Fabrication of convex-shaped polybenzylsilsesquioxane micropatterns by the electrophoretic sol–gel deposition process using indium tin oxide substrates with a hydrophobic-hydrophilic-patterned surface

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Abstract Polybenzylsilsesquioxane (BnSiO$_{3/2}$) particles become a supercooled liquid through a heat treatment above the glass transition temperature (T_g) of the particles. Micropatterns of BnSiO$_{3/2}$ thick films with high transparency were obtained by the electrophoretic deposition of the BnSiO$_{3/2}$ particles on indium tin oxide (ITO)-coated substrates with a hydrophobic-hydrophilic-patterned surface and subsequent heating above T_g of the particles. It was found that the control of electrophoretic deposition conditions, in which the amounts of the particles deposited on the substrates were changed, led to two types of micropatterning processes of the BnSiO$_{3/2}$ thick films. In the first process, the particles were selectively deposited on the hydrophilic areas after the electrophoretic deposition. In the second process, the particles were deposited on the whole area of the ITO-coated substrate with hydrophobic-hydrophilic patterns after the electrophoretic deposition. Due to the difference in wettability of BnSiO$_{3/2}$ molten liquids between hydrophobic and hydrophilic surfaces, the molten liquids on the hydrophobic areas, which were obtained by heating above T_g of the particles, migrated toward the hydrophilic areas. In both the processes, convex-shaped BnSiO$_{3/2}$ micropatterns with high transparency were fabricated only on the hydrophilic areas after a heat treatment above T_g of the particles.

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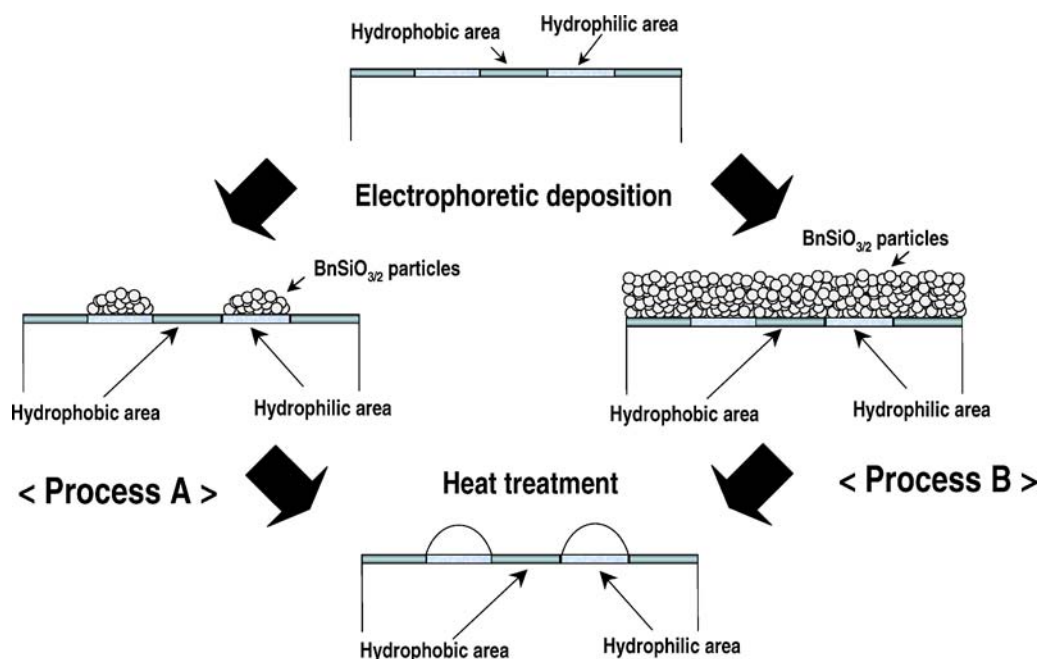Aichi 441-8580, Japan

Introduction

Sol–gel micropatterning techniques have attracted considerable attention for the fabrication of micro-optical components, such as optical gratings, waveguides, and microlens arrays. For example, embossing techniques using soft gel films [1, 2], photolithographic techniques using photosensitive gel films [3], and direct photolithographic deforming of the hybrid glass [4] have been reported. Moreover, various kinds of micropatterning processes using hydrophobic-hydrophilic patterns have also been proposed [5–10]. For the application of these patterns to optical components, formation and patterning of the thick films are very important.

