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Preparation of nano-structured $BaTiO_3$ thin film by electrophoretic deposition and its characterization

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Abstract

Nano-structured $BaTiO_3$ (BTO) thin films were electrophoretically deposited from BTO nanoparticle suspensions. The microstructural properties of the nanoparticles and thin films were examined through XRD, HR-TEM, and SEM techniques. BTO nanocrystallites in a pseudo-cubic perovskite phase with an average particle size of about 10 nm were synthesized by a high-concentration sol–gel process. By dispersing a piece of BTO bulk gel into a mixed solvent of 2-methoxyethonal and acetylacetone, the well-dispersed and stable suspensions of BTO nanocrystallites were obtained. From these suspensions, crack-free nano-structured BTO thin films with different thickness from 100 nm to several micrometers were deposited on $Pt/Ti/SiO_2/Si$ substrates by electrophoretic deposition (EPD). The prepared films exhibited a uniform nanostructure, and a smooth surface with a roughness under 10 nm. The microstructural and dielectric properties of sintered BTO thin films were evaluated.

Keywords: Films; $BaTiO_3$ and titanates; Electrophoretic deposition; Microstructure-final; Sol–gel process

1. Introduction

Barium titanate ($BaTiO_3$) has become the basic ceramic capacitor dielectric material in use today.[1] $BaTiO_3$ (BTO) family ceramic films having been widely investigated for electronic applications, such as multilayer capacitors, dynamic random access memory and tunable microwave devices.[2–4] With the development of thinner multilayer capacitors and the possibility of integration with standard semiconductor structures, deposition of high quality and reliable BTO thin films onto metal electrodes on silicon substrates is of great interest.[5]

As one of the most used method for fabricating films, electrophoretic deposition (EPD), has been developed to fabricate advanced coatings, nanocomposites, laminated structures, functional graded materials.[6–9] EPD is essentially a two-step process. In the first step, particles suspended in a liquid are forced to move toward an electrode by applying an electric field (electrophoresis). In the second step, the particles collect at one of the electrode and form a coherent deposit on it (deposition).[10] Compared with other methods, EPD offers advantages of low cost, process simplicity, uniformity, rigidly control of thickness and deposition on complex shaped substrates.[11]

Several papers described electrophoretic deposition of BTO thick films from micro or sub-micro particles suspensions have been published.[12–14] However, in order to fabricate BTO nano-structural thin films and understand the mechanisms of EPD, the electrophoretic deposition of BTO films from mono-dispersed nano-particles suspension is needed. In the present research, the synthesis of mono-dispersed BTO nano-particles suspension and electrophoretic deposition of nano-structural thin films were investigated.

2. Experimental

Schematic representation of preparing BTO nano-particles and nano-structural BTO thin films is shown in Fig. 1. The BTO nano-particles were prepared by a

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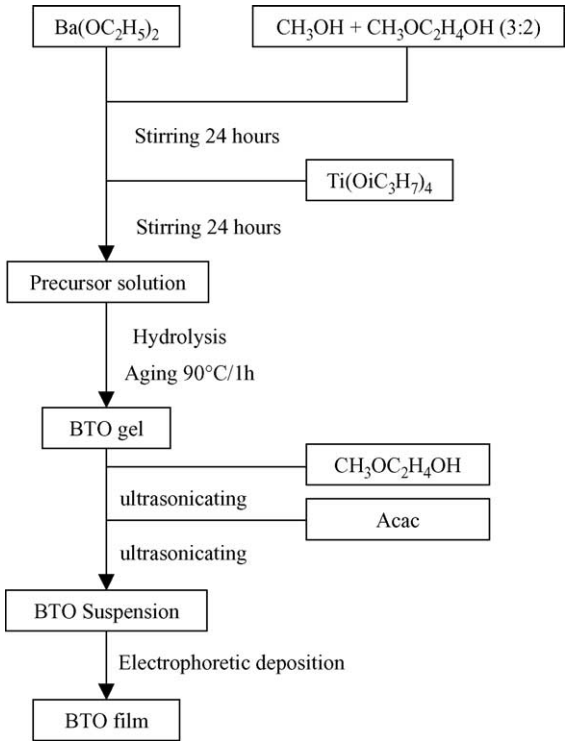

