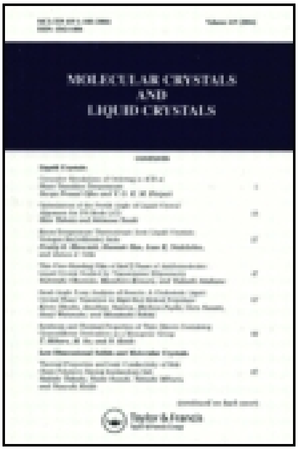

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# Preparation of Multilayered Film of Polyimide Nanoparticles for Low-K Applications

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*In order to reduce dielectric constant of polyimide, preparation of porous films assembled by polyimide nanoparticles was investigated. We utilized the electrophoretic deposition of polyimide nanoparticles to prepare porous low dielectric constant (low-k) films possessing voids between particles. The films thickness was controlled in the range of 500 nm ~ 5 μm by changing the dispersion concentration and applied voltage. Porous morphologies were confirmed by SEM observation. As a result, dielectric constant of the film decreased to 2.32, 14% lower than that of the bulk polyimide film, due to the introduction of air voids into the matrix. This is the first report showing a promising approach with high processability for porous low-k polyimide films.*

**Keywords:** electrophoretic deposition; low-k; multilayered film; polyimide nanoparticles; reprecipitation method

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## INTRODUCTION

Resistance–capacitance (RC) delay in ultra large scale integrated circuits (ULSI), caused by the increasing integration density of interconnect lines, must be reduced for improvements in the device performance. In order to avoid RC delay, the most important issue will be how to lower the dielectric constants of interlayer dielectrics [1,2]. Polyimides (PIs) seem the natural choice for the dielectric application, because their dielectric constants are lower than that of $SiO_2$ or SiOC. PIs have been widely used as dielectric and packaging materials in the microelectronic industry due to their several advantages, including low dielectric constant, easiness of processing and good mechanical properties. In order to further reduce the dielectric constant, a proportion of PI film has been replaced by air (dielectric constant is 1), which leads to a nanofoam or porous structure [3–6]. The probability of this technique is readily apparent via the prediction by Maxwell-Garnett modeling of porous structures based on a matrix polymer [7]. A PI nanofoam was prepared by the thermolysis of a thermal labile polymer as a dispersed phase in casting copolymers film, comprising thermally stable PI as the matrix. While this approach has been demonstrated to lower the dielectric constant of polyimide to some extend ($k = 2.56$), the synthetic procedures are relatively complicated.

We have developed an alternative approach to prepare porous PI films of higher voidage, maintaining the desirable thermal and mechanical properties. It is to prepare multilayered films of PI nanoparticles, in which air voids were generated by PI nanoparticles themselves. However, few studies on the preparation of PI particulates have been carried out so far [8–10]. We have prepared PI nanoparticles successfully by a unique and simple way, the reprecipitation method [11,12]. Moreover, it is possible to assemble uniform films of PI nanoparticles via electrophoretic deposition method, a rapid and straightforward method to obtain multilayered films of particulates [13,14].

In this present paper, we prepared porous films electrophoretic-deposited by PI nanoparticles. The film morphology can be controlled by changing electrical potential and dispersion concentration of PI nanoparticles. Dielectric properties of porous films obtained will be also discussed.

## EXPERIMENTAL

### Materials

PAA ($M_w = 6.9 \times 10^4$ g/mol, $M_w/M_v = 1.84$) used as a precursor polymer of PI was synthesized by polyaddition reaction of 4,4′-oxydianiline

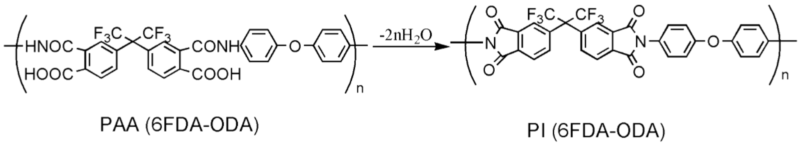

**FIGURE 1** Chemical structures of precursor PAA and corresponding PI.

(ODA) and 4,4′-(hexafluoroisopropylidene) diphthalic anhydride (6FDA) in N-methyl-2-pyrrolidinone (NMP). The chemical structures of PAA and the corresponding PI are shown in Figure 1. NMP as a good solvent, cyclohexane as a poor solvent, pyridine as a catalyst, and acetic anhydride as a dehydrating agent were all purchased from Wako pure chemical industries, Ltd. and used without further purification.

## Preparation of PI Nanoparticles by Reprecipitation Method

PI nanoparticles were prepared via reprecipitation method, as recently reported [12]. In a typical experiment, the dispersion of PAA nanoparticles was obtained by injecting PAA solution (1.0 wt% in NMP, 100 μl) into vigorously stirred cyclohexane [10 ml, containing a dispersing agent, Acrydic A-1381 (Dainippon ink and chemicals, Inc.)]. Then PI nanoparticles were obtained by the chemical imidization of PAA nanoparticles, which was performed by adding 100 μl of pyridine/ acetic anhydride mixture (1:1). After the chemical imidization, PI nanoparticles were separated by centrifugation and dried in vacuum. Finally, a yellowish powder of PI nanoparticles was obtained.

