Fabrication of photonic opal structures on different support materials by convective evaporation

Delphine M Lebrun, Gunnar A Niklasson and Lars Österlund

Department of Engineering Sciences, The Ångström Laboratory, Uppsala University, P.O. Box 534, SE-75121 Uppsala, Sweden

E-mail: dele@angstrom.uu.se

Abstract. Photonic polystyrene (PS) opals with face-centered cubic structure were fabricated by convective evaporation. The influences of substrate and its physical properties, as well as deposition conditions were investigated. It is shown that the surface roughness must be less than about 30% of the bead diameter to form well-ordered opals, rendering substrates such as glass, ITO and quartz superior to thick Kapton, ordinary tape, thermal release semiconductor tape, plastic and hydrophilic plastic HHNW (Kemafoil). Periodic stripe-like structures were found to form perpendicular to the growth direction defined by the receding meniscus of the solution front when the PS concentration is lower than 1.0 w/v%. Finally, we present the principles and results of using soft sacrificial layer deposited on quartz substrates to fabricate free standing inverse opal structures.

1. Introduction
Artificial opals are self-assembled face-centered cubic (fcc) structures of spherically shaped beads, which show interesting applications as photonic band gap materials [1]. Inverse opals are photonic crystals consisting of fcc packed voids embedded in a high refractive index material matrix. [2-4], such structures have been used to enhance the efficiency of photocatalytic materials [5-7], and motivates further studies to improve the deposition process and the quality of the template opals [8-12].

Convective evaporation is a common method to make artificial opals [13; 14], and has been used to deposit square centimeters of polystyrene or silica beads. Polystyrene (PS) spheres are readily available in a wide range of sizes and can be deposited on a wide range of substrates. There is however several problems encountered during the deposition process to achieve well-ordered structures[15-17]. Even if the thickness can be controlled relatively well by the oven temperature and humidity as well as the solution concentration [14; 18; 19], it is not straightforward to obtain high quality opals. Due to the strainexerted on the PS beads as the liquid is evaporated from the wet structure, opals tend to crack during the drying process and therefore form millimeter-sized domains [20].

Until now only the hydrophilicity of the substrate has been identified to be a necessary criterion for successful opal ordering [19; 21-23], but in this paper we show that surface roughness is also
important. Further, we demonstrate the influence of PS concentration on the film morphology and show that too low concentration leads to strip-like structures with a periodicity of hundreds of micrometers. Finally, we show results of PS self-assembly of opal structures on soft sacrificial layers deposited on quartz substrates, which enables fabrication of free-standing opal structures which can reduce stress in the film upon drying thus facilitating larger domains of well-ordered structures.

2. Experimental

2.1 Materials

All chemicals were used as purchased. All bead suspensions were sonicated in an ultra-sonic bath for at least 30 minutes before use. Quartz (Ted Pella), glass (ThermoScientific), ITO (PGO), Kapton (GoodFellow), hydrophilic plastic HNW W (Kemafoil), Scotch tape (3M), and Revalpha thermal release tape (Nitto Americas) were used as substrates. Water based polystyrene (PS) suspensions were purchased from Polysciences and ThermoScientific. Ethanol 99% and Decon90 (Decon Laboratories Limited) were used as received. Decon90 contains potassium hydroxide and was used as detergent to clean substrates prior to experiments.

2.2 Sample preparation and characterization

Convective evaporation was employed to deposit polystyrene beads on the different substrates. PS solutions (typically 20 mL) were prepared by dilution in deionized water and subsequent ultrasonic. The concentrations are presented in units of w/v% defined according to equation 1 (taking into account the solution mass of PS):

\[
\frac{w}{v} = \frac{1}{1 - \frac{W_w}{\rho_w} + \frac{W_w}{\rho_{PS}}} ,
\]

where \(W_w\) is the weight ratio of (dry) polystyrene to latex, \(\rho_w\) is the density of water, and \(\rho_{PS}\) is the density of polystyrene.