Fig. 1. Schematic representation of preparing nano-structural BTO thin films.

high-concentration sol–gel method.[15,16] At first, high purity barium diethoxide ($Ba(OC_2H_5)_2$, >99%) was dissolved in a mixed solvent of methanol (CH_3OH, >99%) and 2-methoxyethanal ($CH_3OC_2H_4OH$, EGMME, >99.8%) with a volume ratio of 3:2 and stirred for 24 h. Then, titanium tetra-iso-propoxide ($Ti(OiC_3H_7)_4$, >99%) was added to form BTO precursor solution and again stirred for 24 h. The concentration of the precursor solution was 1.0 mol/l. The obtained precursor solution was then hydrolyzed by adding a mixed solution of distilled water and EGMME with a volume ratio of 1:1. The molar ratio of H_2O and BTO was 10:1. All above processes were performed in a dry N_2 atmosphere. After stirring for 10 min, the hydrolyzed solution was sealed in an autoclave and aged in a 90 °C oven for 1 h. After extraction, the residual liquid, the BTO gel was dispersed into EGMME by untrasonication for several hours. Then acetylacetone (Acac, $CH_3COCH_2COCH_3$, >99%) was added and again ultrasonicated to form BTO suspension. The volume ratio of EGMME and Acac was 9:1 and the concentration of the suspension was controlled to be 0.075 mol/l.

The BTO green thin film was electrophoretically deposited from the above suspension. A Pt substrate in a size of 1 cm × 1 cm with a $Pt/Ti/SiO_2/Si$ structure was used as cathode and the same size plate of stainless steel was used as anode. The distance between the cathode and the anode was 2 cm. A DC voltage from 1 to 15 V provided by a DC voltage source (HP4140B, Hewlett-Packard, Japan) was applied to the electrodes to electrophoretically deposited BTO thin films. The as-deposited BTO thin films were dried in a 50 °C oven in air. Then some of them were sintered at 800 °C for 30 min in an infrared imaging furnace (RHL-E48, ULVAC RIKO, Japan). For dielectric properties measurement, Al circular electrodes with a diameter of 0.2 mm were deposited by vacuum evaporation on the top of the films.

The microstructures of the BTO nano-particles were evaluated by high-resolution transmission electron microscopy (HR-TEM, EM-002BF, Topcon, H-9000NAR, Hitachi, Japan) and X-ray diffraction (XRD, M18XHF, Mac Science, Japan). The surface morphology and thickness of the deposited films were evaluated by field emission scanning electron microscopy (FE-SEM, S5000, Hitachi, Japan) on the surface and the cross-section, respectively. The dielectric properties as functions of frequency (1–1000 kHz) were characterized by an impedance analyzer (HP 4192A, Hewlett-Packard, Japan).

3. Results and discussion

Fig. 2 shows the representative TEM micrograph of BTO nano-particles prepared by the high-concentration sol–gel method. Uniform nano-particles having a near-spherical morphology were observed. It can be seen that the particles are well crystallized and the average particle size is about 10 nm. The selected area electron diffraction pattern (Fig. 2, inset) can be indexed to cubic symmetry, suggesting BTO nano-particles to be in the perovskite cubic phase. For XRD measurement, the suspension was dried on a glass plate at room temperature to form a thin film. The XRD pattern of BTO nano-particles is shown in Fig. 3(a). All the diffraction peaks can be indexed to cubic $BaTiO_3$ (JCPDS 31-0174). The crystallize size calculated by Scherrer equation was consistent with the results of TEM. The BTO nano-particles can be well dispersed in a mixture of EGMME and Acac with a volumetric ratio of 9:1. The suspension with a concentration of 0.075 mol/l was transparent and stable.

