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Low-temperature synthesis of barium titanate thin films by nanoparticles electrophoretic deposition

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Abstract The nanoparticles electrophoretic deposition (EPD) of barium titanate ($BaTiO_3$ or BTO) thin films was investigated. BTO nanocrystallites in a pseudocubic perovskite phase with an average particle size of about 10 nm were synthesized at a low temperature of 90°C by a high-concentration sol–gel process. By using a mixed solvent of 2-methoxyethanol and acetylacetone as dispersing medium, transparent and well-dispersed BTO nanocrystallites suspensions within the concentration range of 0.0125 to 0.20 mol/l was successfully prepared for nanoparticles EPD. A uniform microstructure and a smooth surface were observed on the deposited films. The film thickness of the deposited films increased rapidly with increasing EPD time in the initial period of EPD, and thereafter gradually increased to a limited thickness. With increasing applied EPD voltage, the limited film thickness increased. A near linear relation between the film thickness of films and the concentration of suspensions was observed under the same EPD conditions. The microstructures of the deposited BTO thin films were investigated.

Keywords Barium titanate · Electrophoretic deposition · Thin film · Sol–gel process · Nanocrystallite

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1 Introduction

Barium titanate ($BaTiO_3$ or BTO) is one of the most important electroceramic materials and has been investigated extensively because of its promising electrical and optical properties. BTO thin films are of significant interest for a variety of technological applications, such as multilayer ceramic capacitors, sensors, actuators, thermistors, dynamic random access memory, and electroluminescent elements [1–3]. A variety of methods, such as sputtering, metal organic chemical vapor deposition, pulsed laser deposition, and chemical solution deposition, have been investigated to prepare BTO thin films [4–8]. Compared with these methods, electrophoretic deposition (EPD) offers advantages of process simplicity, low cost, and easy deposition of multilayer films of controlled thickness on complex shaped or patterned substrates [9].

EPD has been studied extensively for fabricating advanced coating, nanocomposites, laminated structures, and functional graded materials [10–13]. Some groups have reported the EPD of BTO thick films [14–16]. However, there have been few studies on EPD of BTO thin films because of the difficulties in the synthesis of BTO nanoparticles suspensions. In a previous paper, we reported the preparation of monodispersed suspension of BTO nanoparticles and EPD of thin film [17].

In this paper, the effects of EPD voltage and time, suspension concentration, composition of solvent on the

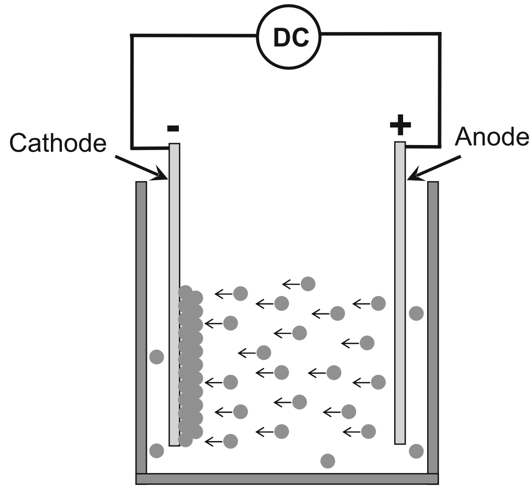


Fig. 1 Schematic diagram of EPD apparatus

thickness, and microstructures of the deposited thin films were investigated.

2 Experimental procedure

A high concentration sol–gel process was applied to synthesize BTO nanocrystallites [18]. The detailed experimental procedures for preparing nanocrystallites suspensions have been reported in our previous paper [13]. In this study, the BTO nanocrystallites suspensions within the concentration range of 0.0125 to 0.2 mol/l were prepared. The solvent of 2-methoxyethanol (hereafter, referred EGMME) and acetylacetone (hereafter referred Acac) with a 9:1 volumetric ratio was used as a dispersion medium.

A schematic diagram of EPD apparatus was shown in Fig. 1. In the present work, a Pt/Ti/Si substrate of 1×1 cm was used as the cathode and a stainless steel plate was used as the counterelectrode with a distance of 2 cm. DC voltage from 1 to 30 V was applied to the electrodes for 30 s to 30 min for deposition. The as-deposited films were dried in a 50°C oven.

