

Effect of Heat Treatment on the Morphology and Transparency of Thick Inorganic-Organic Hybrid Films Prepared by the Electrophoretic Sol-Gel Deposition of Polyphenylsilsesquioxane Particles

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Thick inorganic-organic hybrid films were prepared on ITO-coated glass substrates by the electrophoretic sol-gel deposition of polyphenylsilsesquioxane particles. The morphology of the deposited films changed from the aggregate of the spherical particles to monolith by heat treatment at temperatures higher than 200°C. Transparency of the films was significantly improved accompanied by the morphological change of the particles. The degree of the morphological change was governed by two factors; maximum heat treatment temperature and heating rate. Transparent thick films of ca. 3 μm in thickness were obtained only by heat treatment at 400°C for 2 h with rapid heating from room temperature to 400°C. These films obtained were strongly adhered to the ITO-coated glass substrates and had a very smooth surface.

Key words : Thick film, Inorganic-organic hybrid, Electrophoretic sol-gel deposition, Particle

I. Introduction

Electrophoretic sol-gel deposition is one of the most promising methods to prepare thick films.¹⁻⁴⁾ The films obtained just after the electrophoretic deposition are composed of spherical particles with submicrometer in diameter. The appearance of these thick films is usually opaque because light scattering occurs at the interface between the particles and the open spaces in the films.

Recently, we have reported that thick inorganic-organic hybrid films were prepared by the electrophoretic sol-gel deposition by using the phenylsilsesquioxane (PhSiO_{3/2}) particles derived from phenyltriethoxysilane (PhTES).⁴⁾ These films prepared by the PhSiO_{3/2} particles were opaque before heat treatment of the films. This is because the thick films are composed of aggregates of the spherical particles which cause the light scattering as described above. Transparency of the films was drastically improved by the heat treatment at 400°C. This significant improvement of transparency is attributed to the facts that the PhSiO_{3/2} particles were softened to change the morphology of the films from the aggregates of the spherical particles to the monolith with neither shapes of particles nor open spaces between the particles after the heat treatment at 400°C. However, transparency of the films heat-treated at 200°C was relatively low compared with the films heat-treated at 400°C

although all of the particles and open spaces in the films disappeared after the heat treatment at 200°C. Furthermore, transparency of the films heat-treated at 200°C did not increase even after the subsequent heat treatment at 400°C, indicating that not only the maximum heat treatment temperature but also the other factors should be satisfied to obtain high transparency of thick films.

In the present study, we investigate the effects of maximum heat-treatment temperature and heating rate on the morphology and transparency of thick inorganic-organic hybrid films composed of PhSiO_{3/2} spherical particles. We also determine the optimum heat-treatment conditions to prepare thick inorganic-organic hybrid films with high transparency.

II. Experimental Procedure

1. Preparation of PhSiO_{3/2} particles

Preparation procedures of PhSiO_{3/2} particles are similar to those reported previously.⁴⁾ Water was deionized and distilled before use. Reagent grade PhTES (Shin-Etsu Chemical Co., Ltd.) was used as a starting material. Diluted hydrochloric acid (HCl) and diluted ammonium hydroxide (NH₄OH) were used as catalysts for hydrolysis and condensation, respectively.

The hydrolysis and condensation of PhTES were per-

formed by the successive addition of HCl as an acid catalyst and NH_4OH as a base catalyst. In the first step, 0.01 mass% HCl was mixed with PhTES for hydrolysis and the mixture was stirred at 25°C for 10 h until the mixture became homogeneous. In the second step, the resultant homogeneous solution was added to 4 mass% NH_4OH solution and stirred at 25°C for additional 10 h for condensation of hydrolyzed PhTES. The mole ratio of PhTES/ H_2O (in HCl solution)/ H_2O (in NH_4OH solution) was fixed to be 1/20/180. The total weight of the sols was 100 g. The particles collected by centrifugation were washed three times by repeating redispersion in H_2O and centrifugation. The particles obtained were dried overnight at room temperature and then under vacuum at room temperature for 3 h.

