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Preparation of three-dimensional photonic crystal using self-assembled silica colloid

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Abstract

In this paper, we focused on the fabrication of a opal-type photonic crystal from monodispersed SiO_2 nano-spheres. Sol-gel derived colloidal solution of SiO_2 nano-spheres with average diameter of about 300 nm were prepared by stöber method. At first, zeta potentials of colloidal solutions were measured to decide the optimum pH value for obtaining a well-dispersed colloidal solution. At second, suitable drying conditions of SiO_2 colloid particles on a glass substrate were investigated, where colloidal particles could arrange closely packed structures to form opal-type photonic crystals. The resultant samples were characterized by measuring the transmittance. As a result, transmittance drop at about 540 nm was observed to show the formation of the opal-type photonic crystals. This value is in good agreement with the result of calculation by using Bragg's law. From the results, it was concluded that self-assembled photonic crystals could be easily fabricated from colloidal solution of monodispersed SiO_2 by controlling the capillary force during drying on the substrate.

Key words: opal, photonic crystals, silica, capillary force

1. INTRODUCTION

Photonic crystals are the periodic arrays of dielectric materials, usually in a range from nanometer to micrometer scale. These dielectrics arrays exhibit photonic band gaps where the electromagnetic waves cannot propagate [1-3]. Potential of these structured materials for optical applications have motivated many investigations [4-6]. In order to fabricate 3D photonic crystals, semiconductor process technologies were mainly applied [7,8]. However, such technologies are not cost effective. On the other hand, it is difficult to fabricate long-range ordered photonic crystals by the cost effective method. One solution of this problem is opal-type photonic crystals made from monodispersed SiO_2 nano-spheres [9]. SiO_2 is low cost and ecological material. It is possible that monodispersed SiO_2 spheres with a few hundreds nm in diameter were stacked into a hexagonal or a cubic close-packed structure. Such close-packed structures can be formed by self-assembly from colloidal spheres if the solvent drying process were optimized [11]. In addition, tunable 3D photonic crystal was proposed in the recent years from this type of opal structures as template [12]. In the case of the tunable 3D photonic crystal, the second phase such as liquid crystal was infiltrated into cavities of opal-type photonic crystals.

This showed that if the optical property could be controlled by changing some parameters such as temperature and potential, further applications of photonic crystals could be expected. Therefore, final goal of this study is to fabricate tunable 3D photonic crystals from monodispersed SiO_2 nano-spheres and the other dielectric materials. For this purpose, we, at first, investigated the easy technique to fabricate long-range ordered opal-type photonic crystal from monodispersed SiO_2 nano-spheres.

2. Experimental methods

2.1 Synthesis of monodispersed SiO_2 colloid

Under the ambient pressure, ethanol of 14.2mol/l, distilled water of 4.5mol/l and ammonia of 0.93mol/l were mixed and stirred for 30 minutes at 30℃. In order to keep solution temperature constant, TEOS was warmed at 30℃. Then TEOS of 0.32mol/l were added to the solution, then stirred for 72 hours at 30℃. Size distribution and cumulant average diameter of SiO_2 particles were measured (Ohtuka Denshi, SELS-800Y) after 1h, 2h, 3h and 72h of TEOS addition.

2.2 Measurement of zeta potential

The thickness of the electrical double layer on the surface of colloidal particles in the solvent directly influences the dispersion state of the colloidal solution. If colloidal particles were aggregated, it is difficult to fabricate closely-packed structure. Therefore, we measured zeta-potential of the prepared colloidal solutions (Ohtuka Denshi, SELS-800Y).

2.3 Fabrication of opal-type photonic crystals

After starring for 72h, organic solvents of solutions were replaced with water to obtain the well-dispersed colloidal solutions by controlling the pH values of the solutions. The densities of colloidal solutions were 0.37vol% and 1.3×10^{14} particles/L.

Silica glass substrates were cleaned by acetone and distilled water and then irradiated by UV lights.

The cleaned glass substrates were settled in a vessel with a flow out hole horizontally and then colloidal solutions of 150ml were pored into the vessel. After that, the colloidal solutions were flowed out at the constant rate of about 20～30nL/minuts. Samples were dried for 1 night at room temperature in a desiccator, then samples heated at 400℃ for 1 hour to fix SiO_2 colloidal particles on glass substrate.

Micostructures of the resulting films of SiO_2 particles were observed by SEM (JEOL, JSM-5600).