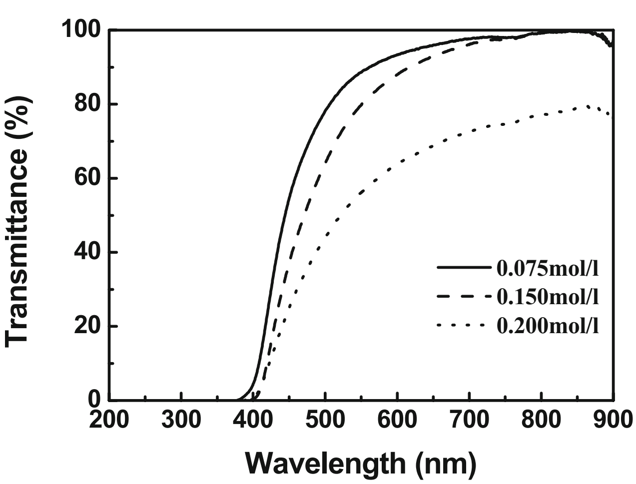


Fig. 2 Transmittance as functions of wavelength for the BTO nanoparticles suspensions with different concentrations

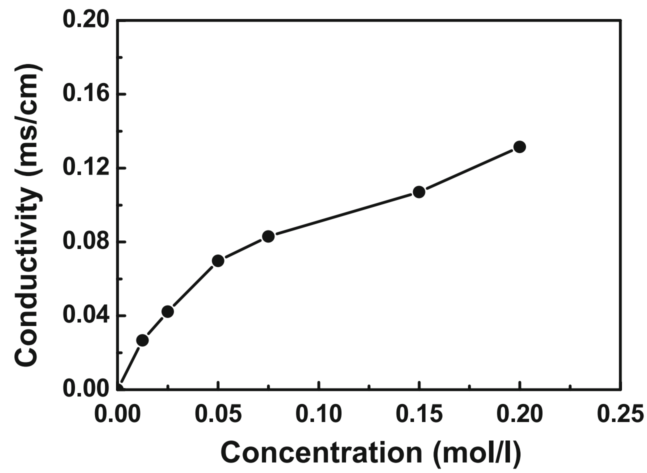


Fig. 3 Conductivity as a function of concentration of the BTO nanoparticles suspensions

Particle size distribution and conductivity of the suspension was evaluated by a laser Zeta potential and particle size analyzer (Nano ZS, Malvern, UK). The film thickness was measured from the micrographs on the cross-section of the deposited films by using a field emission scanning electron microscopy (FE-SEM; S5000, Hitachi, Japan).

3 Results and discussion

Our previous paper reported that well-crystallized BTO nanoparticles with an average size of ~10 nm have been synthesized at 90°C for 1 h by the high-concentration sol–gel process, and the nanoparticles suspension with a concentration of 0.075 mol/l have been prepared in a mixed solvent of EGMME and Acac. In this work, the nanoparticles suspensions with various concentrations from 0.0125 to 0.2 mol/l were successfully prepared. Figure 2 shows the transmittance as functions of wavelength for the nanoparticles suspensions with different concentrations. Under the same preparation conditions, transparent suspensions of 0.075 and 0.15 mol/l were obtained while the suspension of 0.20 mol/l exhibited a lower transmittance than the former suspensions. To prepare transparent suspensions of 0.20 mol/l, much longer time for ultrasonication is needed. We could not prepare stable suspensions with a concentration more than 0.20 mol/l. Sediment occurred within several days in the suspension of 0.25 mol/l. Figure 3 shows the relationship between the conductivity and the concentration of BTO nanoparticles suspensions. The conductivity increased with increasing

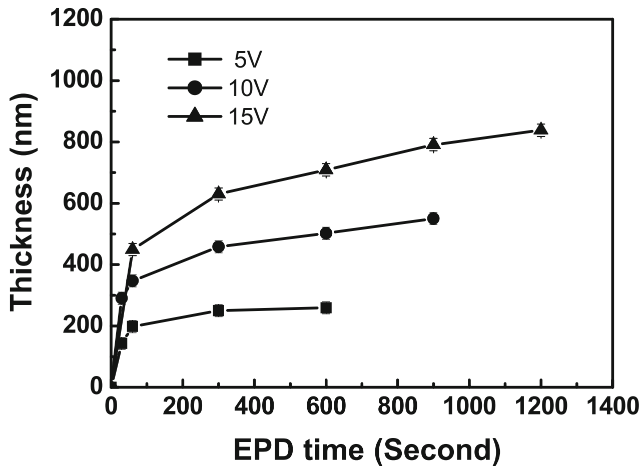


Fig. 4 Film thickness of BTO thin films as functions of EPD duration time under different applied EPD voltages