As a formation process of thick films, the electrophoretic deposition method is well-known [11–15]. We proposed so called "electrophoretic sol–gel deposition process," which is a procedure combining particle preparation by the sol–gel method and film formation by the electrophoretic deposition process [16]. Thick films of SiO$_2$ [17] and TiO$_2$ [18] of about 20 μm in thickness have been prepared by this process using sol–gel derived particles from the corresponding alkoxides. However, these films were opaque because of light scattering at the interface between the particles and the open spaces in the films. This means that applications of these thick films prepared by the electrophoretic deposition to optical components are difficult.

We also prepared polybenzylsilsesquioxane (BnSiO$_{3/2}$) and polyphenylsilsesquioxane (PhSiO$_{3/2}$) particles, one of the inorganic-organic hybrid materials, by the sol–gel

Fig. 1 Schematic illustration for the preparation of $BnSiO_{3/2}$ micropatterns by the electrophoretic sol–gel deposition process using a hydrophobic-hydrophilic-patterned surface

method, and formed $BnSiO_{3/2}$ and $PhSiO_{3/2}$ thick films on indium tin oxide (ITO)-coated substrates by the electrophoretic deposition using the particles. The $BnSiO_{3/2}$ and $PhSiO_{3/2}$ particles were found to show the glass transition behavior; the particles became a supercooled liquid when they were heated at temperatures above the glass transition temperature (T_g). Thus, the thick films prepared from the $BnSiO_{3/2}$ and $PhSiO_{3/2}$ particles were morphologically changed from aggregates of spherical particles to a continuous phase by a heat treatment to form transparent thick films [19, 20]. Patterned $BnSiO_{3/2}$ thick films were also fabricated on glass substrates with patterned ITO layer, when the particles dispersed in the sol were selectively deposited on the patterned area [20]. However, the films were slightly spread on the surrounding areas after the heat treatment. With respect to the patterning technique using electrophoresis, various kinds of works have also been reported by other researchers [14, 21–23].

Recently, we demonstrated the formation of convex-shaped $PhSiO_{3/2}$ micropatterns with high transparency on ITO-coated substrates with hydrophobic-hydrophilic patterns using the electrophoretic sol–gel deposition method [24, 25]. In those works, $PhSiO_{3/2}$ particles prepared by the sol–gel method were selectively deposited on the hydrophilic areas. Furthermore, we have also proposed a micropatterning of transprent $BnSiO_{3/2}$ thick films using the difference in wettability for $BnSiO_{3/2}$ liquids between hydrophobic and hydrophilic surfaces; the electrophoretic deposition of the $BnSiO_{3/2}$ particles on the whole area of ITO-coated substrates with hydrophobic-hydrophilic patterns was

performed and subsequent heating above T_g of the particles was carried out [26].

In this study, we have investigated the micropatterning process of the $BnSiO_{3/2}$ thick films using the electrophoretic sol–gel deposition of the $BnSiO_{3/2}$ particles on ITO-coated substrates with the hydrophobic-hydrophilic patterns in detail. The micropatterning process was evaluated under the different electrophoretic deposition conditions, in which the amounts of the particles deposited on the substrates were changed. As a result, the change in the amount of the particles deposited on the substrates led to the two types of micropatterning processes. Schematic illustration for the two types of micropatterning processes is shown in Fig. 1. In the process A, the $BnSiO_{3/2}$ particles were selectively deposited on the hydrophilic areas, whereas in the process B, the $BnSiO_{3/2}$ particles were deposited on the whole area of the ITO-coated substrates after the electrophoretic deposition. Finally, in both the processes A and B, convex-shaped $BnSiO_{3/2}$ micropatterns with high transparency were fabricated only on the hydrophilic areas after a heat treatment above T_g of the particles. The formation mechanism of the micropatterns is also discussed in the two processes.