2. Preparation of thick films

Sols for the electrophoretic deposition (coating sols) were prepared as follows. First, the particles were dispersed in 1 mass% NH_4OH solution with stirring. The solution was placed in an ultrasonic water bath to disperse the particles homogeneously. Second, after the particles were dispersed completely in NH_4OH solution, ethanol was added to the solution. The mole ratio of H_2O (in NH_4OH solution)/ethanol was 1/1. The amount of the particles added into the coating sols was 1 mass%. The total weight of the coating sols was 70 g.

ITO-coated glass was used as a substrate for thick film coatings and for measurement of optical transmittance. Stainless steel spiral (SUS304BA) was used as a counter electrode. The coating substrate and the spiral were cleaned with 2-propanol in an ultrasonic bath and were immersed in the coating sols. A constant dc voltage was applied between the two electrodes, i.e., the ITO-coated glass plate and the spiral, by using a power supply (Model GPV 0650-0.5, Takasago, Ltd., Kanagawa, Japan), causing the electrophoresis of negatively charged $\text{PhSiO}_{3/2}$ particles toward the anode substrate (the ITO-coated glass plate). Applied voltage and deposition time were fixed to 20 V and 5 min, respectively. After electrophoresis, the coated substrates were withdrawn from sols and dried in a desiccator over silica gel for one day. The dried films were heat-treated in air at temperatures between 100 and 400°C for 2 h with various heating rates.

3. Characterization of the films

A scanning electron microscope (SEM) (Model JSM-5300, JEOL, Tokyo, Japan) was used for observation of the surface and cross-section of the thick films.

Optical transmission spectra of the substrates coated with the thick films were measured by a ultraviolet-visible-light (UV-VIS) spectrophotometer (Model V-560, JASCO, Tokyo, Japan).

In order to investigate the softening phenomena of the $\text{PhSiO}_{3/2}$ particles, penetration test was performed by using a thermal mechanical analyzer (Model TMA-4000, Mac Science Co Ltd., Kanagawa, Japan). Figure 1 shows the

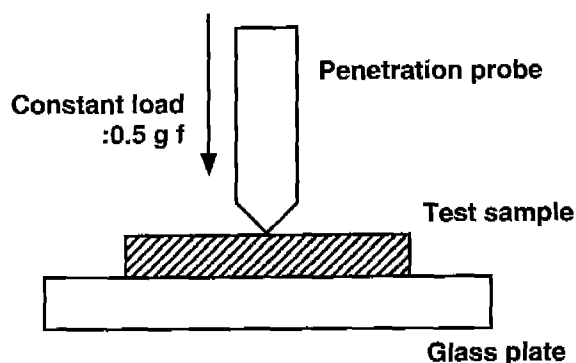


Fig. 1. Schematic drawing of the penetration test.

scheme of the penetration test. In the case of a thick film composed of spherical particles for the penetration test, the probe penetrated between the particles. This type of penetration does not reflect only the softening phenomena of the $\text{PhSiO}_{3/2}$ particles. Consequently, thick films composed of spherical particles were not appropriate as penetration test samples. Softening phenomena of the $\text{PhSiO}_{3/2}$ particles can be investigated by using monolithic test sample without particles nor open spaces. From these considerations, the monolithic samples for the penetration test were prepared as follows: First, an acetone solution of $\text{PhSiO}_{3/2}$ particles was casted in a glass dish and dried at 50°C for 24 h. Complete drying was performed by subsequent vacuum drying of the casted sample at room temperature for 3 h. The sample obtained was a monolith and was ca. 0.3 mm in thickness. This test sample was put on the glass plate and was pushed by a test probe at a constant load (0.5 g). Softening phenomena of the samples were detected as the depth of the penetration of the test probe in the heating step. The heating rates were changed from 1 to $20^\circ\text{C}/\text{min}$.

