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Cathodic electrophoretic deposition of barium titanate films from aqueous solution

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Abstract Cathodic electrophoretic deposition (EPD) of barium titanate from aqueous suspensions was performed on nickel substrate. Cathodic deposition allows preparation of thin layers from aqueous solution on base metal electrodes, such as Ni or Cu, without creating an intermediate oxide layer during the deposition. This opens the opportunity to prepare complex shapes of dielectric layers onto base metals for co-firing, using relatively cheap and environmentally benign aqueous EPD. Stable barium titanate colloidal suspension with a concentration of 10 g/100 mL at pH of 9.2 has been prepared for the deposition. The characteristics of electrophoretic deposition of those positively charged particles onto cathode were investigated. A uniform and dense layer was obtained for films deposited at 3 V for 2 min. The calculated film thickness for the sintered layer at these conditions was ~1 μm. The morphology can be controlled, and in particular the pore size and distribution can be controlled via the applied voltage. At low voltage a uniform layer can be obtained whereas at high voltage a large number of macropores appears in the deposit and their size increase with the increasing of the voltage due to gas bubble formation.

Introduction

Barium titanate (BT) is one of the most important ceramic materials in electronics. As an intrinsic ferroelectric material it can be used in various applications, for example: as a multilayer capacitor, a grain boundary capacitor and in thermistors [1]. Deposition of $BaTiO_3$ thin films onto metal electrodes is of great interest [2] because of the possibility of integration with standard semiconductor structures.

Electrophoretic deposition (EPD) is an effective technique to prepare a green film of ceramics on a substrate. Considerable work with organic solutions as the suspension medium for $BaTiO_3$ powders has been done [3–14], however the use of organic liquids poses environmental and health hazards due to their toxic nature. The difficulties associated with handling organic liquids, as well as their cost, are important problems as well. The use of water as a solution leads, of course, to difficulties because of hydrolysis [15]. Nevertheless, the economical and health benefits of using water have encouraged researchers to consider aqueous solution for EPD.

In the aim to obtain the electrodeposited BT films, BT colloids can be electrostatically-stabilized or sterically-stabilized. Higher zeta potential means not only better stability but also higher electrophoretic mobility. Both stabilization effects were used in preparation of BT aqueous suspension process [16, 17]. Anodic EPD of $BaTiO_3$ films from aqueous suspension was done by Zhao et al. [18], using Pt electrodes. However, in order to use cheaper metals as electrodes cathodic deposition is preferable to prevent oxidation of the electrodes and the creation of oxide layer on its surface [19].

The goal of this work is to obtain thin and low porosity films of BT on a base metal electrode by cathodic electrodeposition. To achieve this it is necessary to prepare a suitable BT water suspension of high positive zeta potential and low conductivity. It is also necessary to maintain the colloidal system at high pH value, to avoid barium leaching.

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Experimental

Powder preparation

BT powders were prepared by hydrothermal synthesis as described in more details earlier [17], and in brief below. Powders of $BaCl_2 \cdot 2H_2O$ (CARLO ERBA, Rodano, MI, 99.6% purity) and $TiCl_4$ (Aldrich, Milwaukee, WI, 99.9% purity) in deionized water were used. NaOH was added to form a basic medium according to the stability conditions of BT in a solution (pH > 12) [16]. Then the sol was transferred to a Teflon liner in a 300 mL stainless-steel vessel. The sealed vessel was heated to 100 °C for 5 h. The resultant precipitate was cooled to room temperature, centrifuged, washed with water to remove excess Ba^{+2} and dried at 80 °C for 12 h in an evacuated oven. The resulting BT was nano-powder with an average particle size of 20 nm and specific surface area of 62 $m^2\ g^{-1}$.

Suspension stabilization and conductivity reduction

For the application of EPD, both stabilization of the colloidal system and low electrical conductivity of the suspension are required. Stabilization of BT aqueous suspension was done as follows: 10 g $BaTiO_3$ powder was added to 100 mL deionized water. The received mixture was dispersed using an ultrasonic horn. Solution of 0.1 M oxalic acid ($(COOH)_2 \cdot 2H_2O$) (CARLO ERBA, Rodano, MI, 99.5% purity) was prepared and 5 mL of the solution was added to the sonicated mixture. After a short time, the powder was precipitated. This system was washed by replacing the supernatant water by pure water repeatedly until the conductivity of the suspension reached 10 μS/cm. 80 μL of PEI (Polyethyleneimine) (ALDRICH, Milwaukee, WI, 50 wt.% solution in water) was then added for steric stabilization, followed by sonication for 30 min and stirring. This resulted in a stable white suspension with the desired properties.