Experimental

Praparation of $BnSiO_{3/2}$ sols

Reagent grade benzyltriethoxysilane ($BnSi(OEt)_3$) was used as a starting material. Diluted hydrochloric acid and diluted
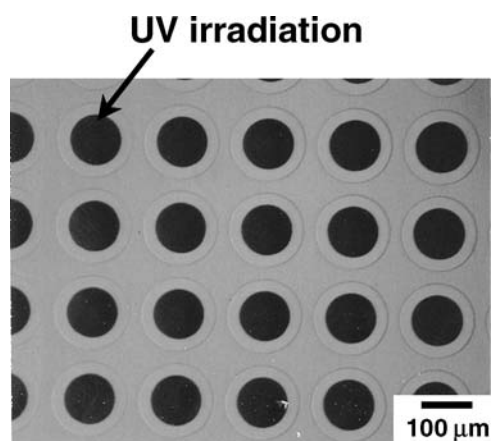
UV irradiation

Fig. 2 Optical microscope photograph of a photomask used for UV irradiation

ammonia water were used as catalysts for hydrolysis and condensation.

The preparation procedure of the $BnSiO_{3/2}$ particles was based on our previous paper [20]. In the first step, $BnSi(OEt)_3$ dissolved in ethanol (EtOH) was hydrolyzed with 0.01 mass% hydrochloric acid at room temperature for 3 h for the sufficient hydrolysis of $BnSi(OEt)_3$. In the second step, the resultant $BnSi(OEt)_3$ sol was added to 4 mass% ammonia water all at once. Microparticles formed immediately after the addition of the sol to the ammonia water, and the sol became opaque. The sol was additionally stirred for 2 h at room temperature. The mole ratio of $BnSi(OEt)_3$:EtOH:H_2O (in hydrochloric acid):H_2O (in ammonia water) was fixed at 1:20:20:180. For the characterization of the $BnSiO_{3/2}$ particles, the particles were collected from the sol by centrifugation and dried under vacuum.

Formation of hydrophobic-hydrophilic patterns

Hydrophobic-hydrophilic-patterned surfaces were prepared on ITO-coated substrates by selective UV-irradiation through a photomask on double-layered films of a very thin TiO_2 gel film (c.a. 5–10 nm) as the underlayer and a hydrolyzed fluoroalkyltrimethoxysilane (FAS) film (< 10 nm) as the top layer [24]. UV light from a high-pressure mercury lamp (about 25 mW cm^{-2} at 365 nm) was irradiated on the films with a 100 μm mesh as a photomask for 3 min in the ambient atmosphere. The optical microscope photograph of the photomask used in this study is shown in Fig. 2. UV-light was only irradiated on the substrate through the black circular areas as a thorough hole in Fig. 2. The fluoroalkyl chain of FAS was cleaved by the irradiation of UV light through a photocatalytic reaction on TiO_2 layer [27]. With the cleavage of the fluoroalkyl chain, the FAS layer became a silica layer. Thus, the UV-irradiated areas of the substrate became hydrophilic, and the areas covered with the photomask remained hydrophobic.

Preparation of $BnSiO_{3/2}$ micropatterns

In the preparation of $BnSiO_{3/2}$ thick films by the electrophoretic deposition, the $BnSiO_{3/2}$ sols were diluted with EtOH. The weight ratio of $BnSiO_{3/2}$ sols:EtOH was fixed at 7:3. An ITO-coated substrate with the hydrophobic-hydrophilic patterns and a stainless steel spiral were used as a working and counter electrode, respectively. A constant voltage of 3–10 V was applied between the two electrodes, i.e., the ITO-coated substrate and the spiral, using a potentiostats/galvanostats (HABF5001, HOKUTO DENKO), causing electrophoresis of negatively charged $BnSiO_{3/2}$ particles toward the anode substrates (the ITO-coated substrate). The deposition time was 3 min. After electrophoresis, the coated substrates were withdrawn from the sols at 3 mm/s with applying the electric field to reduce the peeling of the particles off, and dried at room temperature. The dried $BnSiO_{3/2}$ films were heat-treated in air at 200 °C for 30 min.

Characterization of $BnSiO_{3/2}$ micropatterns

The surface of the thick films and the shapes of the micropatterns were observed using an optical microscope (BX50, Olympus). A scanning electron microscope (SEM) (JSM-5300, JEOL) was used to observe the morphology of the $BnSiO_{3/2}$ particles. Thermal properties of the $BnSiO_{3/2}$ particles were examined from differential scanning calorimetry (DSC) curves under 20 °C/min (Pyris1 DSC, Perkin Elmer). A surface profilometer (TDA-22, Kosaka laboratory) was used to observe the shapes of the micropatterns. Contact angles were measured with a contact angle meter (CA-X, Kyowa Interface Science) at room temperature.