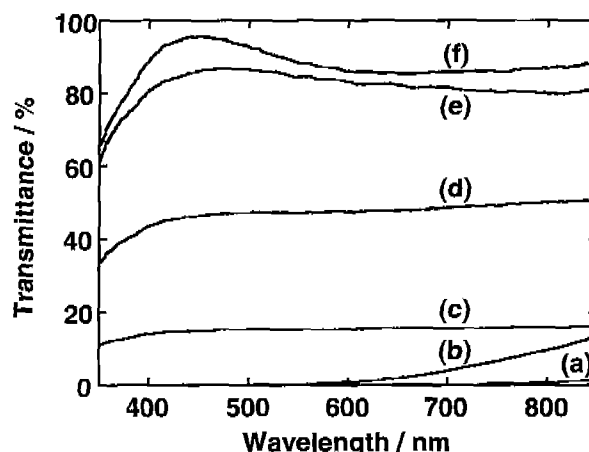


Fig. 2. Optical transmission spectra of ITO-coated glass substrates coated with $\text{PhSiO}_{3/2}$ thick films heat-treated at various temperatures for 2 h; (a) as-prepared, (b) 100°C , (c) 200°C , (d) 300°C , (e) 400°C and (f) ITO-coated glass substrate without the thick film.

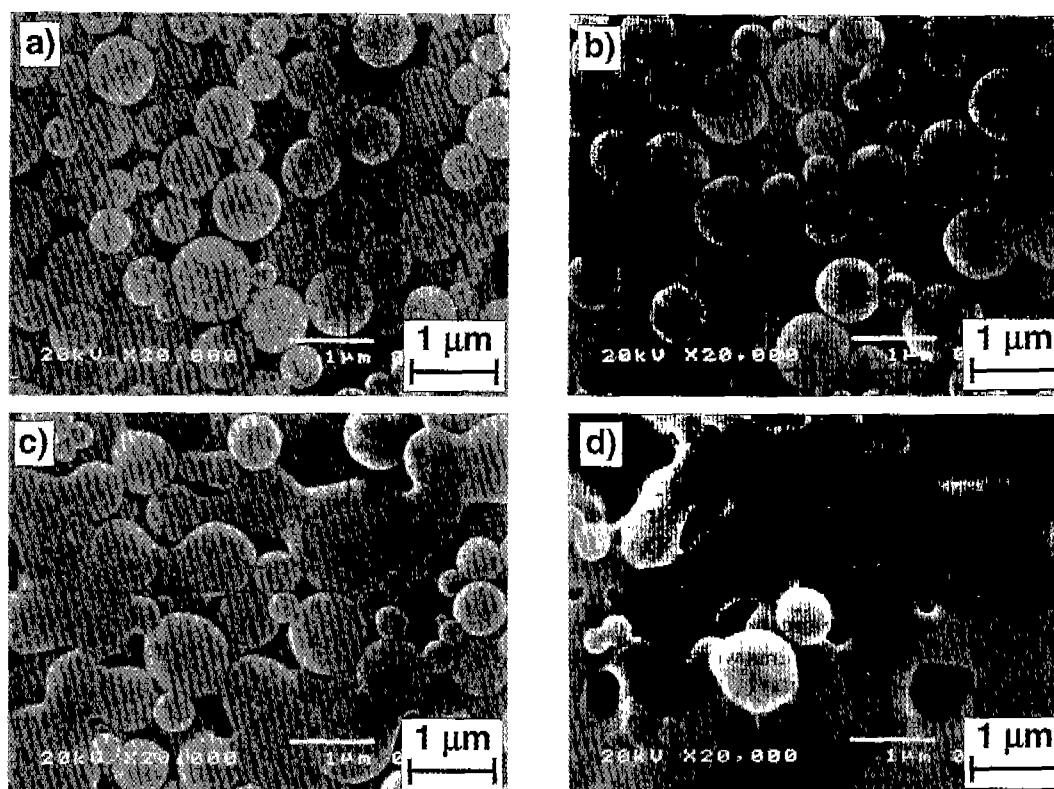


Fig. 3. SEM micrographs of the $\text{PhSiO}_{3/2}$ particles; (a) as-prepared, (b) heat-treated at 150°C for 30 min, (c) heat-treated at 200°C for 30 min and (d) heat-treated at 250°C for 30 min.

