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Synthesis and characterization of multilayered $BaTiO_3/NiFe_2O_4$ thin films

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Abstract

Presented research was focused on the fabrication of multiferroic thin film structures, composed of ferrielectric barium titanate perovskite phase and magnetostrictive nickel ferrite spinel phase. The applicability of different, solution based, deposition techniques (film growth from solution, dip coating and spin coating) for the fabrication of multilayered $BaTiO_3/NiFe_2O_4$ thin films was investigated. It was shown that only spin coating produces films of desired nanostructure, thickness and smooth and crackfree surfaces.

Keywords: *multiferroic ceramics, multilayered $BaTiO_3/NiFe_2O_4$ structure, film deposition*

I. Introduction

Lately, multiferroic materials [1–9] with the coexistence of both ferroelectric and ferromagnetic properties are widely investigated due to their potential applications in various microelectronic devices. However, the coexistence alone is not enough as a strong coupling interaction between two ferroic orders and, consequently, the presence of the valuable magnetoelectric effect is required [5]. The magnetoelectric effect can be simply defined as the appearance of electric polarization upon subjecting the material to a magnetic field or, conversely, by the appearance of magnetization upon applying an electric field. Different single-phase magnetoelectric multiferroic materials have been discovered and widely investigated (such as perovskites $BiFeO_3$ and $BiMnO_3$; hexagonal rare-earth manganates; Fe_3O_4 spinel, etc.) but they are all characterized by a small magnetoelectric coefficient [7,10–12].

An alternative approach, based on composite materials where the magnetoelectric effect arises from the interaction of ferroelectric and ferromagnetic phases, has been developed [4–6,8,13]. In those composites, none of the constituent phases has an intrinsic magnetoelectric effect, but, due to the interaction of the phases, a very high magnetoelectric coefficient can be obtained [5,7]. The mechanism of the interaction can be described by the induced deformation of the piezoelectric (electrostrictive) phase upon applying an external electric field that is transmitted to the magnetostrictive phase through the shared interface and causes a change in its magnetization (or vice versa) [2,6,14]. Particulate bulk composite materials, consisting of spinel and perovskite phases, have been widely investigated [8,13,15]. This is because both perovskites and spinels have high chemical, thermal and mechanical stabilities and form a limited number of secondary phases when mixed together [6]. However, the corresponding magnetoelectric coefficients of the particulate composites are still significantly lower than the theoretically predicted values. This deviation is usually caused by processing difficulties such as the achievement of sufficient bulk density, good dispersion of ferrite phase and coherent interfaces, as well as avoiding possible reactions and interfacial diffusion between the perovskite and spinel phases. Multilayered composites with alternating perovskite and ferrite layers can have even higher magnetoelectric coefficient then the particulate composites and are therefore considered as viable alternatives [3,6,16].

Various vapour deposition techniques [17,18] have been used for the preparation of multilayered composite films, but solution-based approaches have attracted considerable attention in recent years [14,19–21] as they are much cheaper and easily adjustable for different conditions. Thus, in this paper we investigated the applicability of different, solution based, deposition techniques for the fabrication of multilayered $BaTiO_3/NiFe_2O_4$ thin films.

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II. Experimental

2.1 Preparation of precursor solutions/sols

Multilayered $BaTiO_3/NiFe_2O_4$ thin films (Fig. 1) were fabricated by different chemical solution deposition techniques (film growth from solution, dip coating and spin coating) on silica-glass substrates.

Two different precursors for the deposition of $NiFe_2O_4$ layers were prepared. The first one, denoted as WF solution, was an aqueous solution containing Fe^{3+} and Ni^{2+} ions, prepared in a two-step process proposed by Yourdkhani *et al.* [14]. In the first step FeOOH particles were precipitated from an aqueous solution of $Fe(NO)_3\times9H_2O$ (Fluka, Switzerland) in the presence of a dilute ammonia solution, and subsequently centrifuged, washed and dried. In the second step, the obtained FeOOH particles and stoichiometric amount of $Ni(NO_3)_3\times9H_2O$ (Fluka, Switzerland) were dissolved in distilled water with boric acid and an aqueous solution containing Fe^{3+} and Ni^{2+} ions with Ni^{2+} concentration of 0.5 M was obtained. The second precursor, denoted as MF sol, was prepared by dissolving stoichiometric amounts of $Fe(NO_3)_3\times9H_2O$ and $Ni(NO)_3\times9H_2O$ in 2-methoxyethanol. After stirring at room temperature for 20 min a clear, brownish precursor sol with Ni^{2+} concentration of 0.38 M was obtained with pH = 1.5.