Results and discussion

Figure 3 shows a typical SEM photograph of the $BnSiO_{3/2}$ particles, and spherical particles in diameter of about 500 nm are observed. Figure 4 shows a DSC heating curve of the $BnSiO_{3/2}$ particles. An endothermic change due to glass transition is observed at around 35 °C, meaning that the particles become a supercooled liquid above 35 °C.

Contact angles for water and $BnSiO_{3/2}$ liquids ($BnSiO_{3/2}$ particles heat-treated at 200 °C), on the hydrophobic surface with fluoroalkylsilane and the hydrophilic surface with silica are summarized in Table 1. The contact angles for water on the hydrophobic and hydrophilic surfaces are around 110° and < 5°, respectively. The contact angles for the

Table 1 Contact angles for water and $BnSiO_{3/2}$ liquids ($BnSiO_{3/2}$ particles heat-treated at 200 °C) on the hydrophobic surface with fluoroalkylsilane and the hydrophilic surface with silica

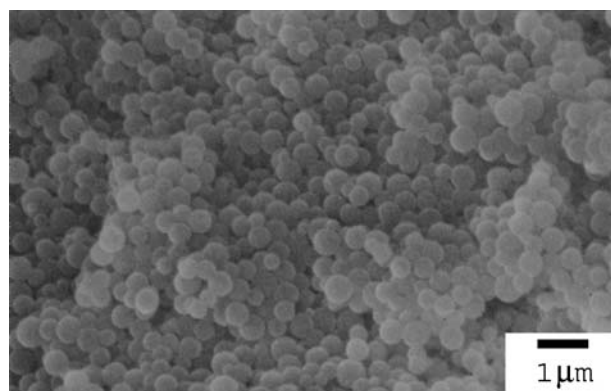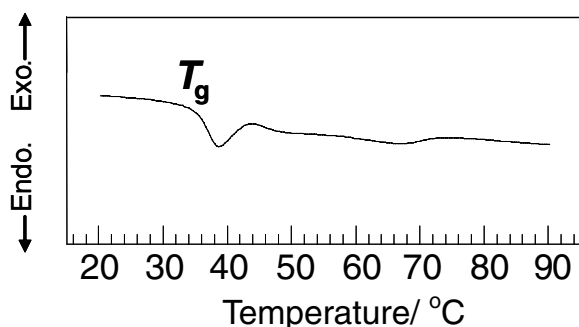|	Contact angle/°	
	Hydrophobic surface	Hydrophilic surface
Water	110	< 5
$BnSiO_{3/2}$ liquids	77	12

Fig. 3 SEM photograph of the $BnSiO_{3/2}$ particles

Fig. 4 DSC heating curve of the $BnSiO_{3/2}$ particles

$BnSiO_{3/2}$ liquid on the hydrophobic and hydrophilic surfaces are around 77° and 12°, respectively. These results indicate that the contact angles for the $BnSiO_{3/2}$ liquid on the hydrophobic and hydrophilic surfaces are quite different, as well as those for water.

To control the amount of the particles deposited on the ITO-coated substrates with the hydrophobic-hydrophilic-patterned surface, the applied voltage was changed in the electrophoretic deposition at 3 and 10 V for 3 min. As a result, the total electricity per unit area was 21 and 146 mC/cm^2, respectively. The increase in the total electricity per unit area should bring about the deposition of larger amounts of the particles. In additioin, electrolysis of water occurred during the electrophoretic deposition at both 3 and 10 V. Thus, the increse in the total electricity per unit area was probably caused from the generation of larger amounts of gases.

