Silica Nanoparticles Thin Film of Highly Ordered Hemisphere Macropores by Wet Coating

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ABSTRACT

Thin film of silica nanoparticles with highly ordered hemisphere macro pores was obtained by a spin coater and a capillary coater. The ordering factor of hemisphere macropores on silica thin films was 98% using spin coater by Voronoi polygon analysis. The pore size can be controlled by selecting the size of polystyrene Latex (PSL) spheres in the range of 50-1700nm. Furthermore we discuss the key to obtain highly ordered PSL spheres with less their boundaries. The employment of silica nanoparticles as a second particle enhances the mobility of PSL spheres. Its elastic repulsion and Brownian motion make it easy to reach the equilibrium structures that are highly ordered hexagonal packing during drying. After the mixture of PSL and silica nanoparticles was coated on a glass plate, the PSL were completely decomposed at a temperature of approximately 400°C for 10-15 minutes. The thin film can be used as a substrate for patterning by its shape, or an anti-reflection film by its optical property.

KEYWORD

Macropore, Self-organization, Spin Coater, Capillary Coater, Silica Particles, Polystyrene Spheres, Voronoi Polygon Analysis,

INTRODUCTION

Self-organization is a pattern formation of built-up, and it is extremely useful technique for mass production using nanotechnology. Macropatterned thin films have received increased interest in the past few years for use in chemistry and life science. They have become of interest for microreactors, separation, sensing and optical application.

In a few years, periodic porous materials with highly ordered have been studied such as macroporous silica thin film (Subramanian, et al., 1999, Meng, et al., 2000, Velev, et al., 2000, Iskandar, et al., 2003), mesoporous silica (Beck, et al., 1992, Zhao, et al., 1998) and anodic porous alumina (Masuda, et al., 1995, Masuda, et al., 1997). The macroporous silica thin film, which has three-dimensional structure, has been produced by a dip coater before removing a template. The mesoporous silica has been produced using low-cost commercially available polymer by dip-coater. An anodic porous alumina has been initiated by the textured pattern of the surface made by the molding process, and the growth of an almost defect–free channel array could be achieved throughout the textured area. Figure 1. shows SEM images of previous studies for materials with highly ordered pores.

The macroporous silica thin film in the previous studies, however, needs a lot of time to fabricate
in small area. Furthermore, it has been difficult to arrange the hemisphere macropores on substrates. Therefore our objectives are to produce thin films with highly ordered pores by high speed wet coating over large surface area. Our thin film is fabricated in wide area by employing a spin coating that is simple, fast and commercially available wet coating process. Our concepts are to produce an inorganic thin film two-dimensional arrangement of macropores by removing the organic particles, to employing a simple and fast process for industry, and to utilize inorganic single nanoparticles in order to arrange organic particles regularly.

Figure 1. SEM images of previous studies for materials with highly ordered pores.
(a) Macroporous silica thin film (Meng, et al., 2000), (b) mesoporous silica (Zhao, et al., 1998) and (c) anodic porous alumina (Masuda, et al., 1997).

In this research, we chose polystyrene latex (PSL) spheres and silica nanoparticles, since the PSL spheres can be removed easily by calcinations and silica nanoparticles have ultra-low dielectric property and size effect. The availability of PSL in various particle sizes permits the control of pore size by selecting a PSL with a specific particle size.

For the evaluation of self-organized arrangement, it is necessary to relay on statistical consideration. It is important not only to view images of SEM or AFM, but also to indicate as a numerical value. Segmentation data of openings of pores are evaluated by Voronoi diagram analysis, which have
been analyzed point patterns (Donna, et al., 1999, Michael, et al., 2000). In this statistical analysis, the ratio of hexagons in all polygons, which is ordering factor; \( OF_{\text{polygon}} \), is defined as the quantitative evaluation of hexagonal closed-packed structures, and the average deviation of all hexagon angles from 120 degree, which is ordering factor; \( OF_{\text{angle}} \), is also defined as the qualitative evaluation of hexagonal closed-packed structures. We also show the mechanism for the self-organization of PSL spheres in the run-up to making the hemisphere pores. The silica nanoparticles are essential for the closed packed arrangement of PSL spheres. The size effect of silica particles enhances the arrangement of PSL spheres. The simplicity of controlling the morphology as well as the pore sizes of the materials is one of the key factors for the development of several applications. This thin film is applicable to an ultra-low dielectric thin film, an ultra low index thin film and a photonic filter by its physical property. And this is also applicable to a template for assembling particles and to a microreactor by its shape of the surface.