The structure change of the $\text{PhSiO}_{3/2}$ samples with heat treatment was investigated by the ^{29}Si -CPMAS-NMR (Model Unity Inova 300, Varian).

III. Results and Discussion

In the present study, we first try to determine the optimum heat-treatment temperature. In the previous paper, we reported that transparency of the $\text{PhSiO}_{3/2}$ thick films was gradually improved as the heat-treatment temperature increased.¹⁾ Optical transmission spectra of ITO-coated glass substrates coated with $\text{PhSiO}_{3/2}$ thick films heat-treated at various temperatures are shown in Fig. 2(a)-(e). For comparison, the spectrum of an ITO-coated glass substrate without the film is also given (spectrum (f) in Fig. 2). Transmittance of the substrate with the $\text{PhSiO}_{3/2}$ thick film without heat treatment is $< 1\%$ in the visible range (450-850 nm), as shown in spectrum (a). On the other hand, the transmittance of the substrate with the film increases as the heat-treatment temperature increases. After heat treatment at 400°C for 2 h (spectrum (e)), transmittance of the coated substrate becomes as high as 85 % in the visible range. Such a transparent thick film is promising for the application to optical devices.

Figure 3 shows SEM micrographs of the $\text{PhSiO}_{3/2}$ particles heat-treated at various temperatures. Heat treatment of the $\text{PhSiO}_{3/2}$ particles was carried out by placing the par-

ticles into the electric furnace which was heated beforehand to each desired temperature. Heat-treatment time was fixed to be 30 min. Only spherical particles are present before the heat treatment (Fig. 3(a)). The shape of the spherical particles is still kept after a heat treatment at 150°C (Fig. 3(b)). Morphological change is observed when the heat-treatment temperature reaches 200°C (Fig. 3(c)). At this temperature, the neighboring particles begin to fuse each other to produce larger particles. The degree of the fusion proceeds and much larger particles are produced at 250°C (Fig. 3(d)). These micrographs indicate that the higher the heat-treatment temperature, the easier the $\text{PhSiO}_{3/2}$ particles soften and change in morphology. As a result of the heat treatment and subsequent morphological change, the interface between the particles and open spaces among the particles decreases. The decrease of the interface is consistent with the result of the improvement of transparency, as shown in Fig. 2. From the thermal analysis, decomposition of the phenyl group in the $\text{PhSiO}_{3/2}$ particles was observed at temperatures near 500°C . Consequently, one of the optimum conditions is thus determined to be the heating at 400°C .

Highly transparent films, as shown in the spectrum (e) in Fig. 2, were obtained only when heat treatment was carried out by placing thick films into the electric furnace which was heated beforehand to a temperature of 400°C . In this heat treatment, it was important to heat the films to 400°C

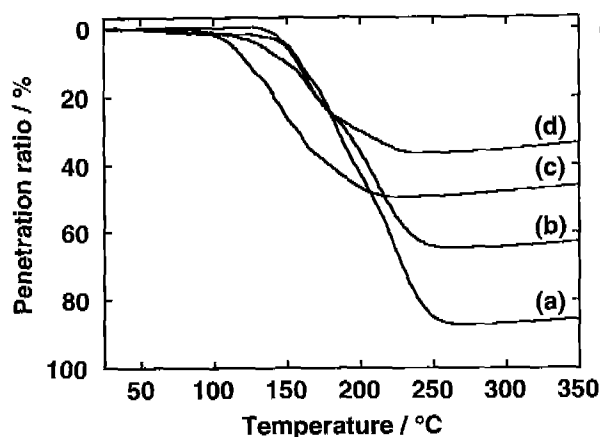


Fig. 4. Penetration ratio of the test probe into the test samples against temperatures with various heating rates; (a) 20°C/min, (b) 10°C/min, (c) 1°C/min and (d) 1°C/min (pre-heat-treated at 100°C for 2 h).

