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Fabrication and dielectric properties of the $BaTiO_3$–polymer nano-composite thin films

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Abstract

To prepare high dielectric thin film of polymer-based materials, nanometer sized barium titanate ($BaTiO_3$) particles, which should have high dielectric coefficients and low energy dissipation factors due to nano-size effects, were dispersed in polyvinylidene fluoride (PVDF) or siloxane-modified polyamideimide (SPAI). The $BaTiO_3$ particles with crystal sizes of 10.5–34.6 nm were synthesized with a complex alkoxide method. Polymer/*N*-methyl-2-pyrrodinone solution suspending the $BaTiO_3$ particles was spin-coated on ITO glass substrates to prepare polymer-based composite films with thickness of submicron meters. The $BaTiO_3$ particles were dispersed more homogeneously in the PVDF film than in the SPAI film. The good dispersion of the particles in the PVDF film brought about a smooth surface of the film that had a root mean square roughness less than 20 nm at a particle volume fraction of 30%. The roughness was less than one-tenth of the roughness of the SPAI composite film. An increase in the $BaTiO_3$ crystal size from 10.5 to 34.6 nm in the PVDF film at a particle volume fraction of 30% increased the dielectric constant of the film from 20.1 to 31.8. The $BaTiO_3$–PVDF composite film attained high dielectric constant that had more than twice the dielectric constant of the $BaTiO_3$–SPAI composite film. The dissipation factor of the PVDF composite film was as low as 0.05 at 10^4 Hz.

Keywords: Films; Composites; Dielectric properties; $BaTiO_3$ and titanates; Polymer

1. Introduction

Reduction in size of high performance electrical devices requires an integration of passive components such as resistors, capacitors and inductors, which outnumber active integrated circuit elements and occupy a large area of the substrate.[1–6] Fabrication of thin films with high dielectric constants is essential for the integration of the passive components.

Ferroelectric lead zirconate titanate and barium titanate ($BaTiO_3$) are candidates for capacitor materials because of their high dielectric constants. The titanates, however, require high temperature processing, which is not compatible for embedding the capacitors in the printed circuit board of a resin substrate.

To realize low temperature processing, a number of attempts have been devoted, one of which is the application of a nanocrystalline seeding technique.[7–12] Our previous work with this technique reported that high dielectric nano-composite films of titanates could be fabricated at a temperature as low as 350 °C.[12]

Fabrication of ceramic–polymer composites is another attempt, and is receiving attention since this technique combines the low temperature processing of polymers and the high dielectric constant of ceramics.[1–6] Traditional approach for preparation of such composite films is to mix a dielectric polymer solution and submicron- or micron-sized ferroelectric particles, and evaporate the solvent of the polymer solution.[1–6] Since a composite film at high particle contents has a roughness of at least the ceramic particle size, the film thickness has to be much larger than the particle size to achieve uniform film thickness. Consequently, the thickness of composite films containing such large particles exceeded 1 μm,[13] and it was difficult

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to achieve high capacitance densities. In addition, fabrication of the films in integrated circuits requires a surface roughness much less than a 100 nm. Therefore, to meet the demands of film thickness and smoothness, it is strongly required to prepare composite films that disperse ceramic nanoparticles.

Ceramics such as $BaTiO_3$ with particle sizes larger than several 10 nm have ferroelectric properties. However, when their sizes approach to nanometers, they tend to have paraelectric properties that result in low dissipation factor. These properties are suitable for dielectric materials.

The purpose of the present work is to fabricate polymer composite films in which $BaTiO_3$ nanoparticles are well dispersed at high $BaTiO_3$ concentrations. Two different kinds of polymer, polyvinylidene fluoride (PVDF) and siloxane-modified polyamideimide (SPAI), are examined as host polymers. The $BaTiO_3$ nanoparticles with a perovskite crystalline structure are prepared from complex alkoxide with a sol–gel method. Measurements of dielectric properties and surface roughness characterize the composite films.