**EXPERIMENTAL**

**Film preparation by spin coater**

The mixed suspensions of PSL spheres (average diameter; 100-1000nm) and silica nanoparticles were prepared within the range from 0.1 to 1.0 wt%. The glass plates (15mm \( \times \) 0.3mm) were used as substrates. The zeta potentials of two kinds of suspensions were measured by zeta potential analyzer (LEZA-600S, Otsuka Electronics Co., Ltd.). The suspensions were put onto the glass substrates and rotated at 3000 r.p.m. by a spin coater (ACT-300D, Active Co., Ltd.). Finally, the thin films consisted by two kinds of particles were calcinated at 450 degree Celsius for 10 minutes by a muffle furnace (KDF S-70, DENKEN Co., Ltd.)

**Film preparation by capillary coater**

The mixed suspensions of PSL spheres (average diameter; 200-500nm) and silica nanoparticles were prepared within the range from 1.0 to 10 wt%. The glass plates (100 x 100 x 1.8mm) were used as substrates. The suspensions were put onto the glass substrates and coated at 10-100cm/min by a capillary coater (CAP Coater III, HIRANO TECHSEED CO., Ltd.). Finally, the thin films consisted by two kinds of particles were calcinated at 450 degree Celsius for 15 minutes by a muffle furnace (KDF S-70, DENKEN Co., Ltd.). Figure 2. and figure 3. show a photograph and a schematic feature of a capillary coater, respectively.

![Figure 2. Photograph of a capillary coater.](image)

![Figure 3. Schematic feature of a capillary coater.](image)
Observation and evaluation of surface morphology

The self-organization of macro pores on the substrate were evaluated by a scanning electron microscope (SEM: JSM-6340F, JEOL CO., Ltd.). The center positions of pores in each SEM image were determined by a computer image processing using a commercially available program (WinRoof; Mitani Corp.). The quantitative evaluation of organization could be carried out by characterizing the shape of the polygons that constitute the Voronoi diagram.

RESULT AND DISCUSSION

Observation of surface morphology

The macroporous silica thin films were fabricated using different size of PSL spheres with 5nm silica nanoparticles. The silica thin films with well-ordered macro pores were fabricated by the spin coater and the capillary coater. Although there are a few defects on the surface, the silica thin films with hexagonal closed-packed macro pores can be obtained. The silica thin films, which were obtained, have the high coverage of pores and the large boundarys of hexagonal packed self-organization of PSL spheres. Many kind of diameters of hemisphere pores can be obtained by selecting the PSL spheres, which are commercial available in the range of 50-1700nm. It is applicable to ultra-low dielectric thin film, ultra-low index thin film, photonic filter, template for patterning and microreactor.

Evaluation of surface morphology

The Voronoi polygon analysis was carried out for evaluating the regularity of pores quantitatively. Each Voronoi polygon is generated from the intersection of perpendicular bisectors of the line segments connecting any center of gravity to all its nearest neighbors. The ratio of hexagons in all polygons, that is ordering factor; $OF_{\text{polygon}}$ (1) as follows, is defined as the quantitative evaluation of hexagonal closed-packed structures.

Ordering factor for polygon : $OF_{\text{polygon}}$

$$OF_{\text{polygon}} = \frac{\text{the number of all hexagons}}{\text{the number of all polygons}} \quad (1)$$

Next the average deviation of all polygon angles from 120 degree, that is ordering factor; $OF_{\text{angle}}$ (2) as follows, is also defined as the qualitative evaluation of hexagonal closed-packed structures.