## Preparation of Multilayered Films of PI Nanoparticles

PI nanoparticles with mean diameter of 250 nm were redispersed in cyclohexane with solids concentration of 0.3, 0.5, 0.8, 1.5 and 2.0 wt% by ultrasonic irradiation. Firstly, PI nanoparticles films were prepared by spin-coating method. 100 μl of the dispersion obtained was spin-coated on a glass plate at 1500 rpm for 30 seconds. On the other hand, multilayered films of PI nanoparticles were prepared by electrophoretic deposition method. Two ITO plates used as electrodes were immersed in a plastic tube filled with the dispersion of PI nanoparticles. Different voltages (50 ~ 2000 V/cm) were applied to electrodes in a face-to-face separation. PI nanoparticles were deposited and a multilayered film was generated on the anode surface. The film was dried in ambient condition, and then thermally imidized in air at 270°C for an hour. After that, the film obtained was spin-coated (100 μl, 2500 rpm) by 1 wt% dispersion of PI nanoparticles in order to bury cracks formed by coalescence of nanoparticles during evaporation of solvents.

The morphology of films electrodeposited was characterized by field emission scanning electron microscopy (FESEM, JEOL JSM-6700F) at an acceleration voltage of 15 kV and an emission current of 10 μA. Dielectric measurements on the PI films were carried out using a HIOKI 3535 LCR meter. Medium frequency (0.1 kHz to 100 kHz) capacitance was measured in air and at room temperature.

## RESULTS AND DISCUSSION

### Preparation of PI Films via Spin-Coating Method

PI nanoparticles films were prepared by spin-coating dispersions with different solids concentration. PI nanoparticles tended to form closer packing films with increasing dispersion concentration. Although a high concentration dispersion with 7 wt% solid was used, PI nanoparticles can not fully cover the surface of the substrate and generate uniform films as shown in Figure 2(a). It is considered that partial aggregation of PI nanoparticles in high dispersion concentration made

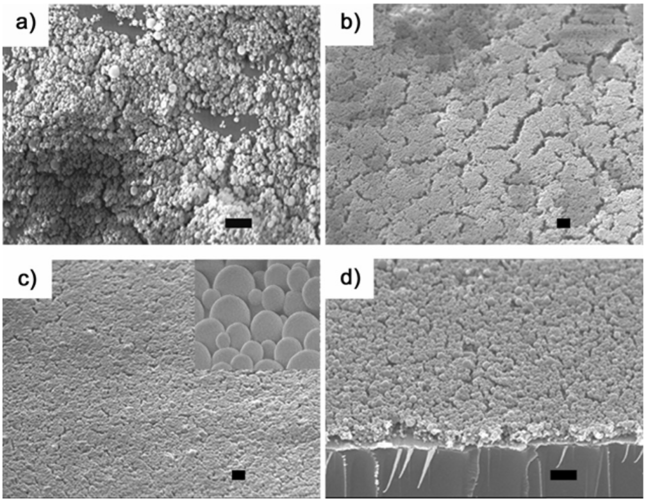

**FIGURE 2** FESEM images of PI films prepared by different methods. (a) spin-coating, (b) electrophoretic deposition, and (c) and (d) electrophoretic deposition following by spin-coating. (a), (b), (c) are top view of films, and (d) is corresponding cross sectional view of (c). The inset in (c) shows a magnified view of porous packing of PI nanoparticles. The scale bar is 1 μm.

it more difficult to prepare multilayered films of PI nanoparticles by spin-coating. Although spin-coating is the preferred method for application of thin films to flat substrates, it is not suitable for the preparation of uniform films assembled by PI nanoparticles.

## Preparation of Porous PI Films via Electrophoretic Deposition Method

PI nanoparticles were electrophoretically deposited and multilayered films were prepared on the anodes in one minute, because surfaces of PI nanoparticles were minus-charged in cyclohexane. Uniform films of PI nanoparticles were easily obtained by this method as shown in Figure 2(b). However, many cracks were observed in the films after a drying process. It was probably due to coalescence of PI nanoparticles during the evaporation of dispersing solvent. Particles larger than 250 nm could induce more cracks after the formation of porous film. Because further deformation, resulted from the mass residue of cyclohexane in bigger voids between PI nanoparticles, was developed in the films. The crack problem can not be solved by control of dispersion concentration and applied voltages.

It was found that these cracks can be buried by a spin-coating of PI nanoparticles dispersion after the electrophoretic deposition. In order to enhance adhesion to the substrate and cohesion to neighbor particles, the electrophoretic deposited films were thermally treated at 270°C for an hour. This temperature, 270°C, was 30 degrees lower than the glass transition temperature of PI, so no morphology transformation was observed after the thermal treatment. After that, the films obtained were spin-coated by a 1 wt% dispersion of PI nanoparticles. Figures 2(c) and (d) show the surface and cross-sectional FESEM images of a flat film obtained. It is apparent from Figures 2(c) and (d) that the cracks were filled by PI nanoparticles. No thickness variation was shown after the spin-coating. Making multilayered films of PI nanoparticles with uniform and compact morphologies was performed by the combination of electrophoretic deposition and spin-coating.