2. Experimental details

2.1. Materials

Starting reagents for the barium titanate were metallic barium (Kanto Chemical Co.) and tetraethyl orthotitanate (TEOT) (97%, Tokyo Kasei Kogyo Co.). Special grade reagents (Wako Pure Chemical Industries, Ltd.) of ethanol (99.5%, dehydrated) and *N*-methyl-2-pyrrodinone (NMP) (dehydrated) were used as solvent. PVDF (average Mw = 534,000, Aldrich Chemical Company Inc.) and SPAI were used as host polymers. These molecular structures are shown in Fig. 1. All the chemicals were used as received. Indium tin oxide substrate (ITO substrate) (Furuuchi Chemical Co.) was used as a substrate electrode. H_2O was distilled and deionized to have an electric resistance higher than 18 MΩ cm.

2.2. Synthesis of $BaTiO_3$ nanoparticles

The synthesis of $BaTiO_3$ particles was reported elsewhere.[14] Metallic barium was dissolved in ethanol or 50% (v/v) benzene/ethanol cosolvent, and was refluxed at 73 °C for 1 h. Then, TEOT was added to the solution, and the mixture obtained was refluxed for another 24 h, which led to preparation of a transparent complex alkoxide solution. To hydrolyze the complex alkoxide, the solution was mixed with an equal volume of an ethanol/water solution, and kept at 50–70 °C for 10 h. The mixed solution turned opaque, which indicated the formation of the $BaTiO_3$ particles. In hydrolysis reaction, the total metal concentration and the H_2O concentration were ranged in 0.06–0.12 kmol/m^3 and 10–20 kmol/m^3, respectively. The $BaTiO_3$ particles were sedimented by centrifugation, and the dispersion medium (benzene/ethanol/water) was substituted with NMP to prepare $BaTiO_3$/NMP suspension for a succeeding fabrication of composite films.

2.3. Fabrication of $BaTiO_3$–polymer nano-composite film

The polymer of PVDF or SPAI was dissolved in the NMP under stirring at 70 °C for 12 h, and then mixed with an equal volume of the $BaTiO_3$/NMP suspension prepared as in the previous section. The weight ratio of polymer to polymer + NMP in these $BaTiO_3$/polymer/NMP suspensions was adjusted to 5% for PVDF and 13.6 wt% for SPAI, respectively. The $BaTiO_3$/polymer/NMP suspensions were spin-coated on the ITO substrates at 3000 rpm for 30 s, and dried on a hot plate at 150 °C for 20 min. Concentration of the $BaTiO_3$ particles prepared in the composite films was varied from 0 to 30 vol%.

2.4. Measurements

The $BaTiO_3$ particles were characterized by transmission electron microscopy (TEM) and X-ray diffraction (XRD). TEM photographs were taken with a Zeiss LEO 912 OMEGA microscope operated at 100 kV. Samples for TEM measurements were prepared by dropping and evaporating the particle suspensions on a collodion-coated copper grid. XRD measurements (RU-200A, Rigaku Co.) were carried out at 40 kV and 30 mA with Cu Kα radiation using a monochromator. For powder XRD measurement, the $BaTiO_3$ colloid was centrifuged to remove supernatant and then the residue was dried at 50 °C for 24 h in vacuum. The crystal sizes of the $BaTiO_3$ particles were calculated with the Scherrer equation from the (1 1 1) peak of the XRD pattern.

Surface of the film was observed by optical microscope (BH-2, OLYMPUS). Thickness of the film and root mean square (RMS) roughness of the film surface were measured with a surface profilometer (Dektak[3], ULVAC).

The dielectric constant of the composite film was obtained from the capacitance of the film, the area of the Au-electrode (1.96×10^{-7} m^2) and the thickness of the composite film. Au-electrodes were patterned as upper electrodes on the film surface by sputtering. The capacitance and dissipation factor of the film were measured with an NF Electronic Instruments 2322 LCZ meter at frequencies of 10^2–10^5 Hz.

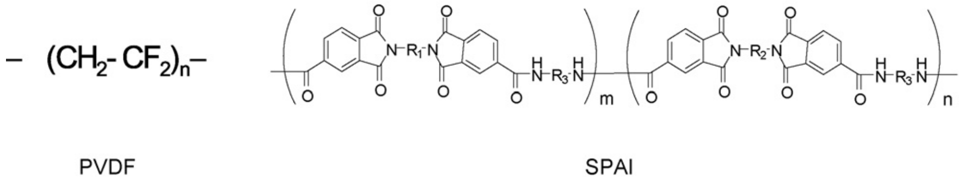

Fig. 1. Molecular structures of polyvinylidene fluoride (PVDF) and siloxane-modified polyamideimide (SPAI).

