Fabrication of Highly Qualified Opal Film with Controlled Thickness

Dong Hun Shin*, Bo Hyun Sung, Mi Jung Im, and Ung Su Choi†

Tribology Research Center, Korea Institute of Science and Technology, Seoul 136-791, Korea
*Department of Chemical and Biological Engineering, Korea University, Seoul 136-701, Korea

Received March 3, 2005; Accepted April 21, 2005

Abstract: Stable dispersions of monodisperse colloidal PS spheres of submicron-size have been synthesized according to a general emulsion polymerization procedure for PBG crystals. The size of the PS spheres can be controlled by the amounts of surfactant and monomer. The periodically ordered three-dimensional porous structure having submicron PS spheres was obtained using a precisely controlled withdrawing method in which the fabrication of the template and the infiltration of the voids of the template are controlled by the related experimental parameters for the assembly, including the temperature, concentrations, and withdrawing speed. SEM (scanning electron microscope) images and transmission spectra of the samples show that these films have a highly ordered three-dimensional structure. The transmission spectra of the films, obtained upon changing the incident angle, favorably coincided with results calculated using the Bragg and Snell law.

Keywords: PBG crystals, withdrawing method, monodisperse PS, inverse opal

Introduction

Ever since three-dimensional (3-D) photonic crystals (PCs) were first proposed by Yablonovich and John [1] there has been much activity across a wide range of scientific disciplines in an attempt to synthesize and investigate the structure/property relationships in this new category of functional materials [2]. The key property of a PC is the presence of a photonic band gap (PBG). The PBG arises from a periodic modulation of the dielectric function in at least one crystallographic direction [3]. If the modulation of the dielectric function occurs in all directions in the crystal, a 3-D PBG will be fabricated [4].

The search for 3-D PCs that could potentially exhibit a PBG at visible wavelengths focused initially on the gemstone opal. Opal is a crystallloid composed of a face-centered cubic (fcc) array of mono-sized, hydrated, amorphous silica spheres [7]. There are many techniques used in the formation of synthetic opals from colloidal dispersions of mono-sized spheres, including sedimentation, centrifugation, sedimentation electrophoresis, and controlled vertical drying [8]. Although colloidal self-assembly is used widely for the formation of thin-film photonic crystals, the factors influencing the growth process and the optimum conditions for the growth of large crystals that have a low defect densities do not appear to have been investigated systematically. It can be anticipated that many of the factors influencing the growth process will not be independent; understanding the interactions between these variables is critical.

Consequently, the comparison of results presented by different research groups is often problematic [9-12]. In addition, the lack of a consistent method for measuring film quality (e.g., defect density or domain size) for these materials makes it difficult to fully utilize the results that have been reported in the literature.

In this paper, the results of a systematic study of the factors influencing the controlled fabrication technique are reported. The factors chosen for investigation in this study were the temperature, withdrawing speed, sphere diameter, and colloidal concentration. The colloidal crystals reported herein were assembled from polystyrene spheres in aqueous solution and have been characterized using a range of UV-vis spectroscopy and SEM (scanning electron microscope) techniques.

† To whom all correspondence should be addressed.
(e-mail: uschoi@kist.re.kr)
**Experimental**

**Colloidal Synthesis**
Styrene (bp 145 ~ 146 °C, 99 %, Aldrich) was distilled at reduced pressure to remove traces of the inhibitor 4-tert-butylcatechol (bp 285 ~ 286 °C). After distillation, the monomer was stored in the refrigerator, in amber bottles and under a nitrogen atmosphere, until required. Colloidal polystyrene (PS) spheres were synthesized by emulsion polymerization using a free radical initiator (potassium persulfate, K₂S₂O₈, 99 %, Aldrich) [13]. The polymerization was performed in aqueous solution at 70 °C for 7 h under a nitrogen atmosphere. The reaction mixture was agitated using a twin-paddled overhead stirrer operating at 350 rpm. Variation of the mean diameter can be achieved by alteration of the reagent concentrations, reaction time, and amount of surfactant [sodium dodecyl sulfate (SDS)]. The diameter of the colloidal spheres was determined using a scanning electron microscope (FE-SEM, HITACHI S-4200) and a dynamic light scattering instrument (DLS, Malvern Zetasizer 3000).