3. Results and Discussions

3.1 Synthesis of silica colloids

Monodispersed SiO_2 nano-spheres were synthesized by the Stöber method [10]. Figures 1 showed time dependence of size distribution for synthesized colloids using dynamic light scattering method. From figures 1, formation reaction of monodispersed SiO_2 nano-spheres continued up to 2 h and the size distribution of the resultant monodispersed SiO_2 slightly changed, showing the formation mechanism of the monodispersed particles (uniform nucleation and following growth of the nuclei). To complete the formation reaction of monodispersed SiO_2, stirring and/or aging has been done up to 72 h, leading to the stable colloidal solutions. After the preparation of the monodispersed SiO_2 colloids, the solvent was changed from organic one to water by distillation using rotary evaporator.

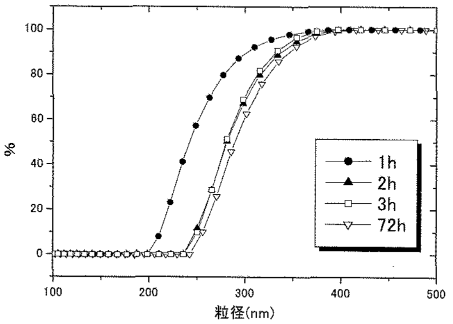


Fig.1 Particle size distribution of SiO_2 colloid particles

3.2 Zeta potential measurement of SiO_2 colloidal solutions

The pH values of solutions strongly affect the dispersion and aggregation of colloidal particles. Interaction of electrical double layer between colloidal particles has significant effect on the agglomeration behavior.

Figure 2 showed zeta potentials of SiO_2 colloidal solutions with different pH values. The point of zero charge (PZC) or isoelectric point for SiO_2 has been reported in the range pH=1.8～2.5[13]. However, the measured PZC value was slightly higher. This is ascribed to the aggregation of SiO_2 particles near the point of zero charge. The largest value of zeta potential was observed at about pH10. Therefore, we selected pH10; this condition was considered to give better dispersion state of the SiO_2 colloids. However, it could be considered that in the electrophoresis measurement at pH=12, zeta potential was so high that electrical double layer was deformed and particle motion was suppressed. In order to compare the pH effect, three colloidal solutions with pH=8, pH=10 or pH12 were prepared.

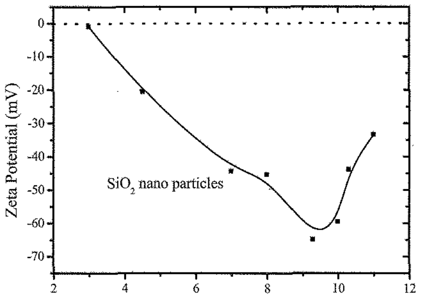
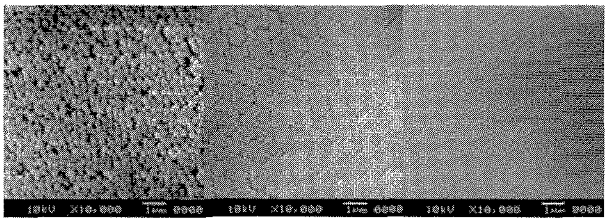


Fig.2 Change in Zeta potential for monodispersed SiO_2 with pH

3.3 Fabrication of photonic crystal using room temperature drying process

The clean glass substrate was soaked into the SiO_2 colloidal solutions and then the colloidal solution was flowed out from the vessel to fabricate the photonic crystals. Samples were dried for 1 night in the desiccator.

The packing structures of nanosphere colloids with different pH were shown in figure 3.



(a) pH8 (b) pH10 (c) pH12

Fig.3 SEM images of silica structures from colloidal solution of different pH

At pH10 conditions, hexagonal close-packed structure was observed. On the other hand, close-packed structure was not observed at pH8 condition as expected. Unexpectedly close-packed structure of SiO_2 particles was also attained at pH12 condition. The reason of the formed close-packed structure is not clear yet. One possible reason for this is that the condensation of siloxanes would be accelerated at higher pH of 12, leading to the change in the surface characteristics of the SiO_2 nano-spheres to attain the well-dispersed state. Another possible reason is that real electrostatic force at pH12 was larger than at pH10, so that close-packed structure was formed.

It was confirmed that close-packed structure was successfully fabricated by the room temperature drying process if the pH of the colloidal solution was adjusted at 10. However, hard coalescence of colloidal particles occurred to form coalescent silica grains hills on the substrate. It is impossible to fabricate uniform ordered photonic crystal through the large area.

