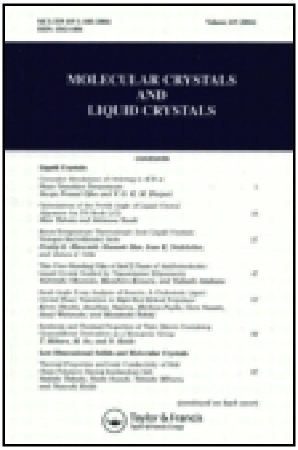

Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

Synthesis of Photonic Band Gap Materials

G. Subramaniam [a]

[a] Department of Chemistry, Penn State University, University Drive, Hazleton, Pennsylvania, USA

Version of record first published: 31 Aug 2006

To cite this article: G. Subramaniam (2005): Synthesis of Photonic Band Gap Materials, Molecular Crystals and Liquid Crystals, 435:1, 127/[787]-133/[793]

To link to this article: http://dx.doi.org/10.1080/15421400590955244

Mol. Cryst. Liq. Cryst., Vol. 435, pp. 127/[787]–133/[793], 2005
Copyright © Taylor & Francis Inc.
ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421400590955244

Synthesis of Photonic Band Gap Materials

G. Subramaniam
Department of Chemistry, Penn State University, University Drive,
Hazleton, Pennsylvania, USA

Non-absorbing, periodic, strongly scattering dielectric structures remove the path for propagation of light of certain frequencies, thus, creating a photonic band gap are known as Photonic Band Gap Materials, PBGM. Numerous methods are available to fabricate a 3-D PBGM, the photonic analog of electronic semi conductor. The method described involves the use of a silica template, infiltration of high refractive index or other materials of interest and removal of template. Template formation involves synthesis of monodispersed silica spheres followed by the self-assembly or electrophoretic deposition into close packed Face Centered Cubic (FCC) structure.

Keywords: electrophoretic assembly; photonic band gap materials, (PBGM); self-assembly; silica template

INTRODUCTION

The hallmarks of current century are miniaturization of devices and high-speed computation. Optical fibers can carry gigabits/second and replaced the slower electronic carriers; however, each of the network nodes requires electronic processing at the end. Transduction from photonics to electronics limits the performance and affordability of the network. One needs optical interconnections to enable high-speed data access and reliability. This will be possible only by optical confinement or by localization of light. Just like electrons are confined within the metallic wire and follow the path of the wire without leaking into the background in an electronic circuit, light needs to be confined and guided in a desired path without leakage into the background.

This work is funded by NASA and NSF grant. GS is grateful for NASA Faculty Fellowship and gratefully acknowledges Marshal space Flight Center for the use of their facilities.

Address correspondence to Girija Subramaniam, Deparment of Chemistry, Penn State University, 76 University Drive, Hazleton, PA 18202, USA. E-mail: sxg11@psu.edu

Research for materials to trap light has grown exponentially over the past decade. Logical deduction supported by theoretical calculations [1,2] suggests that the only way to trap light is to device/synthesize periodic array of non-absorbing and strongly scattering dielectric structures. Such structures prohibit light propagation over a band of frequencies, called Photonic Band Gap, PBG; this, in turn leads to localization of photons and inhibits spontaneous light emission [3–5]. These dielectric materials are referred to as the Photonic Band Gap Materials, PBGM, in general and as Photonic Crystals, PCs, if they are crystalline. PBGM can also reflect light for any direction of propagation over certain frequencies, which is being exploited in the creation of an all-optical integrated circuit [3]. Depending on whether the periodicity is in 1, 2 or 3 directions, these are classified as 1-D, 2-D and 3-D Photonic Crystals.

Very strong scattering requisite for PBG formation implies that the dielectric material should have a high refractive index and at the same time does not absorb in the region of interest. This, in turn, restricts the choice of materials that can be used in the synthesis/fabrication of PBGM. Commonly used materials are semiconductors like Si, Ge, InP, and GaAs etc.

