Fabrication of Titanate Barium Films by Electrophoretic Deposition Technique

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Abstract: EPD (electrophoretic deposition) technique has been shown as an effective method to produce thin or thick layers at voltage 5-100 V onto Ni conductive substrate. The aim of this study is to use the EPD method to fabricate films from suspensions BaTiO₃. The effects of the EPD process parameters such as the suspension concentration, deposition time, electrical field strength on the specific EPD deposited weight, morphology particles were used. The surface microstructures of the as-deposited films were investigated by SEM (scanning electron microscopy). A homogeneous microstructure was obtained at applied electric field of 100 V and 1 min of deposition time at an electrode distance of 1.0 cm.

Key words: BaTiO₃, suspension, EPD, deposition time, viscosity, oligoperoxide.

1. Introduction

EPD (electrophoretic deposition) simple technique has been shown as an effective method to produce thin layers on to conductive substrates [1-3]. It is known that the EPD method is a versatile method to fabricate thin or thick films of both metals and ceramics on the electrode substrates. For example, the EPD technique has been used by authors to cover the termination surface of fine inner Pd-Ag electrodes (electrode width 3-4 μm) with zinc borosilicate glass (Zn-B-Si-O) powder to form insulator layers on both sides of piezoelectric PZT-PNN ((Pb(Nb, Ni)O₃-Pb(Zr, Ti)O₃) actuators [4].

Recently, the mild organic solvent such as acetone, ethanol, acetylacetone was used to prepare BaTiO₃ EPD suspension [5-7]. Harari [8] formed BaTiO₃ films with thickness of 10-50 μm from the suspension with particles size of 200 nm using a mixture acetone-ethanol (2:1).

Nanostructured films of BaTiO₃ [9] with the

thickness of several microns were prepared by EPD of monodisperse powders in mixture of 2-methoxyethanol-acetylacetone. Films were formed at electrode composition of Pt/Ti/SiO₂.

High-oriented film BaTiO₃ [10] were obtained on Pt electrodes by a combination of EPD and hydrothermal method. The distance between the electrodes was 4 cm and the area was 0.5-1 cm². It was found that the concentration of Ba(OH)₂ in suspension influences on the films orientation. In the region of Ba(OH)₂ concentration of 0.08-0.1 mol·L⁻¹ the orientation parameter $f = 1$, and in 0.04-0.065 mol·L⁻¹ $f < 1$, respectively.

Thus, most publications on EPD have a pronounced applied nature and consider the process itself EPD powder suspensions as an auxiliary in obtaining certain materials. Stabilization of the suspension is generally regarded as being essential for attaining uniform particle-packing structure of the electrophoretic ceramic deposits. Suspension stability depends on the amount of surfactant or additive used, suspension concentration, pH and conductivity.

In the present study, the authors used surfactant

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functional (OP (oligoperoxide)) oligoperoxide additive of BaTiO₃ nanoparticles for stable suspension fabrication in mixture acetylacetone-ethanol. In addition, to use the EPD method to fabricate BaTiO₃ ferroelectric layers with as well as to investigate the effects of various EPD process on surface and morphology particles.

2. Experiments

2.1 Reagents and Materials

BaTiO₃ nanoparticles (19 m²/g) was synthesized by non-isothermic method using methodic [11]. Functional substance of OP was synthesized at Lvivsky Politechnik University of Ukraine. Ethanol, (AA (acetylacetone)) acetylacetone were obtained from Merck Chemical Reagents Company. All these reagents were used without further purification.

OP complex was obtained by reaction interaction of active vinylacetate-co-5-tret-butylperoxy-5 methyl-1-hexen-3-co-maleic anhydride with Cu²⁺ in alcohol solution. Composition: vinylacetate-22%; tret-butylperoxy-5-methyl-1-hexen-48%; maleic anhydride-30% (Fig. 1). Characteristics of OP: Molecular weight (M_w) 2,000 g·mol⁻¹, surface tension is 37.5 mN·m⁻¹ and content cations of Cu(II) is 1.1%.