The precursor sol for the deposition of $BaTiO_3$ layers was prepared by mixing of $BaCO_3$ (Merck, Germany) dissolved in concentrated acetic acid with tetrabutyl-orthotitanate ($Ti(OC_4H_9)_4$, Fluka, Switzerland) at room temperature (sol denoted as AT). After 20 min of stirring at room temperature a clear, colourless precursor sol with concentration of 0.5 M was obtained, with pH = 1.

2.2 Deposition of multilayered thin films

Three different deposition techniques were examined: i) film growth from solution, ii) dip coating and iii) spin coating. Prior to the film deposition, silica-glass substrates were cleaned ultrasonically in acetone, ethanol and rinsed with de-ionised water.

In the first set of experiments the aim was to obtain bi-layered structure by growing of $NiFe_2O_4$ layer from the WF solution and subsequent deposition of $BaTiO_3$ layer by dip-coating technique (sample G-FT, Table 1). After that the intention was to increase the film thickness by deposition of new $NiFe_2O_4$ and $BaTiO_3$ layers. The previously cleaned silica-glass substrate was suspended vertically and kept in the WF solution at 40 °C for periods between 30 and 120 min. The initial pH of the solution was around 4 and decreased slowly over the course of the deposition. The obtained film was left to dry in air at 120 °C for 20 min., and after that the $BaTiO_3$ layer was deposited by the dip-coating technique from the AT sol with the withdrawal speed of 0.12 mm/s. After the deposition, the film was dried in an oven at 120 °C and finally slowly heated to 600 °C and annealed for 60 min.

Multilayered $BaTiO_3/NiFe_2O_4$ thin films (with six and ten layers in total) on silica-glass substrate were prepared by alternate deposition of $BaTiO_3$ and $NiFe_2O_4$ layers from the AT and MF sol, respectively. Two different deposition techniques were used: dip-coating with the withdrawal speed of 0.12 mm/s (sample D-FT, Table 1) and spin-coating with the speed of 3000 rpm for 30 s (samples S1-FT and S2-FT, Table 1). The spin-coated films were subjected to two different drying/consolidation procedures. For the S1-FT sample every de-

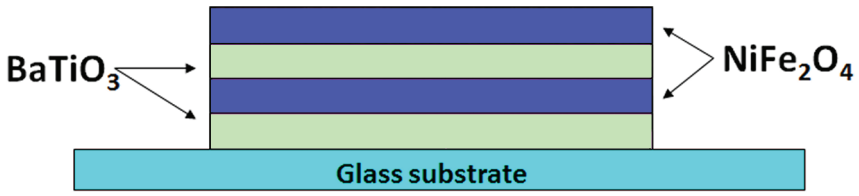
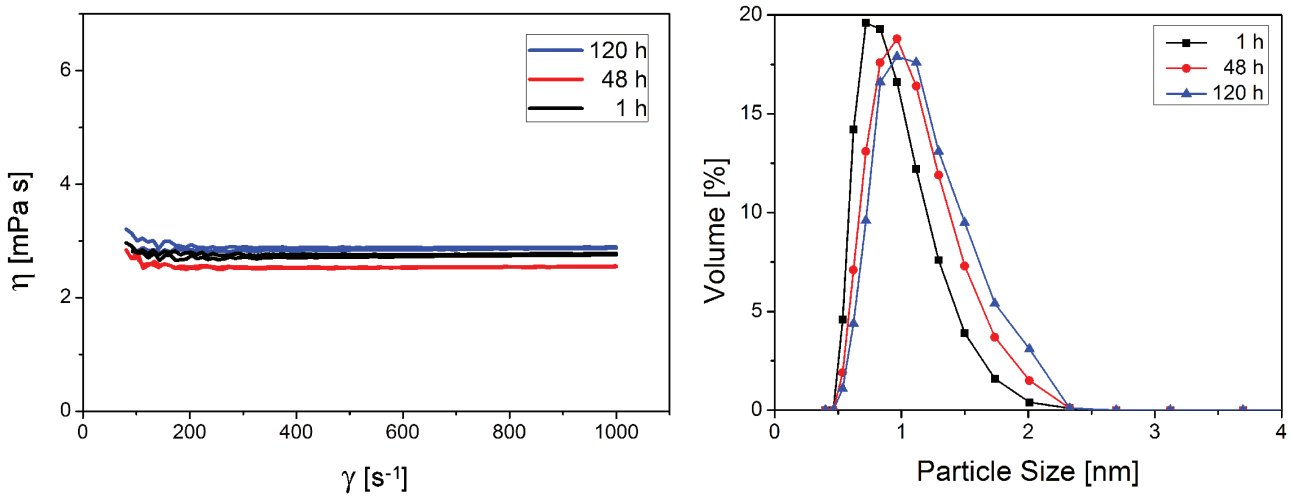