FABRICATION OF PHOTONIC BAND GAP MATERIALS

Of the numerous varied fabrication methods used, the most commonly used are as follows: layer by layer fabrication, stacking layer by layer, lithography, electrochemical etching of the patterned substrate, two-photon lithography [6–10]. Most of these methods are applicable for small-scale fabrication. They are more involved and complex processes. Mass production of 3-D PCs can be achieved either by 2-photon holographic lithography [11] or from colloidal assemblies [12]. The simpler and easier way is colloidal self-assembly wherein colloidal spherical particles of silica or polymer spontaneously assemble into a face centered cubic (FCC) arrangement. Self-assembly is superior to the other lithographic methods because it is less complex and it can produce thicker materials; further just by changing the diameter of the dielectric spheres, PCs that are active anywhere from UV to Near IR region can be made. Dielectric spheres are usually made of silica or polymer.

PCS VIA SELF-ASSEMBLY

Self-assembly of silica spheres lead to a close packing arrangement known as Face Centered Cubic (FCC) packing, which is the Opal structure. Calculations and experiments show that these opal structures do not have a complete photonic band. However the inverse structures i.e. air spheres in high refractive index background dielectric material have a complete photonic band gap. The goal of this project is to make the inverse opal structure, a PBGM with complete gap. The strategies to inverse opals involve the following steps: Synthesis of Monodisperse silica spheres; Self-assembly in Face Centered Cubic (FCC) packing to form the opal template; Infiltration of the interstitial air gaps with high refractive index dielectric material; Removal of the template to form the inverse opal structure.

SYNTHESIS OF SILICA SPHERES

Highly Monodisperse silica spheres were obtained by Stober's process, by the ammonia-catalyzed hydrolysis of Tetraethoxysilane, TEOS [13].

$$\mathrm{Si(OC_2H_5)_4} + 2\ \mathrm{H_2O} \rightarrow \mathrm{SiO_2} + 4\ \mathrm{C_2H_5OH}$$

The Monodispersity and the size were confirmed by Dynamic Light Scattering experiment (Fig. 1) and by Scanning Electron Micrograph. Spheres of diameters 380, 480 and 1000 nm were synthesized.

METHODS OF SELF-ASSEMBLY

The most popular conventional method of crystallization of silica spheres is by sedimentation; it works well for heavy spheres, but is

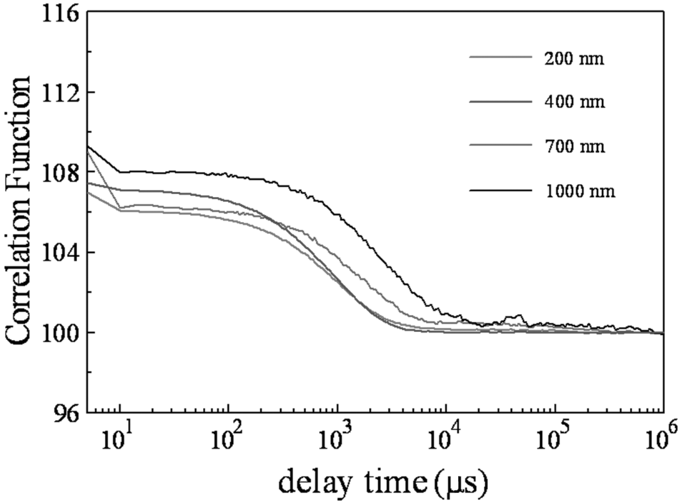

FIGURE 1 Dynamic light scattering correlation functions for silica spheres.