EPD setup

Two-electrode cell arrangement was used for the EPD process. The anode was a stainless steel cylindrical foil (stainless steel type 304, 0.025 mm thick, 20 cm × 7.5 cm) which was covering the inner wall of the beaker. The beaker radius was 3.2 cm. The cathode was a nickel panel (nickel metal foil, 0.1 mm thick, 3 cm × 2 cm), which was placed at the middle of the beaker. A Keithley 2400 sourcemeter was used for applying the constant voltage and measuring the current. The experiments were performed at different values of constant voltage, ranging between 1 V and 5 V, which were conducted for 2 min at room temperature. The average thickness of the electrodeposited BT films was determined by weighing the cathodes before and after deposition, using

$$\bar{\delta} = \frac{V_{\text{total}} - V_{\text{Ni}}}{S} \tag{1}$$

where S is the surface area of the working electrode, V_{total} is the volume of the deposited layer plus the nickel electrode (after sintering in this case) and V_{Ni} is the volume of the nickel electrode as determined by Archimedes' method.

The density of the green body without the large pores can be determined by:

$$\rho = \frac{w_{\text{total}} - w_{\text{Ni}}}{V_{\text{total,green}} - V_{\text{Ni}}} \tag{2}$$

where w_{total} and w_{Ni} are the weight of the cathode after and before the deposition respectively. The relative density is ρ/ρ_{theo}; ($\rho_{\text{theo}} = 6.02$ g cm^{-3}).

The deposited surface coatings were dried in ambient conditions, and then sintered at 1,200 °C for 2 h in reducing atmosphere. Oxygen partial pressure of nominally 10^{-10} atm. was obtained by mixture of flowing gases: 10 mL/min H_2, 10 mL/min dry N_2 and 340 mL/min N_2 wetted by a bubbler with water at room temperature.

Characterization

Particle size distribution was measured by dynamic light scattering (DLS) and ξ-potential was measured by laser Doppler and phase analysis (PALS). Both were measured using a zeta PALS (Brookhaven Instruments Corporation) particle sizer, equipped with a 35 mW, $\lambda = 660$ nm solid-state laser and an avalanche diode detector. Scanning electron microscopy (SEM) was performed using a Jeol JSM-5400 microscope with energy dispersive X-ray spectroscopy (EDS), working at 15 kV. The densities were measured using the Archimedes method.

Results and discussion

Suspension of 10 g/100 mL of $BaTiO_3$ in water was electrophoretically deposited under constant voltage experiments. The stability of the suspension was investigated with the aid of ζ-potential measurements. Taking into consideration the results shown in Fig. 1 and the stability diagram of BT, we have decided to work at pH values around 9.2. This allowed us to work at relatively high ζ-potential while avoiding barium leaching.

No bubbles were observed at a total voltage (including overpotential) of 3 V. The suspension was stable at low voltage, up to 4 V. At 5 V, precipitation at the bottom of the beaker was observed. Table 1 summarizes the working

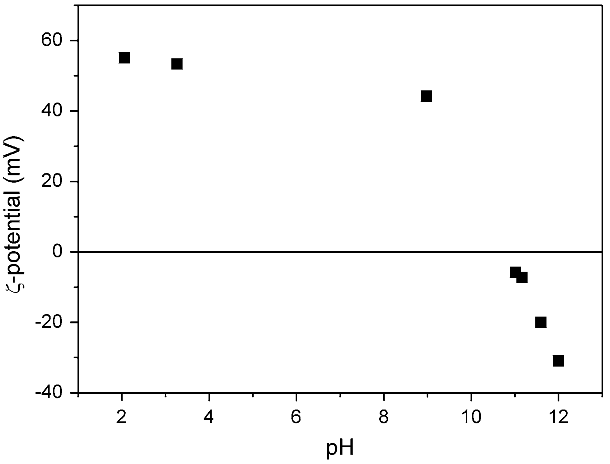

Fig. 1 ζ-Potential as a function of pH of the prepared suspension

Table 1 Representative results

Voltage (V)	Relative green density (%)	Deposit quality
0.5	–	No deposit, only wetting
1	10	Weak deposit
2	30	Weak deposit
3	51	Uniform and crack free
4	48	Beginning of bubble formation
5	41	No uniform deposition

voltage, the green density of the deposited layer and the quality of the deposited layer as seen by SEM micrographs. It can be seen that for voltage below 1 V no deposition occurred on the nickel substrate. The highest green layer density was obtained for layers deposited at 3 V for 2 min. The time dependence of the current during deposition is presented in Fig. 2. In the beginning of the deposition, the current decreased rapidly with time at low voltage. After this initial over-potential buildup, the current is quite stable during the 2 min runs. Low current densities were observed during deposition at low applied voltages, indicating there was a sufficient high resistance EPD cell.