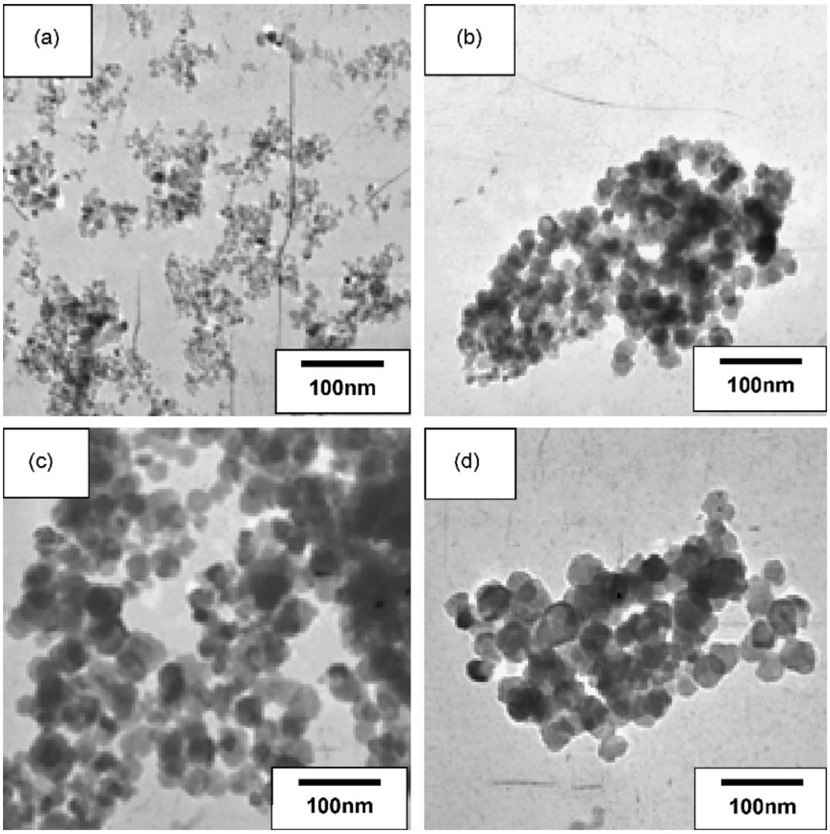

Fig. 2. TEM images of $BaTiO_3$ particles prepared at (a) 0.12 kmol/m^3 metal, 10 kmol/m^3 H_2O and 70 °C, (b) 0.06 kmol/m^3 metal, 20 kmol/m^3 H_2O and 70 °C, (c) 0.12 kmol/m^3 metal, 20 kmol/m^3 H_2O and 70 °C, and (d) 0.06 kmol/m^3 metal, 20 kmol/m^3 H_2O and 50 °C. Pure ethanol solvent was used for the samples (a), (b) and (d), and 50% (v/v) benzene/ethanol solvent was used for the sample (c).

3. Results and discussion

3.1. $BaTiO_3$ nanoparticles

$BaTiO_3$ particles with different sizes were prepared at different temperatures and concentrations of reactants in different solvents. Figs. 2 and 3 show TEM images and XRD patterns of the $BaTiO_3$ particles. The average size of the particles ranged from ca. 10 to 30 nm. All the XRD peaks were attributed to the perovskite cubic phase of the $BaTiO_3$. Crystal sizes of the $BaTiO_3$ particles calculated for (a), (b) and (d) with ethanol were 10.5, 25.5 and 34.6 nm, respectively. The $BaTiO_3$ particles prepared for (c) with 50% (v/v) benzene/ethanol had a calculated crystal size of 27.3 nm. Since the average size of the particles observed by TEM was close to the crystal size, the particles are considered to mainly consist of single crystals.