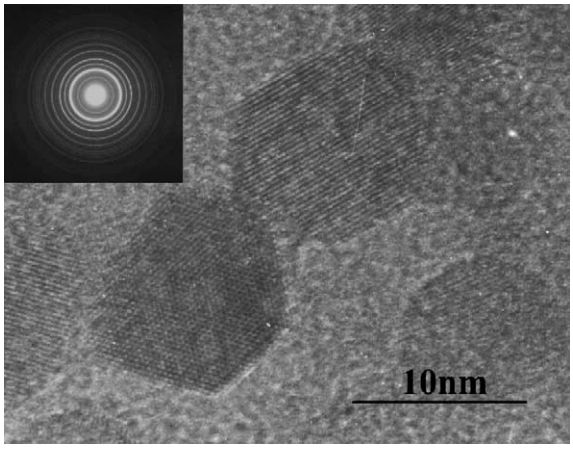

Fig. 2. High-resolution TEM image of BTO nano-particles. Inset: Selected area electron diffraction pattern.

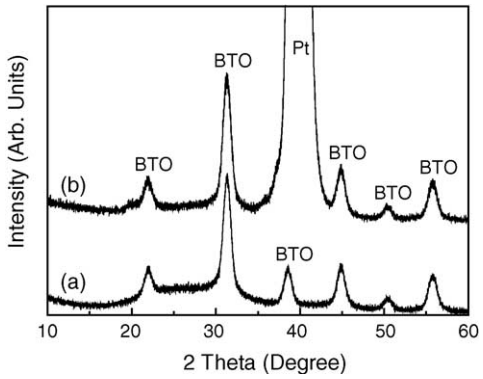

Fig. 3. XRD patterns of (a) BTO suspension and (b) as-deposited BTO green thin films.

Fig. 4 shows the SEM micrographs of as-deposited BTO green thin film. It can be seen that crack-free BTO thin film was compactly deposited on Pt/Ti/SiO_2/Si substrates. A uniform microstructure and a very smooth surface were observed, indicating the ability of electrophoretic deposition to produce a homogeneous and thickness-controlled BTO green thin film. The XRD pattern of the as-deposited thin film was shown in Fig. 3(b). It confirmed the film consisted of cubic BTO phase.

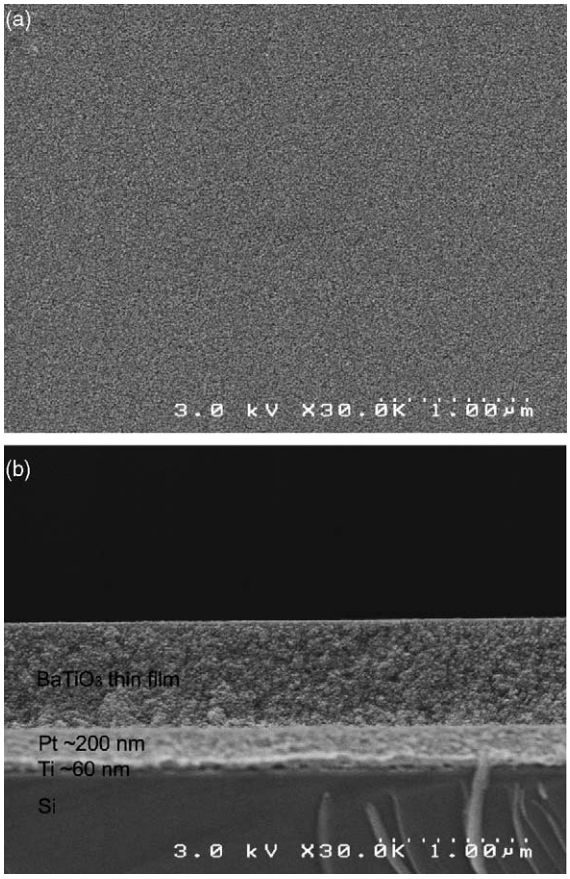

Fig. 4. SEM micrographs of as-deposited BTO thin films: (a) surface and (b) cross-section.