When the thickness of the deposit is to be controlled, the rate at which the deposit forms during the EPD is very important. The thickness of the deposit films was calculated using Eq. 1 and 2. The dependence between the deposited weight and the deposition time at various applied voltages is shown in Fig. 3. Figure 4 shows the deposit average thickness as calculated for film deposited at 3 V. At 1 and 2 V there is hardly any deposition, while at 3–5 V the deposition is linear with time up to 2 min, and the slopes depend strongly on the voltage. However, this dependence is not a simple one, and the ratio between the slope and the voltage does not follow the classical constant behavior.

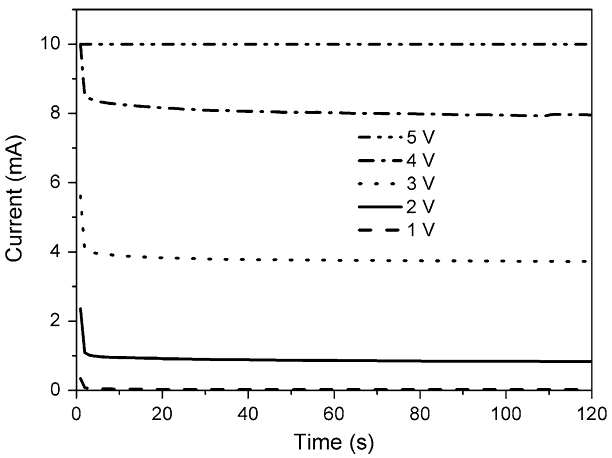

Fig. 2 Current as a function of time during constant voltage deposition

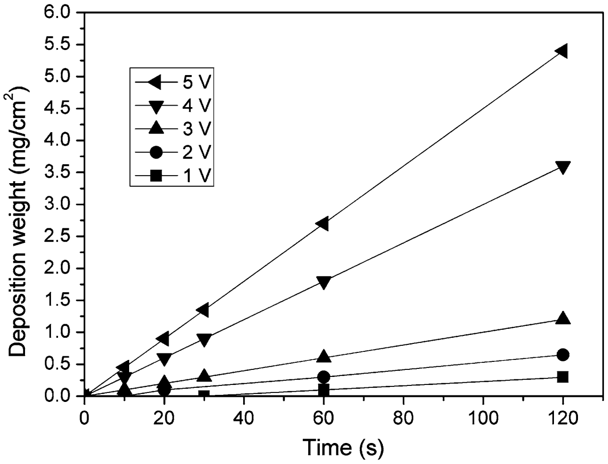

Fig. 3 Deposited weight as a function of time

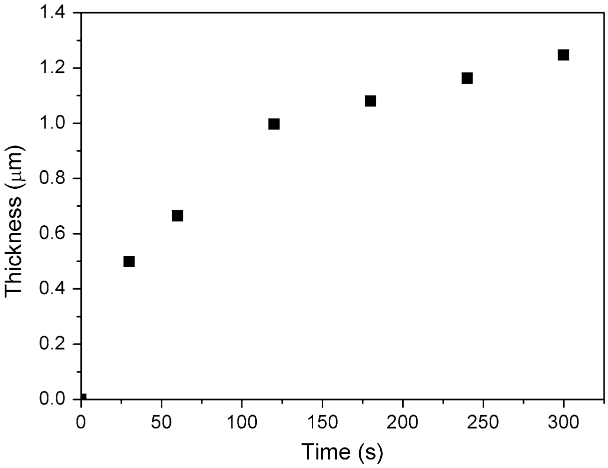

Fig. 4 Average thickness vs. deposition time for layers deposited at 3 V

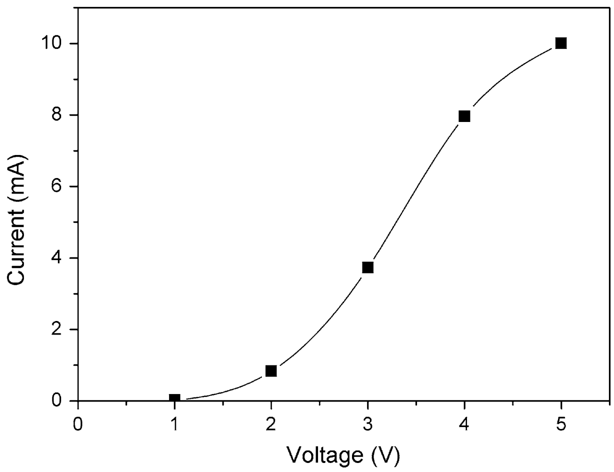

Fig. 5 Current as a function of applied voltage

Figure 5 shows the current after 2 min run as a function of the applied voltage. This is a typical behavior of a deposition process that is controlled both by the reaction kinetics and by mass transport (see, for instance, reference [19], pp. 1–2). From Figs. 4 and 5 it is evident that the mass transport is an important issue that should be dealt with at later improvements of the process.