A clean substrate was placed vertically inside the beaker containing the PS solution at a small angle against the wall of the beaker. The beaker was placed in a pre-heated oven (Memmert UFB400) held at 50°C for between 8 and 14 h depending on the total volume of the solution. After deposition the samples were sintered at 85°C for 1 h 30 min in an oven (Nabathern S17) to create a neck at the PS contact area, which increased the connectivity of the voids in the inverted structure.

Profilometry (Bruker Dektak XT) was used to characterize the surface roughness and the averaged deposition thickness of the sample. The force applied to the stylus was set as low as possible (9.8 mN), and the spatial resolution was approximately 0.33 m/point. From each profilometry trace, the root mean square (rms) surface roughness was extracted. All features above 1 m were removed from the data, since they derived from substrates dirtiness.

A Perkin Elmer Lambda900 spectrophotometer equipped with an integrating sphere was used for UV-Vis-NIR spectrophotometry measurements in the range between 200 nm and 800 nm. A step size of 1 nm was employed to scan the wavelength range, and a 5 mm diameter aperture was placed in front of the samples.

To estimate the position of the photonic bandgap peak position the Bragg-Snell law was used (see equations 2 and 3):

\[
\lambda = 2d_{hk}\left(n_{eff}^2 - \sin^2 \Theta \right)^{1/2} ,
\]

In the case that the close-packed (111) planes are parallel to the top interface, we have:
\[ d_{111} = D \sqrt{\frac{2}{3}}, \]  

where \( D \) is the lattice constant of the photonic crystal, \( d_{111} \) is the distance between bead planes, \( n_{\text{eff}} \) is the effective refractive index of the whole structure, and \( \theta \) is the angle of incidence.

3. Results and discussion

3.1 Influence of substrate surface roughness

To be able to fabricate opals, it has been long established that the surface of the substrate should be hydrophilic. We have tried different types of substrates, all cleaned with Decon90, which provide clean hydrophilic surfaces (contact angle close to zero). However, with similar experimental conditions (temperature, humidity and concentration), it was found to be impossible to fabricate well-ordered opals on several substrates used in this study, including thick Kapton, Scotch tape, and Revalpha thermal release tape, ordinary plastic and hydrophilic plastic HHNW W. Even though those substrates all are hydrophilic, none, or only a few samples, exhibited well-ordered opal fcc domains. In contrast, it was possible to deposit opals on quartz, indium tin oxide (ITO), thin Kapton film and glass, which were pre-treated with Decon90 to give them hydrophilic wetting properties. In all successful deposition experiments on these substrates, domains of extended fcc PS structures formed over the entire substrate.

To understand why the depositions failed for some substrates and were successful in other cases, we decided to look into the surface roughness of the substrates. Figure 1 shows the surface roughness (root mean square, rms, value) of the different substrates from profilometry measurements. It can be seen that quartz, ITO, and glass are smoother than the other substrates. From this study it seems that successful PS opal deposition is achieved for hydrophilic surfaces with surface roughness < 30% of bead diameter.

![Figure 1. Surface roughness (rms value) for the different substrates used in the present study.](image)

3.2 Formation of polystyrene stripe structures

The deposition of PS beads results in self-assembly of PS beads due to van der Waals interactions whereby PS beads assemble along the solution front. A consequence of this is that it is possible to obtain regularly spaced 15 to 30 layers thick PS ridges of self-assembled PS beads separated by troughs with no beads by using solutions with low concentrations (< 1.0 w/v%) on quartz, as
schematically shown in figure 2. These ridges cover the entire length of the solution front across the substrate, and are separated by bare substrate surfaces. On the bare surfaces PS beads have been depleted due to diffusion to complete the fcc structure on adjacent ridges, thus forming stripe-like structures on the substrate with intermittent fcc opal structures and bare substrate surfaces.

**Figure 2.** Schematic picture of the striped PS structure obtained at low PS concentration. The solution front is parallel to the stripes and it descends as the solution evaporates.

Figure 3 shows typical profilometry traces on quartz. The average peak-to-peak stripe periodicity for different PS diameters and solution concentrations is shown in figure 4. The formation of periodic stripe structures can be explained by the combination of limited supply of beads in the growth process in low concentrated solution with the evaporation mechanisms for self-assembly of beads [24; 25].