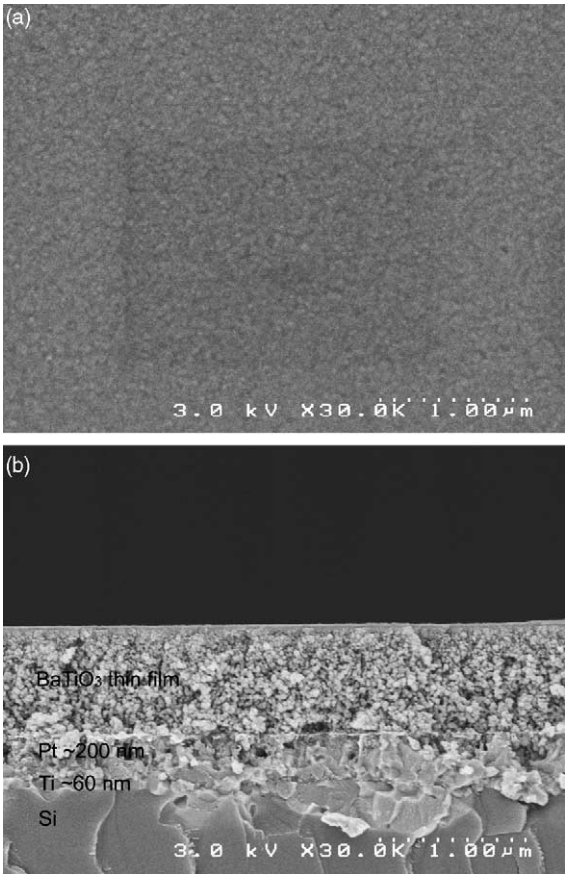

Fig. 5. SEM micrographs of EPD-formed BTO thin films sintered at 800 °C for 30 min: (a) surface and (b) cross-section.

The SEM micrographs of sintered BTO thin film are shown in Fig. 5. The micrograph on the surface showed a dense microstructure. However, the micrograph on the cross-section showed a porous microstructure. This maybe attributed to the characteristics of the infrared imaging furnace. The surface layer irradiated directly by the infrared radiation which promotes the densification. Fig. 6 shows the dielectric properties of sintered BTO film as functions of frequency. A dielectric constant of 94 and a tan δ of 0.017 were observed

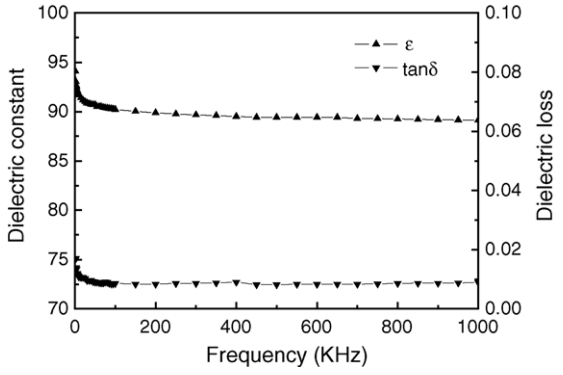

Fig. 6. Dielectric properties of EPD-formed BTO thin films sintered at 800 °C for 30 min.

at 1 kHz. In order to improve the dielectric properties, the sintering parameters should be optimized.

4. Conclusions

Mono-dispersed BTO nano-particles with an average size of about 10 nm were synthesized by a high-concentration sol–gel method. The mixture of EGMME and Acac were found to be an efficient media for BTO nano-particles suspension. Transparent and stable suspensions were prepared by dispersing a wet BTO gel into a mixed solvent of EGMME and Acac with a volumetric ratio of 9:1. Nano-structural BTO thin films were fabricated on $Pt/Ti/SiO_2/Si$ substrates by electrophoretic deposition. The as-deposited film exhibited a very smooth surface and a uniform microstructure. The dielectric properties of BTO thin film sintered at 800 °C for 30 min were measured: $\varepsilon = 94$ and $\tan\delta = 0.017$ at 1 kHz.

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