Original Article

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

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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 ± 30.5 nm and a crystal size of 28.1 nm were synthesized by adding sodium hydroxide aqueous solution to titanium tetraisopropoxide/acetylacetone/-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 nature 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 unhomogeneousness 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 (Ba(OH)₂·8H₂O) (98.0%) and titanium tetraisoproxopxide (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 (1M). 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]. Ba(OH)₂·8H₂O powder was suspended in i-PrOH. At 10 min after the preparation of Ba(OH)₂·8H₂O/i-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 Ba(OH)₂ suspension to the initiation of reaction. Initial concentrations of Ba(OH)₂, TTIP, acetylacetone, H₂O 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 vortex 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 1g/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).
2.3. Characterization

The particles were characterized with transmission electron microscopy (TEM), electrophoretic light scattering (ELS) and X-ray diffractometry (XRD). A JEOL JEM-2100 electron microscope was used for TEM, and an electron accelerating voltage was 200 kV. The particles used for TEM observation were attached on a collodion-coated copper grid (Nishin EM Corporation: 6512) by dropping particle suspension on the grid and then evaporating its dispersing agent. To know conditions of surface charge on particles, ELS was performed with a Malvern Zetasizer Nano ZS90 zeta potential analyzer. HCl aqueous solution or NaOH aqueous solution was added to solution to vary pH of solution for the ELS measurement. XRD measurements were performed with a Rigaku Ultima IV multipurpose X-ray diffraction system using X-ray source of CuKα line generated at 40 kV and 30 mA. The particle powder used for XRD measurements was prepared with a process composed of centrifugation of the particle suspension, removal of the supernatant, and drying of residue at room temperature for 24 h in vacuum.

The glass plates after the deposition and the spin-coating were characterized with ultraviolet-visible (UV–VIS) spectroscopy, scanning electron microscopy (SEM), stylus profilometry (SP) and thermal analysis [thermogravimetry differential thermal analysis (TG-DTA)]. Their UV–VIS transmittance spectra were measured with a Shimadzu UV-3101PC spectrophotometer. The SEM was performed with a JEOL JSM-5600LV microscope operating at 10–15 kV. Thickness of the film was measured by the SP with an ULVAC Dektak surface profilometer. Samples for the SP were produced by peeling off a part of the BT/PMMA film out of the plate with a utility knife to make a gap between the film surface and the plate surface. The thermal analysis was performed in air at a heating rate of 10 °C/min with a Seiko SSCS200 differential scanning calorimeter. Samples for the thermal analysis were obtained by peeling off the whole BT/PMMA film out of the plate with the utility knife, pulverizing the film and mixing it with 3 wt% α-alumina powder so that the film content was 3 wt% in the mixture. The α-alumina powder used for the mixing was the same as that for standard in the thermal analysis. Because the BT/PMMA film contains organic polymer, PMMA, a large amount of exothermic heat will be generated at combustion of the PMMA, which damages the differential scanning calorimeter. To reduce exothermic value from the film, the α-alumina powder stable thermally during the thermal analysis was mixed the film with.

3. Results and discussion
3.1. BT nanoparticles

Fig. 1a shows a photograph of the as-prepared particle colloid solution. The colloid solution was opaque and yellowish. Sedimentation took place in several hours after the preparation. The sediments could be dispersed even by shaking the colloid solution gently with hand, which implied that the sediment was not composed of large aggregates but dispersed fine particles. Fig. 1b shows a TEM image of the as-prepared particles. Most particles were quasi-distorted, and their size was 77.6 ± 30.5 nm. No particles larger than the quasi-distorted particles were observed, which supported the implication for production of dispersed sediments. Fig. 2 shows a ζ-potential of particles as a function of pH of the particle suspension. Their iso-electric point was 4.1, which indicated that the BT nanoparticles had electric charge in neutral pH range. Consequently, the BT nanoparticles were considered to become electrostatically repulsive in water with a neutral pH and to be dispersed, as above-stated. Fig. 3 shows an XRD pattern of the particles. Several peaks appeared clearly.

![Fig. 1 – Photograph of as-prepared colloid solution of BT nanoparticles (a) and their TEM image (b).](image)

![Fig. 2 – ζ-Potential of BT particles vs. pH.](image)

![Fig. 3 – XRD pattern of BT particles. Arrows stand for cubic BT.](image)
at 22.1, 31.4, 38.6, 44.9, 50.6, 55.8, 65.4, 69.9, 74.3 and 78.6°. They were attributed to cubic phase of BT (JCPDS card: 31-0174). A crystal size of the BT particles was estimated by the Scherrer equation from broadening of the 31.4° peak (1 1 0) of cubic BT, and was found as 28.1 nm. Since the particle size was larger than the crystal size, the BT particles were polycrystalline.