**Figure 3.** Selected profilometry traces for periodic opal stripe structures formed with 170 nm PS bead diameter and a PS concentration of 0.3 w/v%. 
Figure 4. Average stripe periodicity deduced from profilometry measurements for different PS concentrations and PS beads diameters. The stripe periodicity was determined by Fourier transform analysis of profilometry traces such as those shown in figure 3.

Transmission spectra of 170 nm bead diameter PS opals grown with different concentrations of PS (0.15, 0.3, and 0.6 w/v%) are shown in figure 5. A well-ordered opal will have a dip in the transmission spectrum at a certain wavelength due to the presence of a local photonic band gap [26].

Figure 5. Optical transmission spectra of opal structures formed from self-assembly of 170 nm diameter PS beads at different concentrations.

3.3 Template for fabrication of free-standing inverse opal structures

A possible method to fabricate free-standing opal structures is to grow self-assembled PS opals on a sacrificial layer. With this approach an open opal structure can be developed from the part of the opal which is lifted off from the sacrificial layer (figure 6). With appropriate thickness, we expect that stable, free standing inverse opals can be fabricated.

This approach may potentially alleviate the problem of capping the opal during ALD.

Two different types of sacrificial films were here tested on quartz substrates which then were used as surfaces for PS self-assembly, namely polymethyl methacrylate (PMMA) and photoresist (S1813) applied by spin-coating. Organized domains (yellow color) could be seen on most of the 1 μm thick photoresist film inter-mixed with regions of bare islands (light pink color).
Figure 6. Schematic picture showing the development of a free-standing inverse opal structure grown on a sacrificial template film: (a) infiltration of the fcc opal structure by e.g. atomic layer deposition, (b) removal of the sacrificial layer, and (c) inverse opal structure formed by removal of the embedded PS beads by calcination of solvents, facilitated by the open structure exposed by removal of the sacrificial layer.

In contrast, for the 200 nm thick PMMA film mainly bare substrate surfaces were visible (figure 7), with patches of organized domains (yellow color).

Figure 7. Photographs of opal structures formed on PMMA and photoresist films on quartz, as well as a bare quartz substrate. A PS solution concentration of 0.2 w/v% and a PS bead diameter of 200 nm were employed.

Figure 8 shows optical transmission spectra acquired from domains of self-assembled 200 nm PS beads on 200 nm thick PMMA films (PS concentrations 0.1 and 0.2 w/v%), and 1 μm thick photoresist films (PS concentration 0.2 w/v%), respectively, on quartz. Distinct transmission minima are clearly seen for opals grown on both PMMA and photoresist films, which show that photonic bandgaps form on both types of sacrificial films, albeit over larger surfaces area in the case of photoresist films. This indicates a way forward for easy fabrication of inverse opal structures, where embedded PS beads should be removed after infiltration of the voids in the fcc structure (by e.g. atomic layer deposition or sol-gel techniques), without having to apply etching steps to remove excess infiltration material which otherwise inevitably will cap the top of the opal structure (see figure 6).
4. Conclusions

Self-assembly of polystyrene spheres by means of convective evaporation is a viable method to fabricate photonic band gap opal structures. Here we show that in addition to substrate hydrophilicity also surface roughness is important to prepare well-ordered opals. If the substrate is hydrophilic and exhibits a rmssurface roughness < 30% of the bead diameter, an opal structure is obtained. All substrates with these desired characteristics can be used for opal fabrication regardless of substrate morphology and employing a wide range of different types of substrates. A good balance between evaporation rate (regulated via temperature and humidity) and bead concentration should be maintained to obtain substrates completely covered with an opal structure. If the concentration is too low, island growth of the opal leads to formation of opal stripes of beads regularly spaced on the substrate. Finally, we show that it is possible to fabricate well-ordered opal structures on sacrificial PMMA and photoresist films on quartz substrates, with well-developed photonic bandgaps. Our results indicate that more extended opal layers form on photoresist films compared with PMMA films. The latter results open up ways for easy fabrication of open opal structures, which allow for removal of embedded PS after fcc void infiltration, without having to apply etching steps.

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