation and optimal sintering temperature the barium titanate film, deposited from B25 sol by spin coating, was examined by XRD. The film crystallize already at 600 °C in perovskite cubic structure (JCPDS card no. 31-0174) (Fig. 4) with a small amount of an intermediate phase (barium-titanateoxycarbonate - $Ba_2Ti_2O_5 \cdot CO_3$). The formation of the intermediate phase was often seen in the polymerized complex method due to esterification of alcohol and carboxyl acids containing (Ba, Ti) ions, which resulted in less segregation of $BaCO_3$ [16]. The intermediate phase completely disappeared at 700 °C. At 800 °C reaction between silicon substrate and the film may occur leading to formation of fresnoite ($Ba_2(TiO)Si_2O_7$, JCPDS card no. 18-0197) (Fig. 4). Optimal calcination temperature is therefore between 700 and 800 °C.

The $BaTiO_3$ films deposited by different (Dimatix and office Epson) inkjet printers are compared and it can be seen that there is no big difference in their characteristics. There is no big difference even between structural characteristics of the barium titanate films deposited by spin and inkjet techniques. Thus, SEM analysis (Fig. 5) confirmed crack-free thin films with good adherence to the substrate for each sample. Their nanocrystalline nature was confirmed by AFM measurements (Fig. 6). Estimated thickness of the examined films deposited by spin coating, Epson and Dimatix printer is around 500 (5 layers), 300 and 200 nm, respectively. XRD patterns (Fig. 7a) of the examined films confirmed characteristic peaks for cubic $BaTiO_3$ phase (JCPDS 31-0174), only their intensities are different due to different film thickness.

However, Raman spectra analysis proved the existence of tetragonal phase. Characteristic peak for tetragonal phase originating from B1, E(TO+LO) mode can be noticed at 305 cm^{-1} (Fig. 7b.). The most intense peak at 522 cm^{-1} originates from silicon substrate and overlaps one of $BaTiO_3$ peaks at 517 cm^{-1} [17]. Considering that cubic phase does not have any Raman active modes it was not possible to determine phase content ratio. Nevertheless, nanocrystalline structure proved by AFM surely favours the formation of cubic phase indicating that tetragonal phase probably originates from particular large grains.

Spin coating method is used for film production in addition to Epson and Dimatix inkjet printing to compare



(a) (b) (c)

Figure 5. SEM images of films deposited with different methods: a) spin coating (5 layers), b) Epson office printer and c) Dimatix inkjet printer

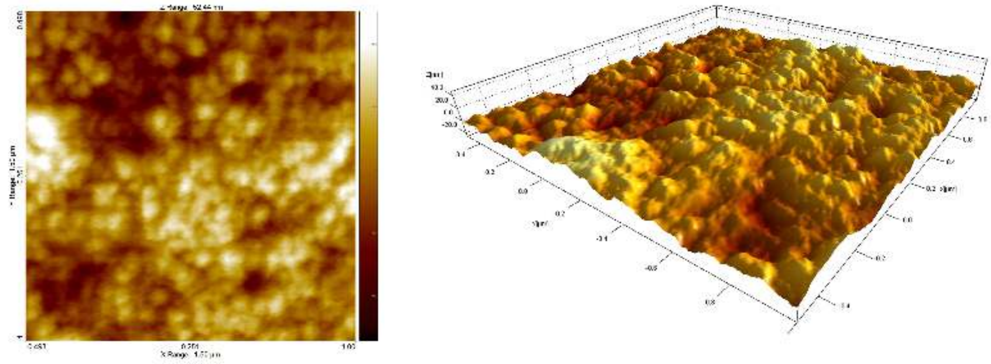
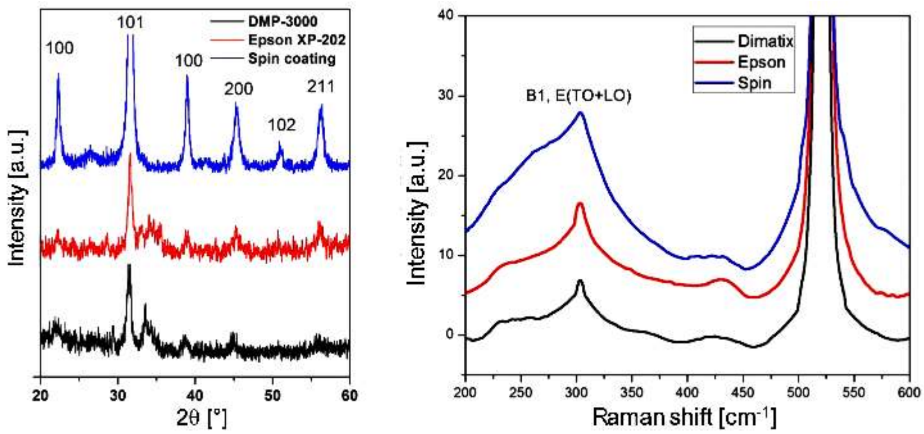