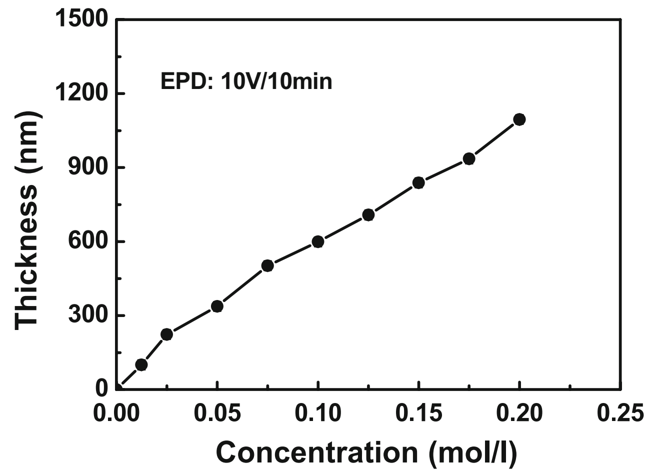


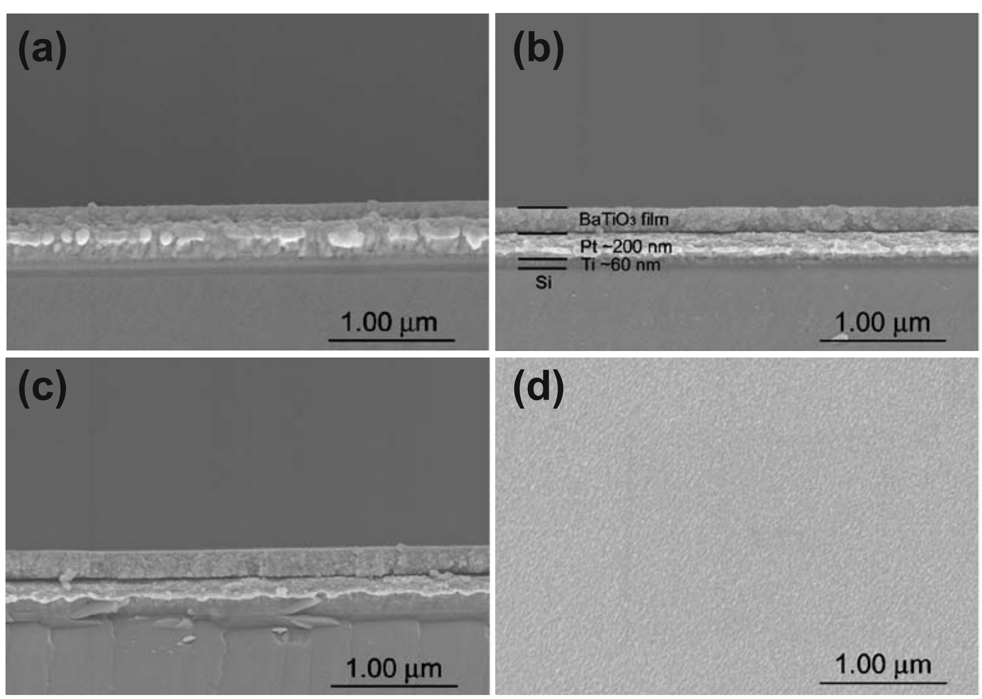
Fig. 6 Relations between the film thickness and the concentration of the BTO nanoparticles suspensions

concentration and a near linear relationship between them was observed when the concentration was >0.05 mol/l. This suggests that the nanoparticles mainly contributed to the conductivity.