Multilayered films with different thickness were obtained by changing dispersion concentration of PI nanoparticles. As shown in Figure 3, films thickness increased with the increase in dispersion concentration until 0.8 wt%, then became a constant value of 1.5 μm at higher concentrations. Because the electrostatic force provided by an electric field of 200 V/cm was not strong enough to attract and fix PI nanoparticles farther than 1.5 μm from electrodes. On the other hand, applied voltages also influenced films thickness dramatically. The films obtained from dispersion with solids concentration of

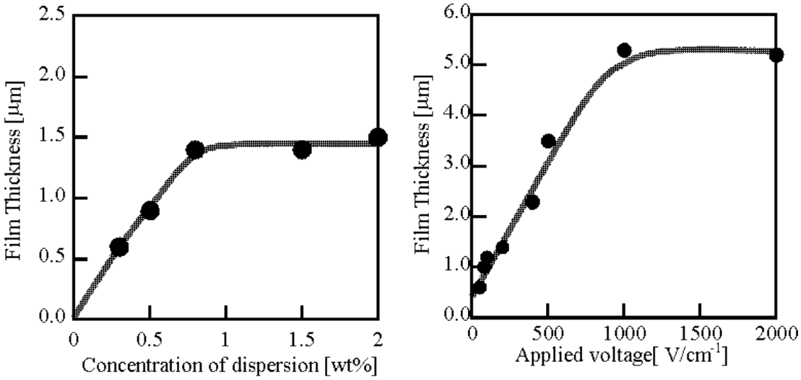

**FIGURE 3** Effect of dispersion concentration and applied voltage on the films thickness.

1 wt% became thicker as applied voltage increased from 50 to 1000 V/cm. However, no further increase of film thickness was observed while applied voltages were higher than 1000 V/cm (Fig. 3). After the electrophoretic deposition process, a transparent liquid left in plastic tubes. This result indicates 100% consumption of PI nanoparticles. Film thickness was controlled in the range of 500 nm ~ 5 μm by dispersion concentration and applied voltages.

## Evaluation of Porous Films Assembled by PI Nanoparticles

For the porous PI film, the ultimate dielectric constant is governed by the intrinsic dielectric constant of the PI matrix, as well as the morphology and porosity of the film. Table 1 shows the dielectric constant of porous films assembled by PI nanoparticles with different film thickness at different frequencies. As anticipated, all the porous PI films exhibit considerably lower dielectric constant. When the film thickness was 500 nm, the dielectric constant decreased about 14% (from 2.71 to 2.32) comparing to the bulk PI film. Unfortunately,

**TABLE 1** Dielectric Constant of Porous PI Films and that of Bulk PI Film

| Frequency (kHz) | 0.1 | 1.0 | 10 | 100 |
|---|---|---|---|---|
| Film a (800 nm thickness) | 2.88 | 2.76 | 2.65 | 2.56 |
| Film b (500 nm thickness) | 2.65 | 2.54 | 2.43 | 2.32 |
| Bulk film | | 2.78* | | 2.71 |

*J. Polym. Sci. B: Polym. Phys., (2002), 40, 2190.

porosity of the film can not be measured by gas adsorption because of relatively large voids (ca. 100 nm) between particles. On the other hand, it is also difficult for mercury to penetrate deep inside the film with great thickness in mercury porosimeter. However, the porosity of porous films can be calculated from the difference of dielectric constants between the bulk PI film and the porous one by using Maxwell-Garnett model [7]. Here, the dielectric constant decreased from 2.71 to 2.32, so the porosity of specific film was 16%. It was even lower than that of rhombohedral packing of spherical particles (porosity = 26%) [15]. Polydispersity of PI nanoparticles may result in denser packing arrangement. It is considered that trace residue of NMP in the film also led to enlargement of dielectric constant because NMP had a dielectric constant of 32.6. Thicker films caused more NMP left inside the film. As a consequence of these factors, dielectric constant increased with films thickness. The residue of NMP could be decreased by extended thermal treatment or drying in vacuum.

Presumably the dielectric constant of porous PI films could be reduced further by using porous PI nanoparticles instead of spherical PI nanoparticles, namely substituting a portion of the matrix with air, resulting in higher porosity. Fortunately, it is possible to prepare porous PI particulates by adding a source of porosity via reprecipitation method. However, control of particles and pores size is still a challenge to meet the demand of insulator applications. It is under investigation.

## CONCLUSIONS

Multilayered films of PI nanoparticles with porous structure have been prepared via electrophoretic deposition method. The film thickness has been controlled simply in the range of 500 nm $\sim$ 5 μm by changing dispersion concentration of PI nanoparticles and applied voltage. The dense packing arrangement of PI nanoparticles generated air voids between neighbor particles, resulting in the reduction of dielectric constant. The porous PI film with dielectric constant of 2.32, 14% lower than that of the bulk PI film, was achieved due to the incorporation of air. Thus, it provides a unique and prospective approach for dielectric applications with extendibility to the ultra-low dielectric constant regime ($k < 2.0$).

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