Figure 5 shows optical microscope photographs of (a) the surface of $BnSiO_{3/2}$ films prepared in a dipping-withdrawing manner without both an electric field and a heat treatment, and the surface of $BnSiO_{3/2}$ films prepared by the electrophoretic sol–gel deposition with an electric field at 3 V for 3 min (b) before and (c) after a heat treatment at 200 °C for 30 min. Without applying an electric field, i.e., with only dipping the substrate in the sol, only small amounts of the $BnSiO_{3/2}$ particles are deposited on the ITO-coated substrate as shown in Fig. 5(a). In contrast, with the applied voltage of 3 V, the $BnSiO_{3/2}$ particles are almost selectively deposited on the hydrophilic areas of the ITO-coated substrate as shown in Fig. 5(b). In our previous work [25], we investigated the difference in variation of current density during the electrophoretic deposition between hydrophobic and hydrophilic surfaces. There was no large difference in variation of current density during the electrophoretic deposition between hydrophobic and hydrophilic surfaces; almost the same amounts of the particles were deposited on hydrophobic and hydrophilic surfaces in the sol. From the result in our previous work, the $BnSiO_{3/2}$ particles must be deposited on the whole area of the ITO-coated substrate with the hydrophobic-hydrophilic-patterned surface before withdrawing the substrate from the sol. This gives an idea that the $BnSiO_{3/2}$ particles only weakly adhered to the hydrophobic surface because of small surface energy but the particles strongly adhered to the hydrophilic surface through
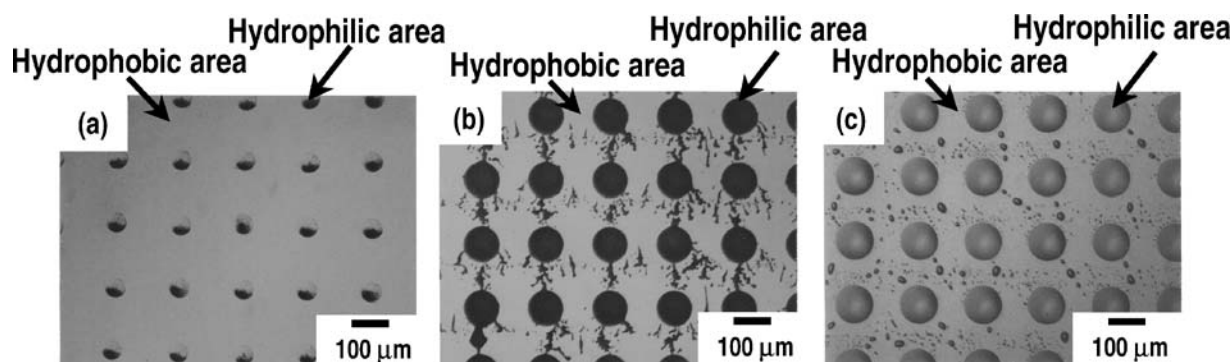

Fig. 5 Optical microscope photographs of (a) the surface of $BnSiO_{3/2}$ films prepared in a dipping-withdrawing manner before a heat treatment, and the surface of $BnSiO_{3/2}$ films prepared by the electrophoretic sol–gel deposition with an electric field at 3 V for 3 min (b) before and (c) after a heat treatment at 200 °C for 30 min

the hydrogen bonds between OH groups on the surface of the substrate and the particles. It is thus considered that almost all the $BnSiO_{3/2}$ particles were dropped off from the hydrophobic surface when the ITO-coated substrate was withdrawn from the sol.

As can be seen in Fig. 5(b), the thick films composed of the $BnSiO_{3/2}$ particles are opaque after the electrophoretic deposition due to light scattering from the particles. However, the open spaces among the particles in the films disappear because of the thermal softening of the particles by the heat treatment at 200 °C. Thus, the particulate films become transparent as shown in Fig. 5(c). Furthermore, the films are not spread on the surrounding areas, because the surrounding areas repel the $BnSiO_{3/2}$ liquid due to the difference in the contact angles between the hydrophobic and hydrophilic surfaces for the $BnSiO_{3/2}$ liquid as described in Table 1. From the results mentioned above, the hydrophobic-

hydrophilic patterns play two roles in the process A. One is the control of the adhesion between the $BnSiO_{3/2}$ particles and the surface of substrates, and the other is the control of wettability of the $BnSiO_{3/2}$ liquid.