Consequently, we started to improve the wettability in order to fabricate photonic crystals on the whole area of the substrate.

3.4 Influence of solvents and draying rates

It was impossible to fabricate wide–area ordered photonic crystals by the room temperature drying process in the previous section. Therefore, 2 different methods were attempted as flow;

(a) Optimization of solvent's surface tension

Water surface tension (72.8×10^{-3} N/m) is very high so that it seems to be difficult to wet the surface of the substrate uniformly by the silica colloidal solution through the wide-area. On the other hands, ethanol surface tension is low (22.0×10^{-3} N/m) so that it is expected to wet the surface of the glass substrate by the ethanol in a wide-area. Accordingly 3 types of solvents (water, ethanol and water:ethanol =1:1) were used to prepare the SiO_2 colloids to fabricate ordered structures through wide-area.

(b) Optimization of drying rate

The other method we tried was to control the drying rate of the solvents. It is well known that packing behavior of SiO_2 particles is influenced by the capillary force during evaporation of the solvent. Hence, we changed the drying temperature of solvents to control the capillary force during drying to fabricate ordered structure of wide-area. For this purpose, samples were heat-treated by using hot plate at 100 or 300℃ to evaporate the solvent immediately.

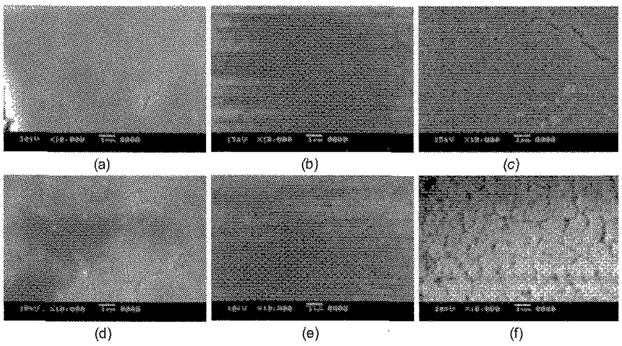

(a) (b) (c) (d) (e) (f)

Fig.4 Effect of solvent and drying temperature on the film structures of silica. (a) water solvent dried at 100℃, (b)water and ethanol mixed solvent dried at 100℃, (c)ethanol solvent dried at 100℃, (d)water solvent dried at 300℃, (e)water and ethanol mixed solvent dried at 300℃, (f)ethanol solvent dried at 300℃.

As a result, it was confirmed that formation of ordered silica layer with about 2×2cm area on a glass substrate. Figure 4 exhibited the SEM images of the SiO_2 layers on the substrate. It was observed that well ordered structures were formed in the order corresponding to water > water+ethanol > ethanol, showing that the effect of the surface tension had no effect on the formation of the ordered structure.

In the case of ethanol solvent, aggregation behavior of SiO_2 colloidal particles is controlled by electrical double layer similar to the case of water [14]. When same type of particles come closer and the region of counter ions overlaps with each other, then the repulsive force arises. On the other hand, the van der Walls attractive force will be occurred at the same time. Thickness of electrical double layer $1/\kappa$ is given by Eq. (1).

$$\frac{1}{\kappa^2}=\frac{\varepsilon_r\varepsilon_0 kT}{2nz^2e^2} \quad (1)$$

As far as the dielectric constant is large, thickness of electrical double layer $1/\kappa$ is large. Whereas the dielectric constant of water is 80.4 and that of ethanol is 24.1, thickness of the electrical double layer is thinner for the case of ethanol solvent so that aggregation of SiO_2 particles easily occurred in the case of the ethanol solvent. This aggregation significantly affected on the packing behavior of the SiO_2 particles.

In the thin wetting film formed just before the solvent evaporation from the film surface, some interactions acts between the particles [15]. In such a system of particles, contact angle of the particles should be same and the interaction between particles is always attractive force to form a self-assembled structure of the particles. Capillary force **f** between the particles is given by Eq. (2)