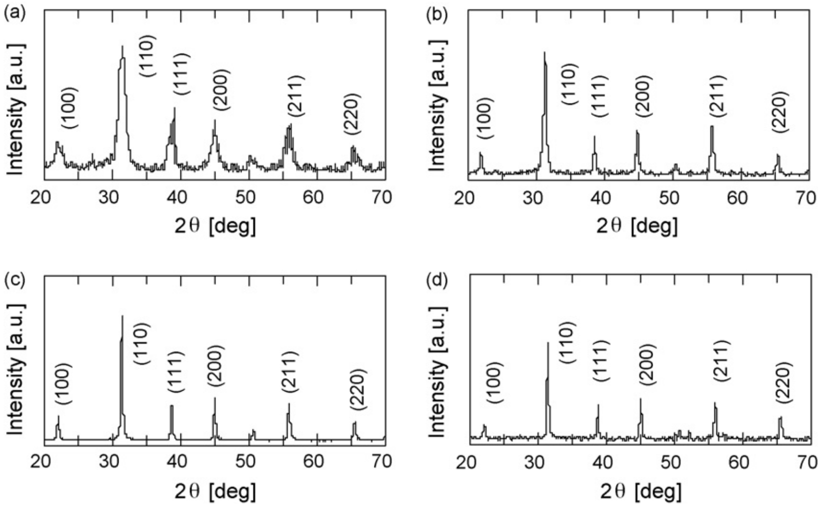

Fig. 3. XRD patterns of $BaTiO_3$ particles. See Fig. 2 for reaction conditions in the preparation.

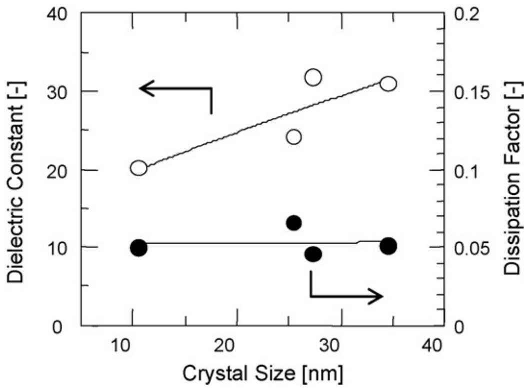

Fig. 4. Dielectric constant (○) and dissipation factor (●) of $BaTiO_3$–PVDF composite films measured at 10^4 Hz as a function of $BaTiO_3$ crystal size. $BaTiO_3$ volume fraction: 30%, spin speed: 3000 rpm and drying temperature: 150 °C.

3.2. *Nano-$BaTiO_3$–polymer composite films*

Fig. 4 shows dielectric constants and dissipation factors of the $BaTiO_3$–PVDF composite films as a function of the $BaTiO_3$ particle size. The dissipation factor was as low as 0.05 for the crystal sizes examined. The dielectric constant increased from 20.1 to 31.8 with an increase in the crystal size from 10.5 to 34.6 nm. It has been reported that the dielectric constant of $BaTiO_3$ ceramic increases with an increase in the crystal size from 0.3 to 1 μm.[15,16] A similar size effect might cause the increase in the dielectric constant of the film.

Fig. 5 shows optical micrograph of the composite films, in which the volume fraction and crystal size of the $BaTiO_3$ particles were 30 vol% and 27.3 nm, respectively. Many aggregates were observed on the surface of the $BaTiO_3$–SPAI composite film. The root mean square roughness of the $BaTiO_3$–SPAI composite film was 200 nm. In contrast, the $BaTiO_3$–PVDF composite film had a smooth surface, which indicated that the particles were homogeneously dispersed. A RMS roughness of the $BaTiO_3$–PVDF composite film was less than 20 nm, which was much lower than those of the $BaTiO_3$–SPAI composite film and the conventional composite film.[13] Probably, the PVDF has a higher affinity for the $BaTiO_3$ particles than the SPAI because of higher polarity of the PVDF, which provided the difference in the particle dispersion in the polymer solutions.

Fig. 6 shows the thicknesses of the composite films as a function of the volume fraction of the $BaTiO_3$ particles. Both the thicknesses increased with an increase in the volume fraction. The thickness of the 30 vol%–$BaTiO_3$–SPAI composite film was 600 nm, which was 20% thicker than the pure SPAI film. The thickness of the 30 vol%–$BaTiO_3$–PVDF composite film was three times larger than the pure PVDF film.