in a very short time. On the other hand, only translucent or opaque films were obtained after the films were heated at a slow rate from room temperature to 400°C, indicating that the heating rate is also another important factor to prepare transparent thick films.

Figure 4 shows the penetration ratio of the test probe into the test samples against heat treatment temperature under various heating rates. Heating rates are (a) 20°C/min, (b) 10°C/min, (c) 1°C/min, and (d) 1°C/min. The test sample (d) was heat-treated at 100°C for 2 h before the penetration test. Penetration ratio was defined by the following equation:

$$\text{Penetration ratio (\%)} = \frac{\text{Penetration depth (mm)}}{\text{Thickness of the test sample (mm)}} \times 100$$

Regardless of the heating rate, penetration begins in the range of 100-150°C and finishes at 200-250°C. However, the final penetration ratio is different according to the heating rate; the higher the heating rate is, the larger the final penetration ratio becomes. From the penetration ratio measurement, the test sample becomes softest when the heating rate is highest, 20°C/min, as shown in the curve (a) in Fig. 4. The reason for the decrease in the final penetration ratio with decrease in the heating rate is that the test sample undergoes longer heating and dehydration condensation which promote the increase of the rigidity. For the same reason, the pre-heat-treated test sample (curve (d) in Fig. 4) also has a low penetration depth because the sample possesses the rigid structure.

Figure 5 shows the ^{29}Si -CPMAS-NMR spectra of the $\text{PhSiO}_{3/2}$ particles before and after heat treatment at 400°C for 2 h. Two peaks are observed at 69 ppm and 78 ppm. Before heat treatment, intensity of these two peaks is almost the same. The peak at 69 ppm disappears and only the peak at 78 ppm is observed after heat treatment at 400°C for 2 h. These two peaks observed at 69 ppm and 78 ppm

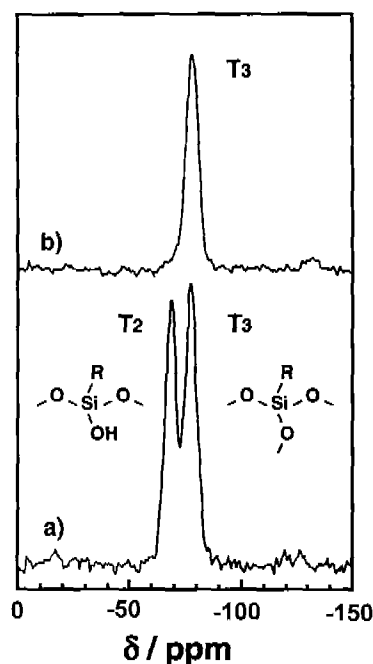


Fig. 5. ^{29}Si -CPMAS-NMR spectra of the $\text{PhSiO}_{3/2}$ particles; (a) before and (b) after heat treatment at 400°C for 2 h.