2.2 EPD Suspensions of BaTiO₃

Pure BaTiO₃ was added in 100 mL organic solvent mixture of acetylacetone and ethanol (1:1) using magnetic stirrer during of 15 min. Then obtained 2 and 10 wt.% suspension of BaTiO₃ was ultrasonically agitated (~10 min). The substance OP with concentration of 0.01-0.2 wt.% was added to

suspension and mechanically treated by ball milling: The EPD suspension added to 200 g YSZ milling balls (3 mm Ø) in a polyethylene container (120 mL) was milled at 250 rpm for 24 h.

For EPD, suspensions with solid concentrations of 2, 10 wt.% were chosen. Two Ni electrodes (90 µm thick), which were acted as a substrate (cathode) for BaTiO₃ layer deposition and a counter electrode (anode), respectively, were hold by fixtures, connected to DC power supply and ammeter and submerged, in the EPD tank (50 mL). The EPD suspensions was carried out with applied electric field strength (5-100 V), deposition time (60-600 s), distance between electrodes 1 cm. Surface area of electrodes was 2-4 cm². After EPD process samples of green films were dried slowly up to 100 °C to prevent it from cracking.

2.3 Characterization

The structural investigation and phase formation of BaTiO₃ were done by powder X-ray diffraction technique in a XRD-DRON 3 M, using CuKα radiation. The measurements were carried out at room temperature in continuous mode, in the 2θ range between 20° and 90°.

Particles size of BaTiO₃ suspensions were performed by laser granulometry in nanosizer HS1000 (Malvern, United Kingdom).

Rheological properties of the nanoparticles suspensions were determined at constant temperature (25 °C) using rheometer RN4.1 (Germany) with cylindrical nozzle of 1 mm. All suspensions used in this study were stabilized by magnetic stirring during 30 min.

Dzetta potential (ζ) of suspension BaTiO₃ was

Fig. 1 Scheme chain of OP.

determined by boundary motion using a modified device Tchaikovsky (Russia).

Conductivity of the suspensions was determined on the bridge AC P5058 (Russia) using cell with two platinum electrodes at a frequency of 1 kHz.

The morphology of BaTiO₃ particles films were investigated using scanning electron microscope JSM-7600F JEOL at acceleration voltage of 200 kV.

3. Results and Discussion

3.1 BaTiO₃ Powder Characterization

The XRD pattern (Fig. 1) indicates that the synthesized powder shows good agreement with the tetragonal BaTiO₃ structure with the P4mm space group (JCPDS data No. 05-0626), with no impurity peak appearing in the diffractogram and lattice parameters $a = 4.000 \text{ \AA}$, $c = 4.030 \text{ \AA}$. These values are very close to the reported values refraining to this tetragonal structure (JCPDS data No. 05-0627). XRD pattern of synthesized BaTiO₃ powders show peak at 45°. In general, the XRD pattern of the tetragonal BaTiO₃ show split peaks at 45° corresponding to the (hkl) Miller index (002) and (200). Thus, we can conclude that synthesized powder show a tetragonal or tetragonal-dominant structure with ratio of $c/a = 1.0075$. A crystallite size of 40 nm was estimated by the Scherrer's equation for peak (101).

3.2 Suspension BaTiO₃ Characterization

It is noted that the quality of electrophoretic deposition heavily depends on the suspension conditions formation. So, a well dispersed stable suspension will provide a better deposition during EPD process compared to an unstable or strong agglomerated powder suspension. The results of laser granulometry show that BaTiO₃ particles are less agglomerated in a mixture of ethanol-AA (ethanol-acetylacetone) compared with pure ethanol after treatment in a ball mill (Fig. 2).

For control stability, suspension rheological test

was used before EPD process with different shear rates at constant temperature. It is known that most suspensions are pseudoplastic and exhibit a decrease in viscosity with an increase in shear rate. So, the viscosity tends to decrease as a function of increasing shear rate [12]. As can be seen in Fig. 3 suspension without additive OP is pseudoplastic.