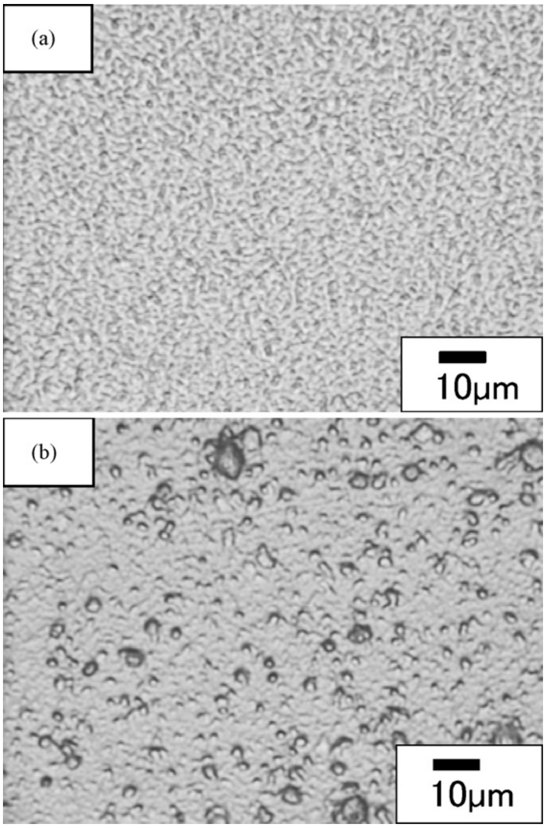

Fig. 5. Optical micrographs of (a) $BaTiO_3$–PVDF and (b) $BaTiO_3$–SPAI composite films. $BaTiO_3$ crystal size: 27.3 nm, volume fraction: 30%, spin speed: 3000 rpm and drying temperature: 150 °C.

Fig. 7 shows the dielectric constants of the composite films as a function of the volume fraction of the $BaTiO_3$ particles. The dielectric constant of the $BaTiO_3$–PVDF composite film increased remarkably with an increase in the particle volume fraction. The 30 vol%–$BaTiO_3$–PVDF composite film exhibited a dielectric constant of 31.8, which was four times larger than that of the pure PVDF film. The dielectric constant of 31.8 corresponded to a capacitance density of 0.63 nF/mm^2, which was larger than that of ferroelectric ceramic–polymer composite films (0.35 nF/mm^2) fabricated by the traditional process.[5] No sharp increment of the dielectric constant was observed with the $BaTiO_3$–SPAI composite film. Possibly, this difference resulted from the low dispersibility of the $BaTiO_3$ particle in the composite films.

Fig. 8 shows the dissipation factors of the composite films as a function of the volume fraction of the $BaTiO_3$ particles. The dissipation factors of PVDF and SPAI polymers, which were the

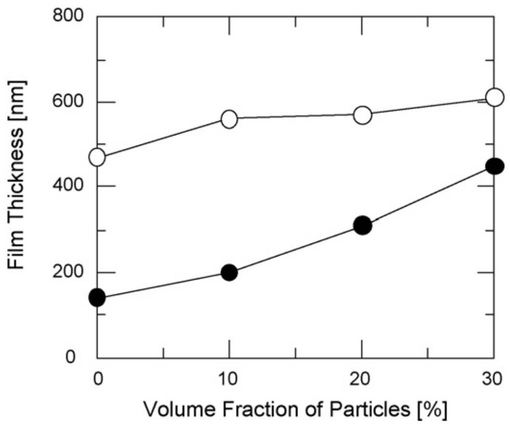

Fig. 6. Thickness of $BaTiO_3$–PVDF (●) and $BaTiO_3$–SPAI composite films (○) as a function of volume fraction of particles. The $BaTiO_3$ crystal size: 27.3 nm, spin speed: 3000 rpm and drying temperature: 150 °C.

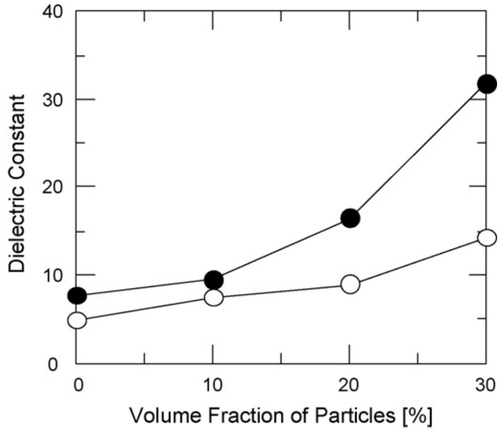

Fig. 7. Dielectric constant of $BaTiO_3$–PVDF (●) and $BaTiO_3$–SPAI composite films (○) measured at 10^4 kHz as a function of volume fraction of particles. The $BaTiO_3$ crystal size: 27.3 nm, spin speed: 3000 rpm and drying temperature: 150 °C.