Figure 6 shows SEM micrographs for two films that were deposited at constant voltage of (a) 3 V and (b) 4 V, sintered at 1,200 °C for 2 h at reducing atmosphere. When working at voltage of 3 V, more uniform, smooth deposit was obtained as compared to the deposited surface that was obtained at voltage of 4 V. The calculated film thickness for the film deposited at voltage of 3 V was 1 µm after sintering. These were chosen to be the optimal conditions for preparing uniform, dense and crack free thin layers of BT by EPD.

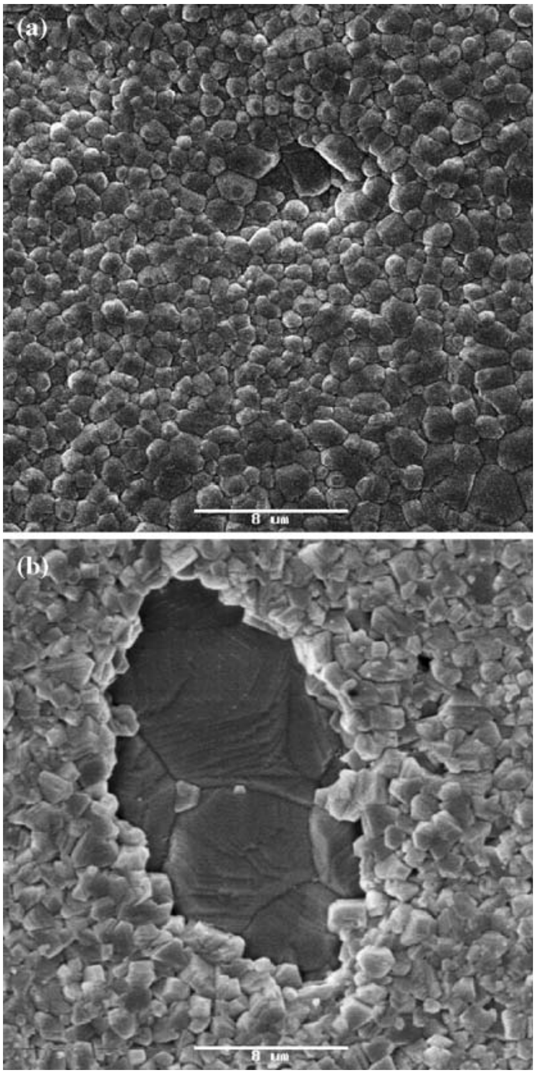

Fig. 6 SEM micrographs for two samples after sintering at 1,200 °C for 2 h. BT layers deposited on Ni plates by EPD for 2 min at (**a**) 3 V, and (**b**) 4 V. The bars are 8 µm. The lower layer in (**b**) is the Ni substrate, as verified by EDS

Summary

Barium titanate films were deposited on nickel substrate by means of cathodic EPD from aqueous suspensions. It allows preparation of thin layers from aqueous solution on base metal electrodes, without creating an intermediate oxide layer and opens the opportunity to prepare complex shapes of dielectric layers onto base metals, using a cheap and environmentally benign method. The maximum total voltage value to avoid gas bubbles near the cathode was 3 V. The appropriate conditions for preparing the colloidal suspension for successful deposition were determined. In addition, the sintering conditions were chosen to be 1,200 °C for 2 h in a reducing atmosphere N_2 wet/N_2 dry/H_2 to prevent the oxidation of the nickel electrode. The average thickness of the 3 V/2 min deposited layer was 1 µm after sintering.

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