Figure 6 shows optical microscope photographs of the surface of $BnSiO_{3/2}$ films prepared by the electrophoretic sol–gel deposition with an electric field at 10 V for 3 min (a) before and (b) after a heat treatment at 200 °C for 30 min. In this applied voltage, the $BnSiO_{3/2}$ particles are deposited on the whole area of the substrate, as can be seen in Fig. 6(a). From the results of total electricity per unit area in the electrophoretic deposition, much more particles should be deposited on the whole area of the ITO-coated substrates in the sol at the applied voltage of 10 V, compared with the applied voltage of 3 V; the deposition of much more particles is supposed to result in the stronger interaction among the particles. It is considered that the $BnSiO_{3/2}$ particles on
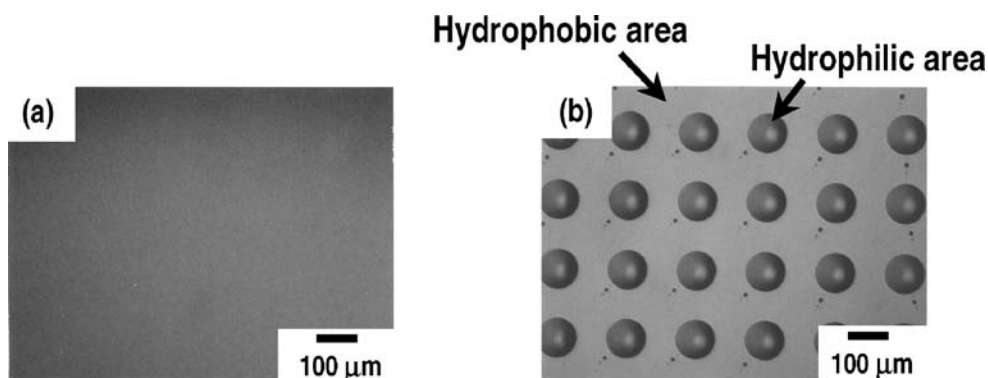

Fig. 6 Optical microscope photographs of the surface of $BnSiO_{3/2}$ films prepared by the electrophoretic sol–gel deposition with an electric field at 10 V for 3 min (a) before and (b) after a heat treatment at 200 °C for 30 min

Fig. 7 (a) Three-dimensional surface profile and (b) cross-section profile of convex-shaped $BnSiO_{3/2}$ micropatterns prepared by the electrophoretic sol–gel deposition using a hydrophobic–hydrophilic-patterned surface and the heat treatment at 200 °C for 30 min
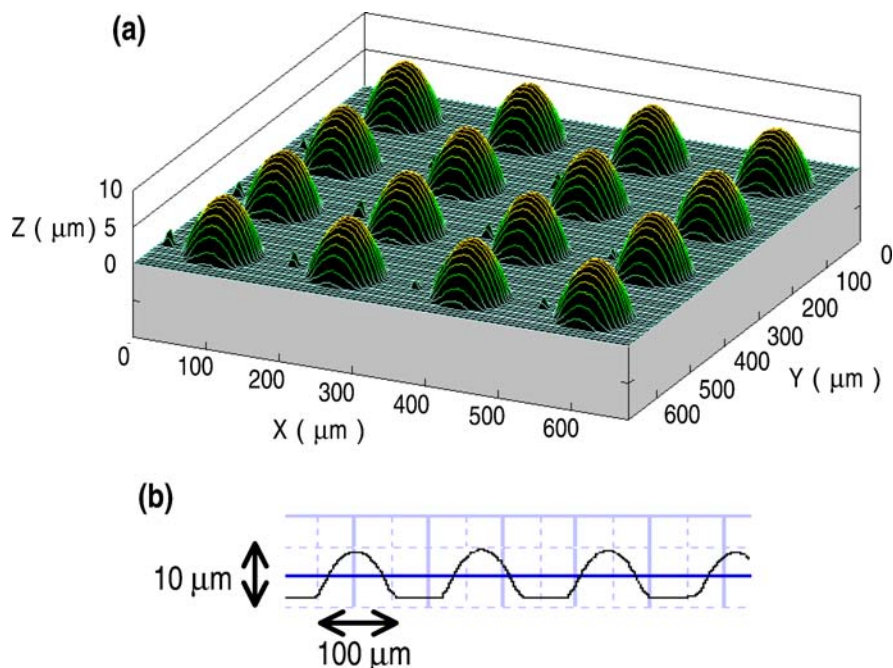
the hydrophobic areas were not dropped off because of the stronger interaction among the particles at the applied voltage of 10 V. The $BnSiO_{3/2}$ particles are thermally softened through the heat treatment above T_g; the $BnSiO_{3/2}$ thick films become a supercooled liquid by the heat treatment at 200 °C. With the thermal softening, the $BnSiO_{3/2}$ liquids on the hydrophobic areas are supposed to migrate toward the hydrophilic areas due to the difference in wettability between the hydrophobic and hydrophilic areas. Finally, transparent $BnSiO_{3/2}$ micropatterns are formed only on the hydrophilic areas, as can be seen in Fig. 6(b).