Figure 6. AFM images of inkjet $BaTiO_3$ films calcined at 750 °C

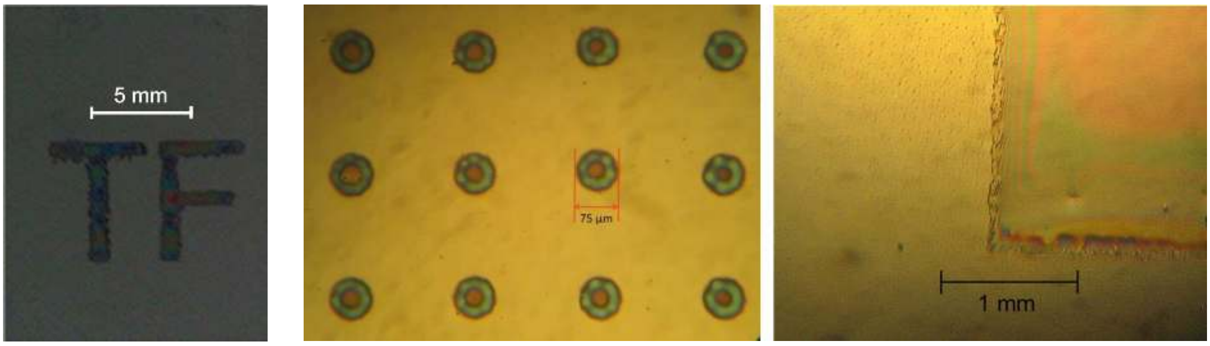
their applicability. Although spin coating method is not suitable for obtaining complex structures, advantage of this method is easy fabrication and flexibility regarding to sol rheology. Thus, even with the low-concentrated sols it is possible to control thickness of films by formation of multilayered structures.

Epson XP-202 printer can achieve good precision during the printing barium titanate sol, but only if a high quality mode of printing is used. This is due to the fact that it is not possible to control the droplet formation, appearance of the satellite droplets and space between the deposited droplets. In addition, Epson XP-202 printer cannot be used for preparation of multilayered films as the precise control of the starting point of deposition is very difficult. Thus, considering simplicity and cost of Epson office inkjet printer, this straightforward technique is appropriate for obtaining shapes that do not require high level of precision (like one presented in Fig. 8a) in a quick and easy manner [18]. Because of the fact that morphology of the Epson-deposited film does not differ significantly from the Dimatix-deposited one, office inkjet printer can be used for testing of inks, as well as fabrication of parallel plate capacitors and sensors [19,20].



(a) (b)

Figure 7. Structural characterization of films: a) XRD analysis and b) Raman spectroscopy



(a) (b) (c)

Figure 8. Barium titanate pattern printed by Epson office XP-202 inkjet printer (a); droplets (b) and edge (c) printed by Dimatix materials printer DMP-3000

Regarding the possibility of obtaining complex forms, Dimatix materials printer DMP-3000 has better performance than spin coating and Epson inkjet printing methods (Fig. 8), with maximum precision even down to 10 µm. Nevertheless, precision is actually the most dependent on size of printed droplets and for the investigated $BaTiO_3$ system it is ~75 µm (Fig. 8b) determining the real printing precision. In order to obtain continuous film drop space of ~35 µm was used, what is a half of droplet size. Such precision can be utilized for printing of meander, interdigitated and other complex structures. Therefore Dimatix materials printer DMP-3000 stands out as the best solution for fabrication of devices like varactor shunts, interdigitated and straight gap capacitors [21,22]. Since it is possible to control initial place to start printing it is also possible to make multilayer structures with different thickness. Nevertheless, for this system that was complicated due to short time stability of B25G10 sol.

Even there is no big structural difference between the spin and inkjet $BaTiO_3$ films, it is necessary to underline the following things. Spin coating is simpler than inkjet printing, but it gives only scarce possibilities. Spin coating is the best option for the deposition of film over the whole surface of a substrate in a quick and simple manner. Thus, spin coating can be used for deposition of bottom electrodes, film-substrate interactions or examining the behaviour of films during thermal treatment. However, it is not possible to deposit material on predetermined places by spin coating. Hence it cannot be used for fabrication of defined shapes, but with spin technique it is easy to adjust the film thickness by different number of deposited layers. However, inkjet technique has big advantages regarding the possibility of obtaining complex forms post-processing.

IV. Conclusions

Barium titanate films were prepared by three different techniques (spin coating, inkjet printing on office Epson XP 202 and commercial Dimatix DMP-3000) on silicon substrate by solution deposition method. It was shown that there is no big structural difference between the spin and inkjet $BaTiO_3$ films. However, spin coating is simpler than inkjet printing and with spin technique it is easy to adjust the film thickness by different number of deposited layers. On the other hand, inkjet techniques have big advantages regarding the possibility of obtaining complex forms in contrast to spin coating technique. Office inkjet printer, as a low cost technique, can be easily utilized for obtaining simpler forms such as squares and rectangles of millimeter dimensions. Precision and manipulation over printing parameters are the most important advantages of commercial Dimatix inkjet printer and incomparable to those of office inkjet printer. It enables printing of large areas, complex forms with high precision and multilayered structures. Thus, inkjet deposition materials printer Dimatix DMP-3000 can be used in many areas (such as microelectronic, medicine, catalysis etc.) for fabrication uniform films, bottom electrodes, meanders, interdigitaded and multilayered films.

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