Figure 1. Schematic representation of multilayered $BaTiO_3/NiFe_2O_4$ thin films

Table 1. Experimental conditions for preparation of $BaTiO_3/NiFe_2O_4$ multilayer films

Sample	Deposition		Final heat treatments
	$NiFe_2O_4$ layer	$BaTiO_3$ layer	
G-FT	Growth + drying (WF + 120 °C)	Dip + drying (AT + 120 °C)	500 °C and 600 °C for 1 h
D-FT	Dip + drying (MF + 120 °C)	Dip + drying (AT + 120 °C)	500 °C and 600 °C for 1 h
S1-FT	Spin + drying (MF + 120 °C)	Spin + drying (AT + 120 °C)	500 °C and 600 °C for 1 h
S2-FT	Spin + caltination (MF + 500 °C)	Spin + caltination (AT + 500 °C)	500 °C and 600 °C for 1 h



a) b)

Figure 2. Viscosity (a) and particle size distribution (b) of ferrite MF sol

posited layer was left to dry in air in an oven at 120 °C before the deposition of the next layer. In the case of the S2-FT sample, drying in an oven was substituted by slowly heating the sample to 500 °C and holding it at that temperature for 5 min. In both cases the layer deposition procedure was repeated six or ten times and after that the formed multilayered films were annealed at 500 °C and 600 °C for 60 min.

2.3 Characterization of sols and films

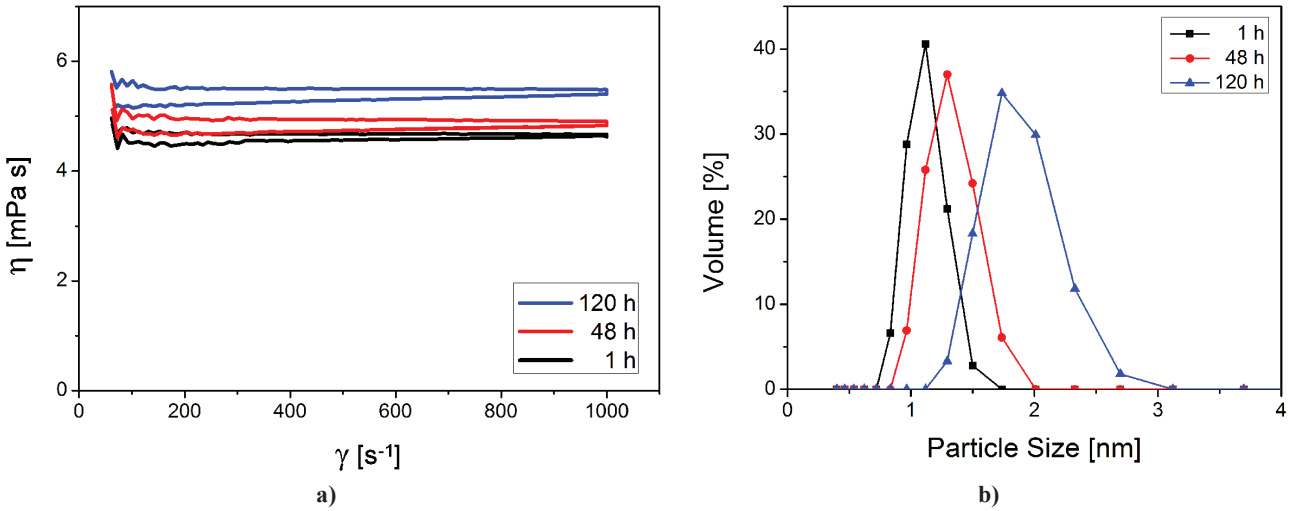
Viscosity of the precursor sols was measured by a Thermo Haake RS600 viscosimeter. Particle size distributions (by volume) of the precursor sols were measured by dynamic light scattering, DLS (Zetasizer Nano ZS, Malvern Instruments). The phase composition of $BaTiO_3/NiFe_2O_4$ multilayer films was characterized by X-ray diffraction (X'Pert PRO diffractometer with Cu Kα (1.54184 Å) radiation and an X'Celerator detector) in 2θ range from 10° to 120°. The structure of surface and cross section of the prepared thin films was examined by scanning electron microscopy, SEM (JEOL JSM-6460LV). The presence of all the ions in the examined multilayer films was confirmed by the EDS analysis (Oxford Instruments).