### 3.2. BT/glass plate

Fig. 4a shows a photograph of the BT/glass plate. The plate was opaque on its whole area. A black curve in Fig. 5 stands for a UV–VIS spectrum of the plate. Its transmittance was ca. 50% at 400 nm, and it increased with an increase in wavelength in a range smaller than 80%. Fig. 4b shows a SEM image of the plate surface. The BT nanoparticles were successfully deposited on the glass plate, though aggregation of the particles was observed in some places on the surface. Difference in index of refraction between BT nanoparticles and air in voids probably provided the observation of opaque plate and the small transmittance.

#### 3.3. BT/PMMA composite film

Fig. 6a shows a photograph of the BT/PMMA composite film on glass plate, in which the spin-coating was performed once. In contrast to the opaque surface prior to the spin-coating, the film was transparent on its whole area. The PMMA was probably filled up the voids among the BT nanoparticles. Because a difference in index of refraction between the BT nanoparticles and the PMMA is smaller than between the BT nanoparticles and air, light scattering was controlled for the BT/PMMA composite film. As a result, the BT-deposited plate became transparent with the spin-coating. A red curve in Fig. 5 stands for a UV–VIS spectrum of the BT/PMMA composite film on glass plate. Its transmittance was almost larger than 90% at all the wavelength range measured. The measurement of this large transmittance indicated that the BT/PMMA film was quite homogeneous, which meant that most voids were fully filled up with the PMMA. Fig. 6b shows a SEM image of the film surface. Though aggregation of the particles was observed slightly on the surface, most surface appeared to be even, which indicated that the PMMA covered the BT nanoparticles-deposited layer almost perfectly. The measurement by SP revealed that the BT/PMMA composite film had a thickness of ca. 350 nm.

The spin-coating was performed twice for producing a BT/PMMA composite film with evener surface. Fig. 7a shows a photograph of the BT/PMMA composite film on glass plate, in which the spin-coating was performed twice. The film was transparent on its whole area, similarly to that for the spin-coating of once. A blue curve in Fig. 5 stands for a UV–VIS spectrum of the BT/PMMA composite film on glass plate. A transmittance that was almost larger than 90% was recorded at all the wavelength range measured as well as that for the spin-coating of once. Fig. 7b shows a SEM image of the film surface. No aggregation of the particles was observed longer on the surface. The surface became evener with the second spin-coating. According to the measurement by SP, a thickness of the BT/PMMA composite film was also ca. 350 nm. The thickness did not change remarkably even with the second spin-coating, which indicated that the PMMA was considered to be consumed to make the surface evener. TG-DTA curves for the BT/PMMA film mixed with the α-alumina powder are
The spin-coating of PMMA/NMP was performed once.

Fig. 6 – Photograph (a) and SEM image (b) of BT/PMMA composite film.

The spin-coating of PMMA/NMP was performed twice.

Fig. 7 – Photograph (a) and SEM image (b) of BT/PMMA composite film.

![TG-DTA curves for the BT/PMMA composite film.](image)

The sample weight did not vary significantly, and no dominant DTA peaks were detected in a temperature range lower than 250 °C. An exothermic peak and a weight loss, which would be assigned to combustion of PMMA, were detected in a range of 303 °C. The weight decreased gradually, and then leveled off at 99.2% above ca.450 °C. The total weight loss of 0.8% corresponded to 26.7% with the respect to the BT/PMMA film, because the film content in the sample for the thermal analysis was 3%. Accordingly, the BT content in film was estimated to be 73.3 wt%, supposing that the weight of BT particles did not change during the thermal analysis. Since densities of BT and PMMA are 6.0 and 1.2 g/cm³, respectively, the BT content of 73.3 wt% was converted into a value as large as 35.5 vol% in film.

The BT nanoparticles/PMMA composite films produced in the present work are expected to exert dielectric properties, since the homogeneousness and the high content of BT particles in the composite films were achieved. Dielectric properties of films incorporated with BT nanoparticles are strongly dependent on dispersion state of BT particles and BT content in the films. Accordingly, information on distributions of the BT particles in the films is quite interesting for understanding dependence of their dielectric properties on morphology of the film. Further studies on them are being prepared.

4. Conclusions

The BT nanoparticles/PMMA composite films were fabricated by a combination of deposition process and spin-coating technique. The BT particles with the average size of 77.6 ± 30.5 nm and the crystal size of 28.1 nm, which were synthesized via hydrolysis reaction of TTIP in the presence of barium...
hydride, were deposited on the sodium glass plate surface-
modified with PVP by immersing the surface-modified plate
into the BT particle suspension. The PMMA/NMP solution at
the PMMA concentration of 150 g/L was twice spin-coated
on the BT-deposited plate at the rotating speed of 5000 rev/min.
Its BT volume fraction in film, its thickness, and its transmi-
tance in the visible light region were 35.5%, ca. 350 nm, and ca.
90%, respectively.

Conflict of interest

The authors declare no conflicts of interest.

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