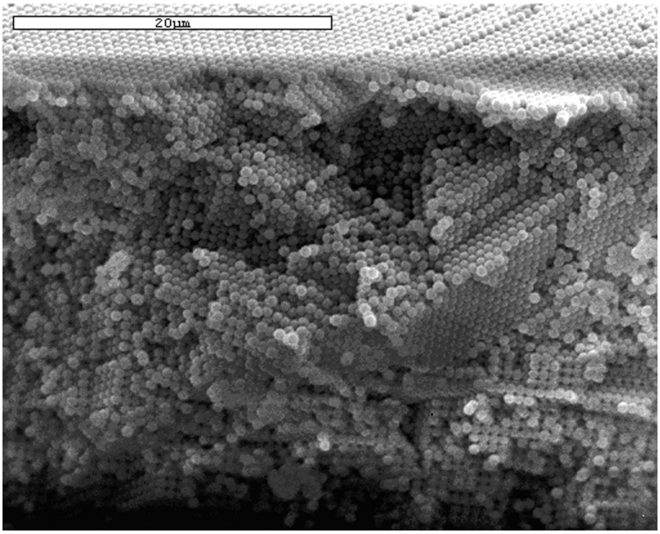

FIGURE 2 SEM picture of silica self-assembly at RT crystallization.

very time consuming. Other popular methods lead to polycrystalline material – structures incapable of being incorporated into a device and the presence of too many effects destroy the desired optical property. These defects were overcome by a technique of self-assembly that relies on capillary forces [14,12]. Our crystals were assembled using these methods and by the faster Electrophoretic methods [15].

The spheres were assembled on a cut silicon wafer substrate, from a 0.33% v/v ethanolic suspension. Opals grown by RT assembly are shown in Figure 2. The quality of the thicker deposits was amazingly uniform; but crystallization is slower. We used faster electrophoretic methods to assemble opals. The assembly from electrophoresis was also equally good as seen in the SEM image in Figure 3. The crystals were dried at 45–60°C and were sintered in an oven at 400°C for making them robust. However, cracking occurred due to solvent bubbling in a few samples as is illustrated in Figure 3.

OPTICAL DIFFRACTION OF OPAL TEMPLATE

The transmission spectrum of opal grown on glass-ITO anode is shown in Figure 4. The spectral position of the band is defined by the Bragg's Law, $\lambda = 2\ d\sqrt{n_{eff}^2}$ where d is the lattice parameter and $n_{eff}^2 = f_1 n_1^2 + f_2 n_2^2 + \cdots + f_n n_n^2$ with f_i and n_i represent the filling fractions of the different materials making the lattice and their refractive indices

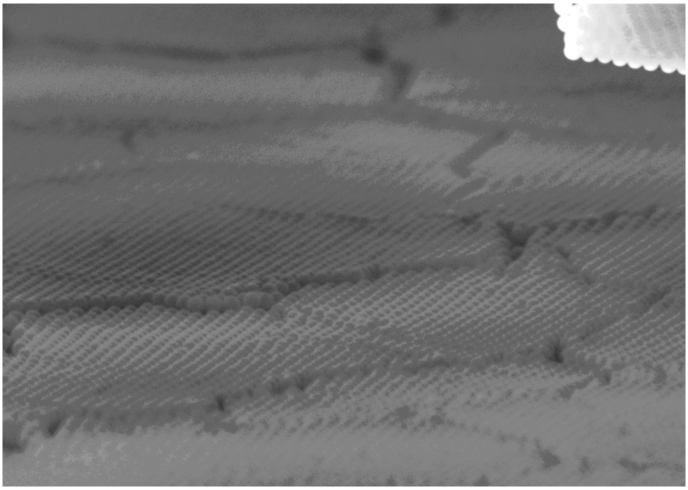

FIGURE 3 Electrophoretic assembly of silica spheres.

respectively. The value calculated for the dip in the transmission spectrum is 1052 nm, assuming refractive index of silica as 1.45 and the filling fraction as 0.74. The stop band gap occurs between 850–1050 nm with the dip around 950 nm.