**Substrate Treatment**
The slide glasses and cover glasses (Marienfeld) used for the experiment were first treated overnight with a solution (piranha) containing 30 % hydrogen peroxide and 70 % sulfuric acid. The glass substrates were then rinsed with deionized water and dried under a flow of dry air or nitrogen gas. The glass substrates obtained after treatment are hydrophilic. The contact angle of water on the substrates was measured to be 0°.

**Fabrication of 3-D PBG Crystal Film and Characterization**
Scheme 1.1 depicts the approach used for fabrication of the colloidal crystal film. First, a suspension of the particles was diluted to a definite concentration using deionized water. A hydrophilic glass substrate was then immersed vertically into the dispersion and lifted up at a constant speed (0.1 ~ 50 μm/s), which was precisely contro-trolled by a motor. The temperature for the experiment was set between 25 and 60 °C. The film thickness was determined by using SEM or a thin-film measurement system. The samples for SEM observation were scraped by using a sharp razor blade and then sputtered with thin gold films. The SEM was also used to observe the particle arrangement in the colloidal crystal films. Because SEM can obtain information only about the surface of the colloidal crystal films, a microscope was used to observe the 3-D crystal structure. The images were recorded using a CCD camera.

**Fabrication of Inverse Opal**
To infiltrate the interstitial space of the opals with TiO₂, we used liquid precursors consisting of mixtures of titanium(IV) ethoxide (TET, 98 %, Aldrich) and ethanol, in proportions ranging from 20 to 100 vol% TET. The end of the assembled opal was immersed into the liquid precursor solution to fill the voids between the spheres through capillary forces. Typically, infiltration of an opal took ca. 30 min. After infiltration, the precursor reacts with water from the air for ca. 24 hr. To obtain inverse opals of TiO₂, infiltrated opal was immersed into toluene for extraction.

**Results and Discussion**

**Synthesized PS Sphere Size by DLS and SEM**
The major components of this process include a monomer, a dispersion medium (in most cases, water), an emulsifier (surfactant), and an initiator (usually water-soluble). The monomer is dispersed as an aqueous emulsion (~1 ± 100 nm in diameter) with the help of the emulsifier. According to the proposed mechanism, most surfactant molecules exist as micelles (~10 nm in diameter), and the majority of these micelles were swollen by the monomer. The formation of polymer latexes begins with the decomposition of the water-soluble initiator during which a burst of primary free radicals are gen-
erated. These radicals polymerize the small amount of monomer that is dissolved in the aqueous phase to form the nuclei oligomers in the form of tiny particles. These nuclei subsequently enter the micelles and eventually grow into larger particles until all of the monomer dissolved in each micelle was consumed. At the same time, the monomer encapsulated in the emulsion droplets acts as a reservoir to provide a supply of repeating units to the growing polymer chains through diffusion. The growth of polymer latexes will stop at the point when all of the monomer has been depleted [13].

Monodisperse PS was synthesized in sizes ranging from 75 to 300 nm by changing the amount of surfactant. Standard deviation increased slightly in proportion to the PS sphere size, as shown Figure 1.

**Temperature**

The growth temperature was the most significant parameter studied. The growth temperature affects the thin film formed in a number of ways. The first effect observed is that an increase in domain size occurred upon increasing the temperature, as measured by SEM. At 25 °C the domains are, in general, less than 50 μm in any direction. This distance increases to 50–100 μm at 40 °C;

<table>
<thead>
<tr>
<th>SLS (g)</th>
<th>0.1</th>
<th>0.13</th>
<th>0.15</th>
<th>0.2</th>
<th>0.25</th>
<th>0.3</th>
<th>0.35</th>
<th>0.4</th>
<th>0.5</th>
</tr>
</thead>
<tbody>
<tr>
<td>DLS (nm)</td>
<td>302</td>
<td>258</td>
<td>227</td>
<td>201</td>
<td>180</td>
<td>169</td>
<td>130</td>
<td>117</td>
<td>75</td>
</tr>
<tr>
<td>SEM (nm)</td>
<td>300</td>
<td>252</td>
<td>230</td>
<td>200</td>
<td>184</td>
<td>165</td>
<td>134</td>
<td>110</td>
<td>74</td>
</tr>
</tbody>
</table>

**Figure 1.** Sizes of synthesized PS spheres as determined by DLS and SEM (polydispersity < 5 %; conditions: water, 200 g; KPS, 0.2 g; styrene, 20 g; 70 °C, 350 rpm).