are assigned to the T_2 and the T_3 units, as shown in Fig. 5, respectively. Before heat treatment, the amount of T_2 unit, which behaves as a flexible unit, is almost the same as that of T_3 unit, which behaves as a rigid unit. However, after the heat treatment at 400°C for 2 h, the T_2 unit disappears and only the T_3 unit is observed. This result supports the occurrence of the dehydration condensation during heat treatment, as described above. From such facts, the flexible T_2 unit which is present in the $\text{PhSiO}_{3/2}$ particles before heat treatment changes to the rigid T_3 unit during the heat treatment. Once the $\text{PhSiO}_{3/2}$ particles which are composed of only T_3 units are generated, these particles cannot be expected to soften or change in morphology by further heat-treatment. Consequently, softening and morphological change of $\text{PhSiO}_{3/2}$ particles in thick films has to occur before the flexible T_2 units change completely to the rigid T_3 units. As the summary in Figs. 4 and 5, the heating rate is also one of the essential factors to make the $\text{PhSiO}_{3/2}$ thick films transparent. The heat-treatment temperature has to be raised rapidly to a temperature high enough to soften the $\text{PhSiO}_{3/2}$ thick films easily as soon as possible.

Figure 6 shows SEM micrographs of the surface of the $\text{PhSiO}_{3/2}$ thick films. Taking into account the heating rate, all the heat treatments of the $\text{PhSiO}_{3/2}$ thick films were carried out by placing the films into the electric furnace which was beforehand heated to each desired temperature. The film without heat treatment is composed of aggregated spherical particles, and many open spaces among the particles and cracks are observed in Fig. 6(a). In contrast, the shapes of the particles shown in Fig. 6(b) are indiscernible, but large dimples still remain in the film heat-treated at

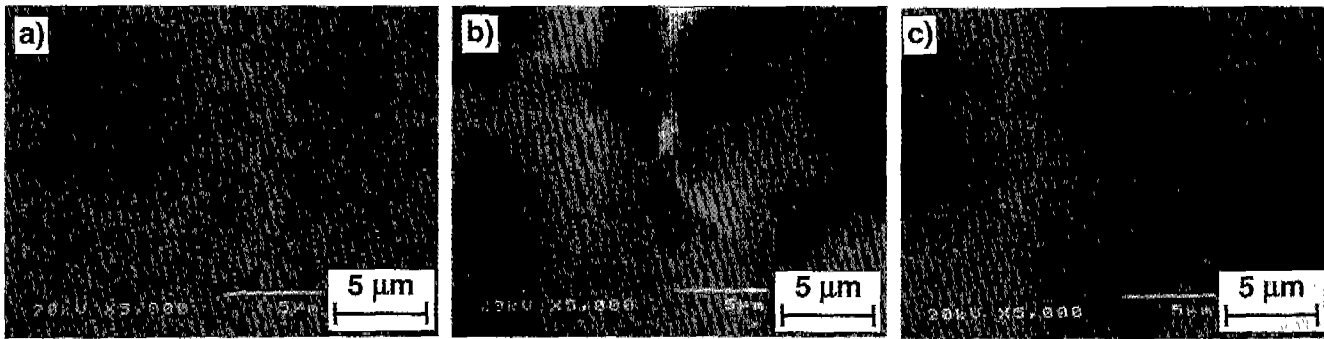


Fig. 6. SEM micrographs of the surface of the $\text{PhSiO}_{3/2}$ thick films; (a) as-prepared, (b) heat-treated at 200°C for 2 h and (c) heat-treated at 400°C for 2 h.