Figure 7 shows three-dimensional profiles of (a) the surface and (b) the cross-section of the thick films prepared by the electrophoretic deposition at 10 V for 3 min on the ITO-coated substrate with hydrophobic-hydrophilic patterns with a 100 μm mesh as a photomask, after a heat treatment at 200 °C for 30 min. In this sample, the average height of the convex patterns is around 7.5 μm, and the surface of the patterns is very smooth. In addition, the patterns formed have the shape of a convex lens and each pattern has almost the same shape. We confirmed that the micropatterns shown in Fig. 5(c) also have the convex shape and the smooth surface with the average height of around 5 μm. Thus, it was found that higher patterns were obtainable from the process B under the present preparation conditions. However, it was difficult to obtain the micropatterns with the average height of more than 7.5 μm even in the process B. When the amount of the particles deposited on the whole area of the substrate (film thickness) was increased, the micropatterning of the $BnSiO_{3/2}$ thick films was difficult; a part of the $BnSiO_{3/2}$ liquids pooled without separating into each pattern by a heat treatment to form convex-shaped micropatterns.

According to our previous paper [24], convex-shaped particulate films were formed only on the hydrophilic areas before a heat treatment, when the particles were selectively deposited on the hydrophilic areas. We also demonstrated that the average height of the convex-shaped micropatterns formed through a heat treatment was increased with an increase in the amount of the particles deposited on the hydrophilic areas, when the particles were electrophoretically deposited only on the hydrophilic areas. Based on the previous report, in the process A, the average height of the convex-shaped micropatterns should be increased with increasing the amount of the particles deposited on the hydrophilic areas. However, in the present study, the particles on the hydrophobic areas remained after withdrawing the substrate from the sol, when many particles were electrophoretically deposited on the whole area of the substrates in the sol, as shown in the process B. It is necessary that the largest number of particles is selectively deposited on the hydrophilic areas to obtain the micropatterns with high aspect ratio by controlling the experimental conditions: conditions of electrophoretic de-

position and concentrations of the sols for electrophoretic deposition.

Two types of micropatterning techniques described in this study are suitable for the production of convex-shaped micropatterns with a curved surface such as a quasi-spherical shape, which is very difficult to produce by other processes such as embossing and photolithographic techniques.

Conclusions

Convex-shaped $BnSiO_{3/2}$ micropatterns with high transparency were fabricated only on the hydrophilic areas by the electrophoretic deposition of the $BnSiO_{3/2}$ particles on ITO-coated substrates with the hydrophobic-hydrophilic patterns and subsequent heating above T_g of the particles. It was found that the control of electrophoretic deposition conditions, in which the amounts of the particles deposited on the substrates were changed, led to the two types of micropatterning processes of the $BnSiO_{3/2}$ thick films. In the first process, where the $BnSiO_{3/2}$ particles were selectively deposited on the hydrophilic areas by the electrophoretic deposition, hydrophobic-hydrophilic patterns played two roles. One was the control of the adhesion between the $BnSiO_{3/2}$ particles and the surface of the substrates, and the other was the control of wettability of the $BnSiO_{3/2}$ liquid. In the second process, where the $BnSiO_{3/2}$ particles were electrophoretically deposited on the whole area of the ITO-coated substrates, the $BnSiO_{3/2}$ particles on the hydrophobic areas migrated toward the hydrophilic areas through a heat treatment above T_g of the particles. This migration was due to the difference in wettability for the $BnSiO_{3/2}$ liquid between the hydrophobic and hydrophilic surfaces. These patterning techniques, which provide microlens array, are applicable for the fabrication of micro-optical components.

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