Ordering factor for angle : $OF_{\text{angle}}$

$$OF_{\text{angle}} = \frac{\sum_{i=1}^{n} \theta_i - \theta_{\text{hcp}}}{180} \quad (2)$$

$\theta_i$: Each angle of Voronoi polygon, $\theta_{\text{hcp}}$: One angle of regular polygon, n: The number of all polygons constructed by the Voronoi polygon analysis
When all pores arrange under the ideal case of hexagonal closed-packed structure, the quantitative parameter; \( OF_{\text{polygon}} \) and the qualitative parameter; \( OF_{\text{angle}} \) are 1. The macroporous silica thin film was evaluated by the Voronoi polygon analysis, which was prepared by the concentrations of Silica particles; 0.25wt% and PSL; 0.5wt% and the diameters of silica particles; 5nm and PSL spheres; 506nm. In a well-ordered area of the thin film, \( OF_{\text{angle}} \) analyzed by Voronoi diagram is 0.98. The result of the parameter indicates that almost all pores are arranged under hexagonal closed-packed structure. Furthermore \( OF_{\text{angle}} \) analyzed by Voronoi diagram is 0.99. It is indicated that the average deviation of all hexagon angles from 120 degree is 1.5 degree. As the result almost all pores are arranged under regular hexagonal structure.

**Mechanism of the self-organization**

Our previous study shows the highest limits of coverage by single particle monolayer films fabricated by an evaporation-induced self-assembly method (Okubo, et al., 2003). Compared with the result, this work, which was used by two kinds of particles, achieved higher packing level than the previous study. Therefore, we consider the mechanism of the arrangement of PLS with silica nanoparticles. In order to investigate the effect of silica nanoparticles as the second particle, PSL spheres were fabricated with and without silica nanoparticles. It was found that the boundaries of PSL spheres without silica nanoparticles are smaller than those of the hexagonal packed PSL spheres under the existence of silica. Zeta potential of PSL and silica dispersions measured by laser electrophoresis zeta-potential analyzer were \(-42\text{mV}\) and \(-30\text{mV}\), respectively. The Zeta potentials are high enough to prevent the aggregation of both particles of silica and PSL. But the Zeta potential of PSL is not enough to arrange to hexagonal packing by electric repulsive force only.

The macroporous silica thin films, which were prepared using various sizes of silica nanoparticles with the PSL particle size fixed at 458nm. The more the size of silica particles increased, the more hexagonal closed-packed pores disordered under these experimental conditions. It is indicated that the high mobility of silica nanoparticles due to the Brownian motion would enhance the self-organization of PSL spheres.

Furthermore, the PSL spheres keep the distance each other: it is because elastic repulsion by silica nanoparticles causes this fabrication. Under drying process, PSL spheres are gathered by capillary attraction force. In PSL without silica nanoparticles case, during water evaporating, the PSL spheres can’t form the closed-packed arrangement before their collision, since the electric repulsive force is considerably weaker than capillary attraction force. After the collision, the friction force of the PSL surface is strong. Therefore, the PSL spheres can’t rearrange hexagonal packing. When nano-sized silica particles as second particles exist in the PSL solution, a different phenomenon occurs in PSL with silica nanoparticles case. First PSL spheres are also governed by capillary attraction force and gathered each other. However, the existence of silica nanoparticles prevents the collision between PSL spheres by the elastic repulsive force of silica nanoparticles. It is indicated that, immediately before the collision, the elastic repulsive force of silica nanoparticles gives the chance for the self-organization to PSL spheres. The silica nanoparticles thus play an important role in the arrangement.

**CONCLUSIONS**

We showed the simple and rapid process for producing the silica thin film with hexagonal packed hemisphere macropores on the glass substrate. In this process, the pore size is controllable by selecting the size of PSL spheres. The Voronoi Polygon Analysis was employed for the evaluation of pore arrangement. The results of \( OF_{\text{polygon}} \) and \( OF_{\text{angle}} \) are 0.98 and 0.99 respectively so that the macro
pores arranged highly ordered. Analyzing the mechanism of arrangement by two kinds of particles, it was found that the existence of silica nanoparticles enhances the high ordering from 89% to 98%. The elastic repulsive force by silica nanoparticles functions between PSL spheres under the drying process, and PSL spheres are arranged to the closed-packing structure by their Brownian motion under the prevention of the collision.

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