III. Results and discussion

3.1 Characterization of precursor solution/sols

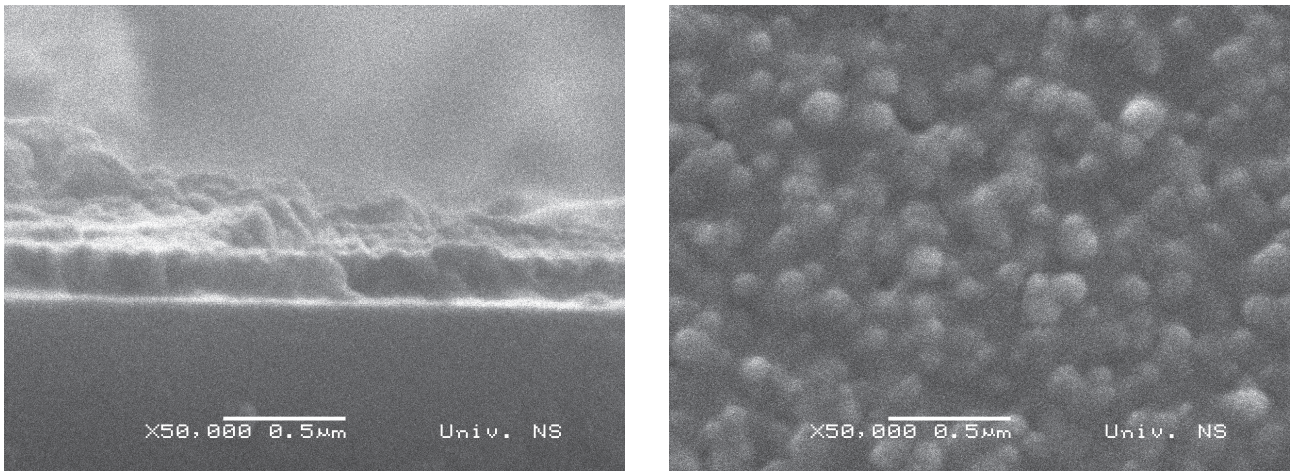
The WF precursor solution, used for the deposition of the $NiFe_2O_4$ layers by the growth method, is light green and transparent with the viscosity of 1 mPa·s remaining constant for at least 10 days. This solution was not used for the deposition of $NiFe_2O_4$ layers by dip and spin coating due to its low viscosity and low surface tension. It was the reason why another ferrite sol (MF) was prepared using 2-metoxyethanol. The MF precursor sol is brownish, transparent and stable for at least one week. It underwent a slight change of viscosity (Fig. 2a), and almost insignificant particle growth upon ageing at room temperature (Fig. 2b).

The titanate, AT, precursor sol, used for the deposition of $BaTiO_3$ layers, is colourless, transparent and stable for at least one week. Figure 3 illustrates that the viscosity of the AT sol increases slightly which can be



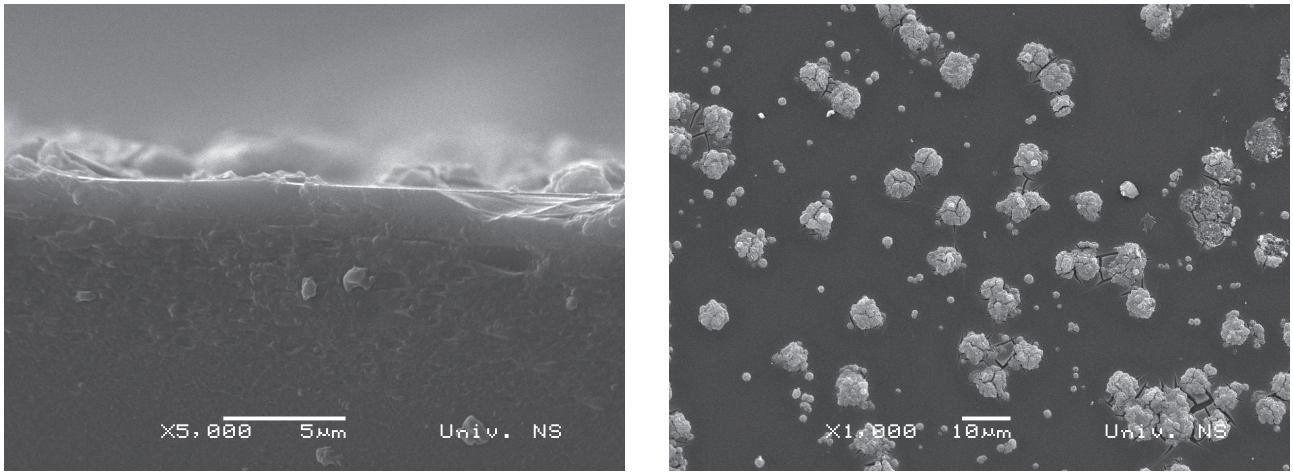
a) b)