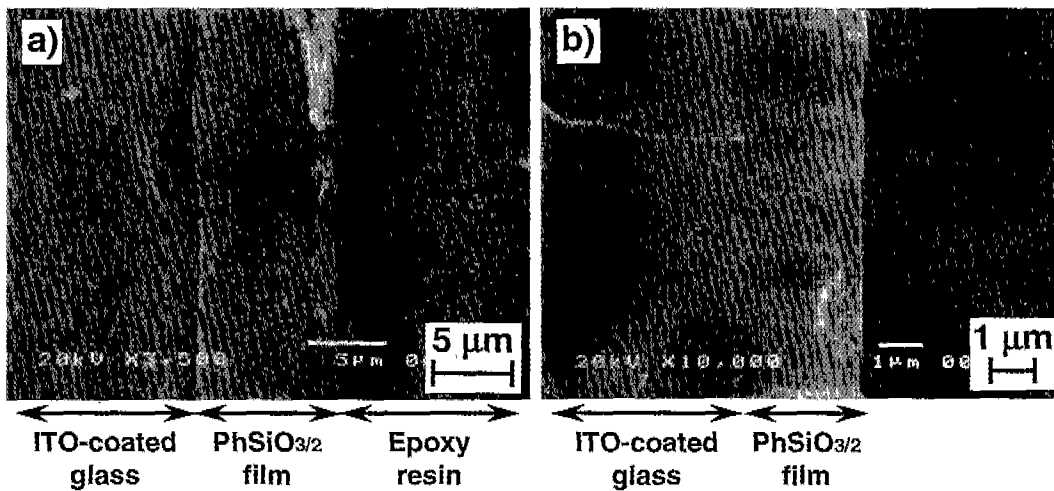


Fig. 7. SEM micrographs of the cross section of the $\text{PhSiO}_{3/2}$ thick films; (a) as-prepared and (b) heat-treated at 400°C for 2 h.

200°C for 2 h. This implies that the softening of the $\text{PhSiO}_{3/2}$ particles at 200°C is not enough to achieve morphological change completely. The film heat-treated at 400°C for 2 h becomes a monolith with no open spaces or dimples, as shown in Fig. 6(c). These SEM micrographs suggest that the increase in optical transmittance shown in Fig. 2 is due to the decrease in open spaces and cracks that cause light scattering.

Figure 7 shows SEM micrographs of the cross section of the $\text{PhSiO}_{3/2}$ thick films on ITO-coated glass substrates before and after heat treatment at the same conditions as described in Fig. 6. The film was fixed with the epoxy resin for SEM observation of the film (Fig. 7 (a)) before heat treatment because the films were very fragile; the photo (a) is composed of the three layers, substrate, film, and epoxy resin from left to right. In the film after the heat treatment at 400°C (Fig. 7 (b)), it was not necessary to use the resin to affix the film; the films was adhered so strongly to the substrate and the cross section of the glass coated with the film was directly observed by breaking the glass substrate. These phenomena suggest that the hardness and the adhesion strength of the films are greatly increased by heat treatment. In fact, we can recognize good contact between

the glass substrate and the film in Fig. 7(b). The thickness of the films decreases, from ca. $8\ \mu\text{m}$ in Fig. 7(a) to ca. $3\ \mu\text{m}$ in Fig. 7(b), accompanied by the heat treatment at 400°C for 2 h. This change of thickness is ascribed to the loss of open spaces among the particles by softening and viscous flow of the particles. Figure 7(b) shows that the film is homogenous in the direction of depth.

IV. Conclusions

The effect of heat-treatment conditions on the morphology and transparency of $\text{PhSiO}_{3/2}$ thick films prepared by the electrophoretic sol-gel deposition was investigated from the point of heat-treatment temperature and heating rate. The appropriate temperature of heat treatment was found to be 400°C . At temperatures lower than 400°C , $\text{PhSiO}_{3/2}$ particles could not soften enough to change in morphology completely. At temperatures near 500°C , decomposition of phenyl groups on each silicon atom in the $\text{PhSiO}_{3/2}$ particles was observed. We also found that the high heating rate was effective to soften the particles and change in morphology of the films. Flexible T_2 units in the $\text{PhSiO}_{3/2}$ particles was found to change to T_3 units which have rigid structure dur-

ing heating step. From these results, softening and morphological change of thick films have to be achieved while $\text{PhSiO}_{3/2}$ particles include enough amounts of flexible T_2 units. Consequently, the heat treatment has to be carried out at 400°C , and the heating rate up to 400°C also has to be high enough. Transparent $\text{PhSiO}_{3/2}$ thick films are only obtained when these heating conditions are fulfilled.

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