Figure 4 shows the relationships between the film thickness and the EPD duration time under different applied EPD voltages. The film thickness increased rapidly with increasing duration time in the initial period, and thereafter slightly increased. It can be attributed to the much higher resistance of the deposited layer. The initial deposited film plays as a barrier layer and suppresses the sequent deposition. It seemed that there was a limited thickness for a certain voltage. As the applied voltage increased, the limited thickness and the duration time for reaching this limited thickness increased. When a voltage higher than 25 V was applied, gas was generated and these gas bubbles may become entrapped between the depositing particles, leading to inhomogeneity and porosity in the final compact. The FE-SEM micrographs on the deposited surface and the cross-section of deposited BTO thin films are shown in Fig. 5. The flat, crack-free, and uniform surface structures were observed.

Figure 6 shows the relationship between the film thickness and the concentration of suspensions. A near linear relationship between them was found. Figure 7 shows the FE-SEM micrographs on the cross-section of

Fig. 5 FE-SEM micrographs of BTO thin films deposited by EPD under different conditions: (**a**) 5 V/30 s, (**b**) 5 V/1 min, (**c**) 5 V/10 min, and (**d**) 5 V/10 min (*top view*)



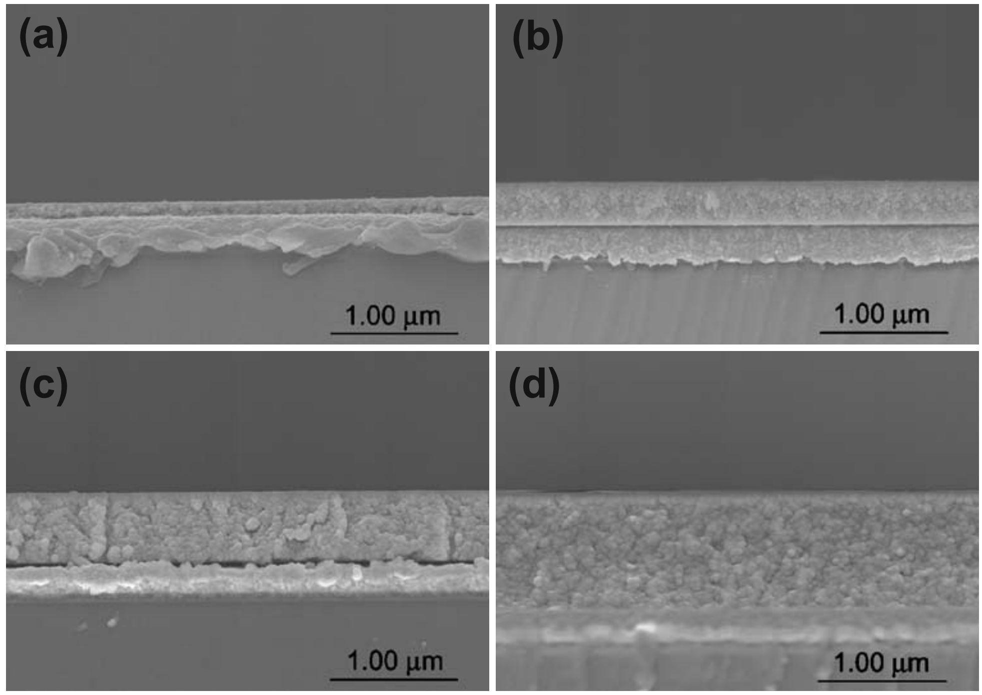


Fig. 7 FE-SEM micrographs of BTO thin films deposited by EPD at 10 V/10 min from various suspensions with different concentrations: (**a**) 0.0125 mol/l, (**b**) 0.05 mol/l, (**c**) 0.125 mol./l, and (**d**) 0.175 mol/l

the BTO films deposited from various suspensions with different concentrations. From the above results, it was found that the nanocrystallites EPD provides a very easy way to adjust the film thickness. The EPD duration time, applied voltage, and the concentration of suspensions can be adjusted to fabricate BTO thin films with desired thickness in one step.

4 Conclusions

BTO nanoparticle suspensions within the concentration range of 0.0125 to 0.20 mol/l were prepared for nanoparticles of EPD of BTO thin films. The film thickness increased rapidly with increasing duration time in the initial period, and thereafter slightly increased. As the applied voltage increased, the limited thickness and the duration time for reaching this limited thickness increased. The film thickness linearly increased increasing concentration of suspensions up to 0.20 mol/l. It was found that BTO thin films of desired thickness from 100 nm to about 1 µm could be fabricated in one step at a low temperature by adjusting the EPD duration time, applied voltage, and the concentration of suspensions.

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