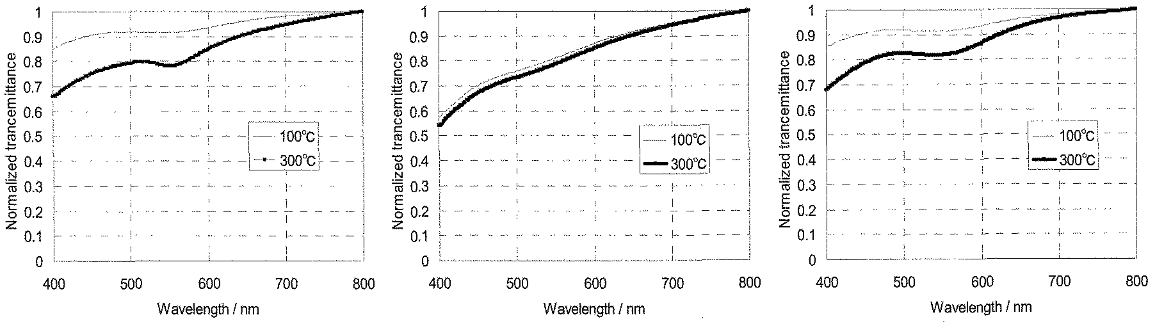
$$f=\frac{2\pi r Q^2}{L} \quad (2)$$

Q is capillary charge and given by Eq. (3)

$$Q=r_c\sin\psi \quad (3)$$

r is interface tension, **L** the distance of particle's center, $\mathbf{r_c}$ the radius where boundary of liquid interface intercepts the particle, **Ψ** interface angle. For the case of the ethanol solvent, thickness of double layer is thin. Therefore, partial aggregation of SiO_2 particles occurred during drying of the colloidal solution. In accumulation process of the particles, L value would be large because of the aggregation, leading to the lower capillary force for the case of the ethanol solvent than that for water solvent. This ascribed to the difficulty in forming the close-packed structure for the case of the ethanol solvent.

These results suggest that the capillary force is more important than wettability of the solvent with substrate to fabricate the closed-packed structure of the monodispersed particles.



(a) (b) (c)

Fig.5 Transmittance of silica structure using 3 type solvents and 2 type dried temperature. Solvent is (a)water, (b)water and ethanol, (c)ethanol

3.5 Observation of the photonic band gap

Light transmittance behavior of the prepared samples was measured and shown in figure 5. Samples prepared from water solvent exhibited obvious transmittance drop at around 540nm. On the other hand, transmittance drop for the samples prepared from ethanol was not clear. In addition, it was demonstrated that transmittance drop was larger for the samples with higher drying temperature of 300℃ in all cases.

3.6 Photonic band gap calculation by using Bragg's equation

It is known that opal-type photonic crystal diffracts light according to Bragg equation [16].

$$m\lambda = 2d_{hkl}\left(n_e^2 - \sin^2\theta\right)^{1/2} \qquad (4)$$

where m is order of diffraction, λ the wavelength at the position of diffraction peak, d_{hkl} the distance between (hkl) lattice planes, n_e the effective refractive index of crystalline assembly, and θ the angle between the plane of interest and the incident light. As given by Eq. (4), λ is determined by the lattice spacing and the effective refractive index. If the hexagonal close-packed structure was postulated in this study, then the lattice spacing and effective refractive index were given by Eq. (5).

$$d_{111} = (2/3)^{1/2} D = 204 \quad [nm]$$

$$\upsilon_{SiO_2}\frac{n_{SiO2}^2 - n_e^2}{n_{SiO2}^2 + 5n_e^2} + \upsilon_{air}\frac{n_{air}^2 - n_e^2}{n_{air}^2 + 5n_e^2} = 0 \qquad (5)$$

$$\therefore n_e = 1.33$$

Substitute $m=1$ and $\theta = 0$, then $\lambda = 541\,nm$ is obtained from Eq.(4). This value is in good agreement with the frequency of the transmittance drop in figure 7.

Therefore, we concluded that transmittance drop in figure 7 is ascribed to the photonic band gap of opal-type photonic crystals.

4. Conclusions

Sol-gel derived colloid particles of SiO$_2$ nano-spheres with ca 300 nm in diameter were prepared by stöber method. In order to prepare well-dispersed monodispersed SiO$_2$ colloid, pH value of colloidal solution was adjusted. In addition, drying rate of the solvent was controlled to fabricate closely-packed SiO$_2$ structure with wide-area of about 2×2 cm. The transmittance measurement demonstrated that transmittance drop was clearly obserbed at about 540nm and the frequency is in good agreement with the calculation result of Bragg equation. Therefore, it was concluded that opal-type photonic crystal was fabricated from colloidal solution of monodispersed SiO$_2$ by controlling the drying temperature or capillary force.

The result demonstrated that it the control of the capillary force was essential for the easy fabrication of photonic crystal from SiO$_2$ colloidal solution by a cost effective method.

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