Figure 3. Viscosity (a) and particle size distribution (b) of titanate AT sol



a) b)

Figure 4. Single ferrite layer deposited by the growth method and calcined at 500 °C for 1 h: a) cross section b) and surface morphology



a) b)

Figure 5. SEM micrographs of multilayered $BaTiO_3/NiFe_2O_4$ film S1-FT (prepared by spin-coating and drying of every deposited layer): a) cross section and b) surface morphology

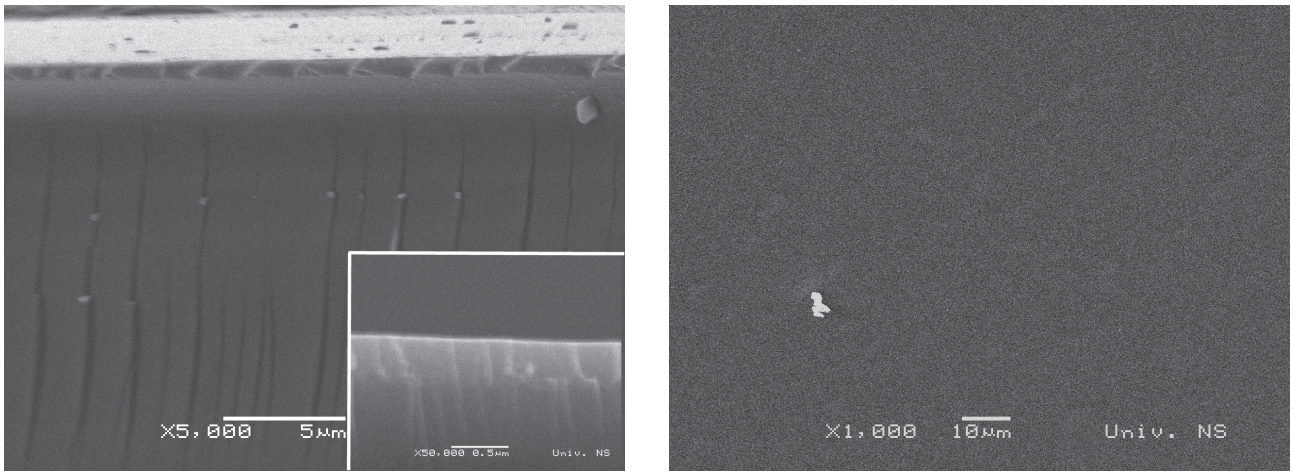
assigned to a small particle growth upon ageing at room temperature. Sols with particles that are stable or grow only slightly during ageing are highly desirable, because rapid particle growth may result in film thickening, surface imperfections and increased grain size of the final film.

3.2 Characterization of $BaTiO_3/NiFe_2O_4$ multilayer films

Growth method – It was observed that deposition time has a great influence on the uniformity of the ferrite layer deposited from the aqueous WF solution by the growth method. For deposition times shorter than 90 min. the obtained layer is not uniform. On the other hand, after 120 min. a uniform ferrite layer with thickness of ~200 nm and a relatively rough surface was prepared (Fig. 4). Deposition of the second $BaTiO_3$ layer was successfully performed by dip-coating from the AT sol, however, the third $NiFe_2O_4$ layer could not be deposited by the growth method. The reason was the destructive behaviour of the aqueous WF ferrite solution to the previously deposited $BaTiO_3$ layer. The long deposition time required by this method resulted in the titanate layer being peeled off.