**Figure 2.** Increasing growth temperature leads to a direct increase in the sizes of the domains produced, as shown in these SEM images that confirm that smaller cracks are not present and that the majority of cracking occurs during drying (scale marker 100 μm).
at 60 °C, domains of length 250 ~ 300 µm were obtained.

The optical micrographs shown in Figure 2 not only demonstrate the increase in domain size that occurs as the temperature increased but also suggest a change in the domain shape or direction of cracking. However, this finding is somewhat misleading; in fact, there is no change in the direction in which cracking occurs within these films. This result is established clearly when examining the SEM images for thin films grown at the three temperatures (Figure 3). It is apparent that, at all of the temperatures we investigated, the cracking always occurs along the close-packed <110> directions. At 25 °C the cracking is isotropic with crack widths of ca. 5 µm. At 40 °C, the SEM image (Figure 3) shows that the cracking is still isotropic, but the crack width is less uniform. In the sample grown at 60 °C, it is clear that while the cracks are still aligned along the close-packed <110> directions, the widths of the cracks are no longer uniform. Cracks that extend up to lengths of 1 mm are observed in the growth direction, i.e., perpendicular to the meniscus. These cracks are still typically ca. 5-µm wide. Analysis by SEM shows that the cracks, which in Figure 2 appear to be parallel to the growth front, are in fact narrow cracks (<1 µm) that alternate between two of the close-packed directions (Figure 3).

This finding confirms that the crystallographic orientation of the material is preserved regardless of the presence of drying cracks, which would indicate that the cracks occur after self-assembly and during the drying process. There is also a noticeable change in the adhesion of the films to the substrate as the temperature is changed. At higher temperatures, the films appear to be bonded more “strongly” to the substrate and the films do not appear to flake or delaminate on manipulation of the samples. The crystallinity of the PS opal structure decreased at higher temperature as a result of the rapid evaporation rate.

It has been reported that upon increasing the growth temperature, the evaporation rate increases and there is a greater influx of colloidal spheres into the meniscus region, with no net change in sample thickness [9].

**Control of Film Thickness**

The film thickness of the colloidal crystal films can be controlled by changing either the particle concentration or the lifting speed. In Figure 4, cross-sectional images of the colloidal crystal films fabricated under different conditions are exhibited. Figure 4(a) present the film fabricated at a lifting speed of 0.2 µm/s using a suspension containing 1.5 % (v/vo) of particles. Under these conditions, a film having a thickness of 15 layers was derived. Figure 4(b) shows a film fabricated at a speed of 0.2 µm/s using a 3 % (v/vo) suspension. The thickness of the film is 31 layers. Film thickness is apparently a function of both the concentration and the lifting speed.
Either of these two factors may be used to control the number of layers.

The detailed experimental results showing how the concentration and lifting speed affect the film thickness are shown in Figure 5. The volume fractions used for fabrication were varied from 0.1 to 20% (v/v0). Each different suspension was used to fabricate films at five different lifting speeds, varying from 0.1 to 5 μm/s. From this graph, we observe that in the concentration region between 0.1 and 5% (v/v0), the film thickness increases linearly upon increasing the volume fraction. The theoretical relationship between the thickness and the concentration [9] is given by

\[ k = \frac{j \cdot \beta \cdot L}{0.063 \cdot b \cdot (1 - \varphi)} \]

where k is the layer number, j is the growth rate of the film determined by the lifting speed, \( \varphi \) is the particle volume fraction, j is the solvent evaporation rate, d is the diameter of colloidal spheres, L is the meniscus height, and \( \beta \) is the ratio between the velocity of a particle in solution and the fluid velocity. A linear relationship between the film thickness and concentration is expected from this equation, which agrees with the experimental results. From these results, we also found that the slopes of the lines increased upon decreasing the lifting speed; this observation means that the film thickness is more sensitive to the concentration change at low lifting speeds.

**Observation of Arrayed Structure**

The morphologies of the colloidal crystal films were first observed by SEM. One typical low-magnification image, which gave information about the surface of the film over a wide area, is shown in Figure 6. The low-magnification images show that the flat surfaces of the films can extend over a very large region on which cracks exist. The distances between the cracks vary from 10 to 100 μm. This morphology is similar to that observed for films fabricated by other methods [2]. The appearance of the cracks is ascribed to the shrinkage of the spheres that occurs during the drying process. The arrangements of the spheres in the films were initially
observed from a high-magnification SEM image. A top-view image of the film is shown in Figure 7; an hexagonal arrangement of the spheres was observed almost everywhere, indicating that the spheres were arranged well in the planar layer. Apparently, the planar arrays pile up regularly from the substrate to the surface of the film. The results obtained from these SEM observations indicate that the spheres form a ccp structure in the films.

