



## Original Article

# Fabrication of barium titanate nanoparticles/poly(methylmethacrylate) composite films by a combination of deposition process and spin-coating technique<sup>☆</sup>



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## ABSTRACT

The present work proposes a method for fabricating poly(methylmethacrylate) (PMMA) film containing barium titanate (BT) nanoparticles (BT/PMMA film). BT particles with an average size of  $77.6 \pm 30.5$  nm and a crystal size of 28.1 nm were synthesized by adding sodium hydroxide aqueous solution to titanium tetraisopropoxide/acetylacetone/*i*-propanol solution suspending barium hydroxide. A sodium glass plate, of which surface was modified with polyvinylpyrrolidone, was immersed into water suspending the BT particles, which resulted in deposition of the BT particles on the plate. A BT/PMMA film was fabricated by twice performance of a process composed of spin-coating of *N*-methyl-2-pyrrolidone (NMP) dissolving PMMA on the plate, and then drying the coated plate in the atmosphere at room temperature. Spin-coating of a PMMA/NMP solution with a PMMA concentration of 150 g/L at a rotating speed of 5000 rpm provided fabrication of a BT/PMMA film with a BT volume fraction of 35.5%, a thickness of ca. 300 nm, and a transmittance of ca. 90% in the visible light region.

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## 1. Introduction

An integration of passive components such as resistors, capacitors and inductors, which occupy a large area of recent high performance electric circuits, is required to reduce size of

electric circuits [1–3]. Fabrication of thin films of the passive components is useful to integrate them in the electric circuits [4–6].

Ceramic dielectric thin film is one of the capacitors incorporated in the electric circuits. Barium titanate (BT) is representative among various ceramics with excellent

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dielectric properties [7-9]. Titanate ceramics like the BT is facing at some problems. One is that the titanates are required to be crystallized by annealing at high temperature to make them have dielectric characteristics [10,11]. A lot of energy is consumed through the high temperature annealing, which provides the large load to environment. The high temperature annealing sinters particles of titanate crystallites, which produces their powder larger than micron meter. Since it is hard to fabricate thin films of such a large powder in the electric circuits, the high temperature annealing is desired to be performed after the integration. However, the high temperature annealing damages the electric circuits composed of passive components and substrates that are usually made from organic resin. A nanocrystalline seeding technique has been attempted for lowering their crystallization temperature [12,13]. Our research group also has studied on the seeding technique in recent decade [14-17], and reported that titanate films could be crystallized at 420°C [16]. This crystallization temperature is still so high that the electric circuits are not prevented from being thermally damaged.

Another problem of titanates is their fragileness derived from characteristic of ceramics. It is hard to process the titanates into the target form because of their fragileness. In contrast, polymers can be processed at temperatures lower than that for ceramics, and are flexible and pliable. However, dielectric constants of the polymer films are low, compared with those of dielectric ceramic films.

Fabrication of titanate-polymer composite films is promising to solve the above-mentioned problems derived from the natures of ceramics and polymer, since the composite films are expected to have both characteristics of the high dielectric constant of titanates and the processability of polymers. The titanate-polymer composite films are desired to have a structure of polymer films incorporated dispersedly and homogeneously with titanate particles, for making the composite films exert stable dielectric properties.

Various methods for fabricating titanate-polymer composite films or polymer films incorporated with titanate particles have been reported [8,18-24]. In most reports, the composite films are fabricated by mixing a dielectric polymer solution and titanate particles, and evaporating the solvent of the polymer solution. Since particles tend to aggregate in liquid phase, the particle aggregation will take place during the evaporation of solvent, which provides unhomogeneous of the composite film. Accordingly, the titanate content in film should be limited in this fabricating method. This limitation does not expect high dielectric constants of composite films.

Our research group has studied on deposition of titanate nanoparticles on substrate of solid material [25]. The nanoparticles are immobilized on the substrate with the deposition process. Once the immobilization with deposition is performed, the deposited nanoparticles cannot move on the substrate, which controls particle aggregation. The target titanate-polymer composite film will be produced by coating the nanoparticle-deposited surface with polymer. The present work proposes a method for fabricating polymer films incorporated with BT nanoparticles at high BT content in film by a combination of deposition and spin-coating techniques, which are expected to have excellent dielectric properties.

## 2. Experimental work

### 2.1. Chemicals

Barium hydroxide ( $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$ ) (98.0%) and titanium tetraisopropoxide (TTIP) (97.0%) were used as starting reagents for producing BT particles. Solvent in a sol-gel reaction of TTIP was iso-propanol (*i*-PrOH) (99.7%). To stabilize the TTIP, i.e., to control the sol-gel reaction, acetylacetone (99.5%) was used, because the acetylacetone reduce reactivity of alkoxide through formation of chelates with ionic metals derived from alkoxide [26,27]. The sol-gel reaction was catalyzed with a sodium hydroxide (NaOH) aqueous solution (1 M). Hydrochloric acid (HCl) (35-37%) and the NaOH aqueous solution were used to vary pH of the BT nanoparticle colloid solution for ELS measurements, which is stated in the section of characterization. Polymer used for fabrication of thin films was poly(methylmethacrylate) (PMMA) (Mw: ca. 100,000, Wako Pure Chemical), and solvent for preparation of PMMA solution used for spin-coating was *N*-methyl-2-pyrrolidone (NMP) (>99.0%). Sodium glass plates (Matsunami Glass Ind., Ltd., 18 mm × 18 mm, 0.12-0.17 mm thick) were used as a substrate. To improve affinity between BT particles and the glass plates, polyvinylpyrrolidone (PVP) ( $K=30$ ) was used as a pretreatment agent of the substrate. All the chemicals except for the PMMA were purchased from Kanto Chemical Co., Inc., and used as received. Water that was ion-exchanged and distilled with Yamato WG-250 was used in all the preparations.

### 2.2. Preparation

BT particles were fabricated according to our previous work [28].  $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$  powder was suspended in *i*-PrOH. At 10 min after the preparation of  $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}/i\text{-PrOH}$  suspension, TTIP/*i*-PrOH solution, acetylacetone and NaOH aqueous solution were successively added to the suspension. The reaction time was 0-5 h. Temperature of the solutions was kept at 80 °C through all the procedures from the production of  $\text{Ba}(\text{OH})_2$  suspension to the initiation of reaction. Initial concentrations of  $\text{Ba}(\text{OH})_2$ , TTIP, acetylacetone,  $\text{H}_2\text{O}$  and NaOH in the final *i*-PrOH solution were 0.06, 0.06, 0.12, 30 and 0.27 M, respectively. The as-prepared BT particles were washed by repeating a process composed of centrifugation of the particle suspension, removal of the supernatant, addition of water and shake of the suspension with a voltex mixer three times. The suspension of washed BT particles was diluted 30 times with water for the following BT particle deposition.

The glass plate was submerged into a 1 g/L PVP aqueous solution for 24 h, which surface-modified the glass surface through adsorption of PVP on the surface. After rinsing excess PVP out of the surface with water, the surface-modified glass plate was submerged into the diluted suspension of BT particles, to deposit the particles on the substrate. After 6 h, excess particles were rinsed out of the glass plate with water. The BT-deposited substrate (BT/glass plate) was then spin-coated with 150 g/L PMMA/NMP solution at 5000 rev/min, and dried at room temperature, which led to formation of a PMMA film on the substrate (BT/PMMA composite film).

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