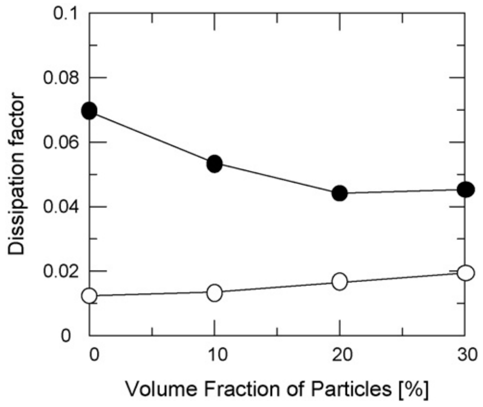

Fig. 8. Dissipation factor of $BaTiO_3$–PVDF (●) and $BaTiO_3$–SPAI composite films (○) measured at 10^4 Hz as a function of volume fraction of particles. The $BaTiO_3$ crystal size: 27.3 nm, spin speed: 3000 rpm and drying temperature: 150 °C.

values at the volume fraction of zero in Fig. 8, were 0.070 and 0.012, respectively. An increase in the volume fraction lowered the dissipation factor of the PVDF composite film but slightly raised the dissipation factor of the SPAI composite film. These results suggested that the $BaTiO_3$ particles had an intermediate dissipation factor between the PVDF and SPAI polymers. The large dissipation factor of the pure PVDF film was probably due to a large dipole moment of C–F bonds.

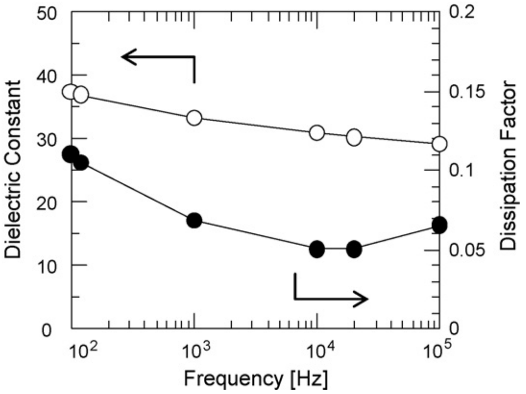

Fig. 9. Dielectric constant (○) and dissipation factor (●) of the 30 vol%–$BaTiO_3$–PVDF composite film as a function of measurement frequency. The $BaTiO_3$ crystal size: 27.3 nm, spin speed: 3000 rpm and drying temperature: 150 °C.

Fig. 9 shows frequency dependence of dielectric constant and dissipation factor of the 30 vol%–$BaTiO_3$–PVDF composite film. The dissipation factor had a minimum around the frequency of 10^4 Hz, while the dielectric constant slowly decreased with an increase in the frequency from 10^2 to 10^5 Hz. The dielectric constant was more than 30 in the whole frequency range examined.

4. Conclusions

Composite films of $BaTiO_3$ nanoparticle/polymer were spin-coated on ITO substrates with NMP solvent. The $BaTiO_3$ particles that were synthesized via hydrolysis reaction of complex alkoxide were homogeneously dispersed in PVDF, whereas the particles aggregated in SPAI. A root mean square roughness of the $BaTiO_3$–PVDF composite film attained less than 20 nm at a particle volume fraction of 30%. The $BaTiO_3$–PVDF films had high dielectric constants compared to the $BaTiO_3$–SPAI film, which might be related to difference in the dispersibility of the $BaTiO_3$ particles in the film. The dielectric constant of the composite films increased with an increase in the $BaTiO_3$ crystal size and with $BaTiO_3$ volume fraction in the composite film. The dielectric constant reached 31.8 for the 30 vol%–$BaTiO_3$–PVDF film with a $BaTiO_3$ crystal size of 27.3 nm, which was four times larger than the dielectric constant of the PVDF film without $BaTiO_3$ and corresponded to a capacitance density as large as 0.63 nF/mm^2.

Acknowledgments

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