In the colloidal crystal films having the ccp structure, the planar arrays of spheres were originally thought to be arranged in ABCABC (face-centered cubic (fcc) structure), ABAB (hexagonal close-packed (hcp) structure), or randomly packed arrays. Theoretical calculations show that the energy differences between the three types of structures are small [14]. Although SEM images can give information only about the top surface or the vertical cross section, the structure of the PS sphere array can still be easily defined. A well-ordered face-centered cubic structure is constructed using this method. There is a significant difference that occurs upon changing the temperature.

**Optical Properties**

The high optical quality of the film can be judged by the naked eye. A uniformly brilliant color, that extends to centimeter dimensions, can be observed for all of the films whose stop bands exist in the visible range. Figure 8 shows photographs of colloidal crystal film that were taken upon changing the angle. The colors of the film change from yellow-orange to blue upon increasing the incident angle. Detailed information on the optical properties of the opal films was derived from measurements of the UV-vis spectra. The spectra show the transmission of the colloidal crystal film composed of 245-nm-diameter spheres. The relative stop bandwidth ($\Delta \lambda / \lambda_0$, where $\Delta \lambda$ is the width at half-maximum of the peak and $\lambda_0$ is the center wavelength of the peak) is ca. 7%. This value agrees approximately with the theoretically calculated result for an fcc crystal [15]. The peak positions in the spectra depend on the angle between the normal vector of the substrate and the detecting light; they shift to shorter wavelength upon increasing the detection angle. The spectra measured at different angles are given in Figure 8. The relationship between the peak position and the detecting angles is summarized in the
Figure 9. Transmission spectra of colloidal crystal films composed of polystyrene spheres as recorded upon changing the angle. The film was prepared using 5 % PS solutions [(a) 180 nm; (b) 245 nm] at a withdrawing speed of 0.2 μm/s. The light angles, 0°, 7°, 15°, 35°, 45°, and 50°, increase in the direction of the arrows.

Figure 10. SEM images of PS array, recorded after infiltration and extraction of the PS spheres. The fraction of alkoxide in the solvent was 30 % TET. (a) and (b): Inverse opal in the cracked opal spot. (c) and (d): Cracked inverse opal.
inset; it was fitted by the Bragg formula

$$\lambda_{\text{max}} = 1.633D(n_{\text{sphere}}f + n_{\text{void}}(1 - f))^{-2}\sin^2 \theta)^{1/2}$$

where D is the diameter of the sphere (in this case, 245 nm), $n_{\text{sphere}}$ and $n_{\text{void}}$ are the refractive indices of the spheres and voids, respectively (the values are 1.6 for polystyrene spheres and 1 for air voids), $V_{\text{sphere}}$ and $V_{\text{void}}$ are the volume fractions of the spheres and voids in the crystal (they are 0.74 and 0.26, respectively, in the fcc structure). Apparently, the experimental results agree well with the calculation.

Although the transmittance is was low as 40 % over a wide range, the stop band gap was significantly present at 405 ~ 420 nm (transmittance <0.5 %), as shown Figure 9(a). In comparison with the UV-vis spectra in Figure 8, the transmittance was double folded and $\lambda_{\text{max}}$ was shifted slightly (from 585 to 575 nm) in Figure 9(b), due to the film thickness, upon concentration of the PS spheres. All of the stop band gaps were shifted to shorter wavelength upon changing the incident angle, consistent with the Bragg formula written above.

This result supported our conclusion that the films possess well-crystallized fcc structures as determined previously from our SEM and microscopy observations.

**Inverse Opal**

The inverse opals easily meet the qualifications for PBG for crystals rather than those of rare opals, due to their cracking and low performance. Inverse opal structures containing air holes were prepared using the TiO$_2$ precursor. When the PS spheres were extracted using toluene, the holes arose, as shown in Figure 10(a).

**Conclusions**

We have demonstrated a withdrawing method performed under a controlled temperature for the fabrication of high-quality, uniform opal films. The film thickness is easily controlled by varying the particle concentration or the lifting speed. Basically, the withdrawing speed and concentration of PS spheres both affect the film quality and thickness. The spheres in the films fabricated using this method crystallize in the form of fcc structures. The single-crystal size can extend to the centimeter regime.

**References**