Viscosity of the suspension (Fig. 3) gradually decreases from 35 mPa·s to 5 mPa·s in shear rates of 0-250 s⁻¹ then it does not change. With the introduction of small amounts of surfactant OP, the slurry becomes almost Newtonian. The viscosity remains virtually unchanged in the range of shear rates. The viscosity suspensions of 2.5-5.0 mPa·s is optimal

Fig. 1 XRD pattern of synthesized BaTiO₃.

Fig. 2 Particle size distribution of the BaTiO₃ suspension at different solvents: (a) ethanol; (b) ethanol: AA.

Fig. 3 Viscosity (mPa·s) shear rates of BaTiO₃ suspensions in acetylacetone-ethanol with different solid OP (mas.%): 1—0.01; 2—0.05; 3—0; 4—0.2.

to EPD process (Fig. 3).

The zeta potential at this level is shown in Fig. 4. It presents the zeta potential that reaches a maximum value when added amount OP about 0.05 wt.%. This is explained by the formation of OP adsorption shell (charged micelle) on the surface of barium titanate particles that will contribute to the motion of particles in EPD process. The pH medium was varied from values 4 to 10 and electric conductivity region of 1.5×10^{-5} – 4.4×10^{-7} S/cm. The authors note that relationship between of ζ (mV) and amount of OP is close to phosphoester (0.4–1.6 wt.%) in suspension of PZT [14].

3.3 EPD of BaTiO₃ Suspensions

In the EPD process, the same suspension concentrations used for rheological characterization were in order to evaluate the combined influence of suspension concentration, voltage on the quality of BaTiO₃ deposits by EPD. The experiments were carried out at constant room temperature. The investigation influence of solid BaTiO₃ (wt.%) on EPD process of suspensions with 0.05% OP at different time deposition and electric field strength of 100 V presents in Fig. 5. The results show that effective mass deposition is for suspension with 2 wt.% of BaTiO₃ because of higher value of ζ (mV) particles.

It can be seen that when the particle

concentration in the suspension is higher the mass deposition is lower. It may be due to the high level of non-uniformity of the deposited particles under very high driving forces. It is also noted that the deposition and time relationship sometimes has an non-linear appearance. Similar observation has been reported in Refs. [1, 13, 15] and this is attributed to the change in deposition rate and particle concentration as deposition continues.

The best quality films were obtained using 2 wt.% solids suspensions with 0.05% of OP. SEM micrographs of BaTiO₃ coatings electrophoretically

Fig. 4 Relationship between zeta potential (ζ) of BaTiO₃ and the amount of added oligoperoxide (OP).

Fig. 5 BaTiO₃ mass deposited (mg/cm²) as a function of the time deposition from the suspension of different concentration (mas.%): 1- 2, 2-10.

Fig. 6 SEM micrographs of BaTiO₃ coatings by EPD on Ni substrate at (a) 5 V, (b) 50 V, (c) 100 V and time deposition 60 s.

deposited at 5, 50, 100 V (drying 100 °C) 60 s are shown in Fig. 6. In contrast, at 5 V the coatings developed microcracks (Fig. 6a). By performing EPD at 50 V and 100 V dense and uniform films were obtained as shown in Fig. 6b and 6c, respectively.

4. Conclusions

It was shown that at surfactant concentration (OP) of 0.05 wt.% the value ζ of particles increases and viscosity suspensions reduces (Newtonian flow behavior). The obtained results show that the ball milling effect on to the suspensions also helps to introduce more protons from the organic solvent which is attached to the surface of the BaTiO₃ powder thus improving its deposition.

Moreover due to concentration of 2 wt.% a good-quality BaTiO₃ deposits on planar Ni substrates, as observed by SEM, were obtained by EPD using voltage 100 V and 60 s deposition time. It is very important to achieve crack-free and smooth BaTiO₃

coatings before sintering process.

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