Dip-coating - Multilayered $BaTiO_3/NiFe_2O_4$ films were successfully deposited by the dip-coating process. The obtained 10 layered films have good adherence to the silica-glass substrate, uniform thickness of ~1.5 µm and fine grain structure (Fig. 5a). However, cracks and bubble like bumps can be seen on the film surface (Fig. 5b). We assumed that the reason was thickness of more than 1 µm and drying that was too fast. In order to reduce the thickness of the resulting films, spin-coating was introduced.

Spin-coating - SEM micrographs of the ten-layered $BaTiO_3/NiFe_2O_4$ films deposited by spin-coating indicate that the thickness of fabricated film was reduced to 400 nm, however the surface imperfection remained. Bubble like bumps can be assigned to the reaction between the deposited $NiFe_2O_4$ and $BaTiO_3$ layers, name-



a) b)

Figure 6. SEM micrographs of multilayered $BaTiO_3/NiFe_2O_4$ film S2-FT (prepared by spin-coating and drying/annealing of every deposited layer): a) cross section and b) surface morphology

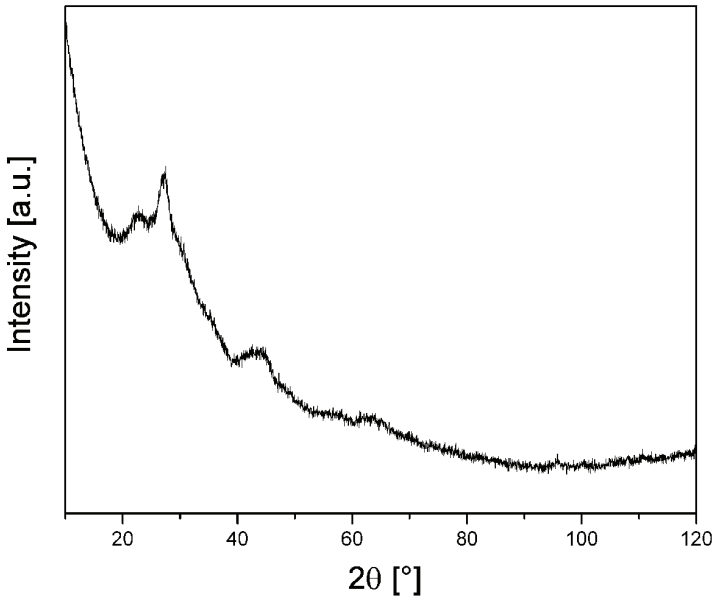


Figure 7. XRD pattern of multilayered $BaTiO_3/NiFe_2O_4$ film S2-FT (prepared by spin-coating and drying/annealing of every deposited layer)

ly the precursor sols' solvents, as they were only dried at 120 °C. Therefore, an additional drying/consolidation procedure was introduced to the fabrication process of the multilayered films. In addition to drying the samples in an oven at 120 °C, they were slowly heated to 500 °C and held at that temperature for 5 min. Heating each dried layer to 500 °C ensured that all remaining solvent was evaporated and that the formed layer was completely consolidated. This led to nanostructured thin (Fig. 6a) and crack free films (Fig. 6b). The XRD pattern of the $BaTiO_3/NiFe_2O_4$ film, heated for 1 h at 600 °C, is presented in Fig. 7, and is characterized by very weak peaks. The observed XRD peaks may be assigned to the initial formation of nickel-ferrite phase and perovskite phases and the very fine (nanostructured) nature of the obtained multilayered $BaTiO_3/NiFe_2O_4$ films. Furthermore, preliminary results on phase composition obtained by X-ray diffraction of identical films on alumina substrates, treated at higher temperatures (1000 °C) are consistent with previous assumptions.

IV. Conclusions

Multilayered $BaTiO_3/NiFe_2O_4$ thin films were fabricated by different chemical solution deposition techniques (film growth from solution, dip coating and spin coating) on silica-glass substrate. With the growth method only bi-layered $NiFe_2O_4/BaTiO_3$ films were successfully prepared, because of the destructive behaviour of the aqueous ferrite solution to the previously deposited $BaTiO_3$ layer. On the other hand, multilayered $BaTiO_3/NiFe_2O_4$ films, with six and ten layers in total and controllable thickness can be prepared by dip and spin coat-

ing techniques. However, cracks and bubble like bumps were formed on the film surface if every deposited layer was only dried in air at 120 °C before the deposition of the next layer. Spin coating and heating each dried layer to 500 °C ensured the fabrication of films with desired nanostructure, thickness of 400 nm and smooth and crackfree surfaces.

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