Field-assisted synthesis of perovskite type oxide/polymer composite film

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Abstract: Perovskite type oxide/polymer composite films were synthesized from titanium-organics and Ba\(^{2+}\) in aqueous solution using a direct current (dc) field. Titanium-organic films on stainless substrates were reacted with barium nitrate solution under dc field. BaTiO\(_3\) nanoparticles were formed in the precursor film at low temperatures and atmospheric pressure. The crystallization of BaTiO\(_3\) particles was dependent on the synthetic conditions, such as applied field, reaction time, and temperature.

Keywords: hybrid, nanocomposite, nanoparticles, BaTiO\(_3\)

1. INTRODUCTION

Nano-sized particle/polymer composites have attracted attention because of the beneficial properties of both the nano-sized particles and polymer matrix [1]. Nanoparticle/polymer composites are expected to be well suited for various applications in optic and magnetic materials. The uniform mixing of nanoparticle in a polymer matrix is quite difficult via conventional mixing of nanoparticles and polymer because the particles aggregate yielding agglomerates by van der Waals forces during mixing process. Therefore, new methods are required for synthesis of the hybrid nanocomposite of nanoparticles and polymer.

Barium titanate (BaTiO\(_3\)) is one of the most widely used perovskite oxides for applications in electrorceramics, including capacitors, thermistors, sensors, and actuators, because of its excellent dielectric properties.

We report the synthesis of crystalline perovskite type particle/polymer composite film from titanium-organic film and Ba\(^{2+}\) ions at low temperatures under direct current (dc) field. The composite films were synthesized on stainless substrates in aqueous solution at ambient pressure. Several titanium organics and barium compounds were used as starting compounds for the synthesis. The synthesis conditions of BaTiO\(_3\) particles in a polymer film were also investigated.

2. EXPERIMENTAL

2.1. Synthesis of BaTiO\(_3\) particle/polymer composite

Acetylacetonate (CH\(_3\)C(OH)C(OH)\(_3\)), acacH) and titanium isopropoxide [Ti(O\(_3\)C\(_2\)H\(_5\))]\(_3\), Ti(O\(_3\)Pr)\(_3\)] were commercially available. Ethanol was dried over magnesium ethoxide and distilled before use. Polyvinylbutyral (PVB, molecular weight, 23000) and poly(methylmethacrylate) (PMMA, molecular weight, 120000) was used as received.

Figure 1 shows a schematic diagram of the experimental setup for the composite film synthesis. Ti(O\(_3\)Pr)\(_3\))(acac) were prepared from Ti(O\(_3\)Pr)\(_3\) and acetylacetonate (acacH) according to the literature [2]. Ti-precursor solution was prepared by mixing 20 wt% Ti(O\(_3\)Pr)\(_3\))(acac) in ethanol (EtOH) with 10 wt% PVB or PMMA in EtOH at a volume ratio of 2:1. The precursor film was prepared using the Ti-precursor solution by spin coating on a stainless substrate (sus304, 20×20×0.1 mm thick) at 1500 rpm for 30 s. The coating was repeated 2 times. After drying below 100°C, the precursor film was exposed to UV irradiation (308 nm) for 30 min under N\(_2\) atmosphere. The precursor film on a sus304 substrate was immersed in 0.01 M Ba(NO\(_3\))\(_2\) solution of CH\(_3\)CN and deionized water with a volume ratio of 3/2. The substrate of the precursor film was used as a cathode, while a sus304 plate of the same size was an anode. The dc voltage was supplied using a potentiostat at 3.0 V at temperature from 40 to 60°C. The distance between anode and cathode was 10 mm. The reaction vessel was maintained in a thermostat.

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temperature using an impedance analyzer.

3. RESULTS AND DISCUSSION

3.1. Synthesis of BaTiO$_3$ particle/polymer composite film

Fig. 2 shows the change of XRD for the BaTiO$_3$ particle/PMMA films on sus304 substrates synthesized from 30 to 90 min at 3.0 V/cm and 50°C. No diffractions of perovskite structure were observed for the film treated for 30 min. The reflections of BaTiO$_3$ began to appear in the film treated for 35 min as shown in Fig. 2(b).

Fig. 3 shows IR spectra of Ti(OiPr)$_3$ (acac)-PMMA film and BaTiO$_3$ particle/PMMA composite film shown in Fig. 2(d). The stretching at 1730 cm$^{-1}$ is due to the ester carbonyl of PMMA. The β-diketone of acetylacetonate marked with arrows are observed at 1591 and 1526 cm$^{-1}$. The broad band at around 600 cm$^{-1}$ is assigned to Ti-O octahedra of barium titanate as reported [3].

Ti(OiPr)$_3$(acac)-PMMA film and BaTiO$_3$ particle/PMMA composite film were analyzed by DTA-TG to estimate the ratio of organic to inorganic phase ($r_r/r_o$), where $r_o$ is the organic phase and $r_r$ the inorganic phase. For Ti(OiPr)$_3$(acac)-PMMA film, the $r_r/r_o$ ratio is 80/20, while the $r_r/r_o$ is 40/60 for BaTiO$_3$ particle/PMMA composite film.

Fig. 4 shows scanning electron microscopy (SEM) of BaTiO$_3$ particle/organic film. The film was synthesized from a 2-time-coated Ti(OiPr)$_3$(acac)-polymmer film and barium nitrate at 50°C and 3 V for 45 min. The surface of BaTiO$_3$ particle/PMMA composite film [Fig. 4(b)] is smoother than that of BaTiO$_3$ particle/PVB composite film. The film thickness of BaTiO$_3$ particle/PVB composite film and BaTiO$_3$ particle/PMMA composite film were 1.6 and 1.0 μm, respectively. The dielectric properties of BaTiO$_3$ particle/organic film were measured at 1 kHz at room temperature. For BaTiO$_3$ particle/PVB composite film, the dielectric constant was 38.0. On the other hand, the dielectric properties of BaTiO$_3$ particle/PMMA composite film was 25.2. It was considered that the dielectric constants of polymer do not much effect on the dielectric properties of BaTiO$_3$ particle/organic film. The dielectric constants of PVB and PMMA were 4.0 (348K, 105 Hz) and 3.2 (343K, 105 Hz), respectively [4, 5].

4. CONCLUSIONS

Crystalline BaTiO$_3$ particle/polymer composite film was successfully synthesized from Ti(OiPr)$_3$(acac)-polymer and Ba(NO$_3$)$_2$ at low temperatures under dc field at atmospheric pressure. The surface morphology of the composite film from PMMA was better than that from PVB.

REFERENCES


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