INFILTRATION OF INTERSTITIAL SITES

The infiltration of silicon into the interstitial spaces was tried by sputtering technique. Sputtering was done for 2 hours at RT. The SEM

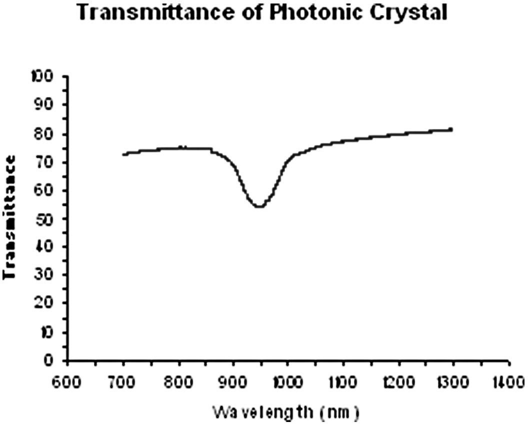

FIGURE 4 Transmission spectrum of silica opal.

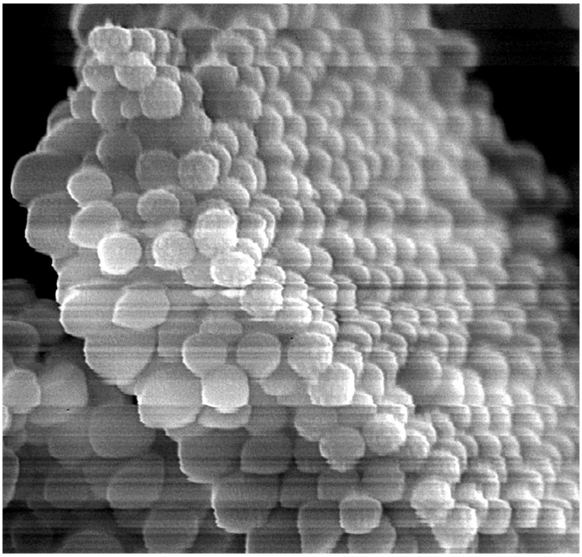

FIGURE 5 Silicon sputtered opal.

image of the sputtered template (Fig. 5) shows infiltration of silicon is not very uniform. Currently trials are underway to get uniform infiltration. Low Pressure Chemical Vapor Deposition (LPCVD) has been shown to infiltrate silicon all the way to the substrate [12] and the future efforts will be using LPCVD. Metal infiltration is also aimed at using the same technique.

In the photonic band gap the linear modes of propagation of light of certain frequencies is prohibited. So it is expected to enhance nonflinear properties. Efforts are underway to investigate monomeric and polymeric NLO materials inside these crystals.

EXPERIMENTAL

All the chemicals were purchased from Aldrich with 99.9% purity. TEOS was distilled before the synthesis. Absolute ethanol and water were filtered before use. Silica spheres were synthesized using Stober's method [13]. Room temperature Self-assembly was done using silicon as well as glass substrate, by dipping them in a beaker containing 0.33% v/v ethanolic sol. Electrophoretic assembly was carried out on ITO-glass electrode as described [15]. Size measurements were done using Zeta Pals (Brookhaven Instruments Corporation) and

SEM micrographs were obtained using JEOL JXA-8500/R instrument. Samples were coated with gold to prevent charging.

REFERENCES

[1] John, S. (1984). *Phys. Rev. Lett.*, *53*, 2169.
[2] Anderson, P. W. (1985). *Phil. Mag.*, *B52*, 505.
[3] John, S. (1987). *Phys. Rev. Lett.*, *58*, 2486.
[4] Yablonovitch, E. (1984). *Phys. Rev. Lett.*, *58*, 2059.
[5] Bykov, A. P. (1975). *Sov. J. Quant. Electron.*, *4*, 861.
[6] Qui, M. & Smith, H. (2002). *J. Vac. Sci. Technol. B, 20*(6), 2991.
[7] Aoki, K. *et al.* (2002). *Appl. Phys. Lett.*, *81*, 3172.
[8] Leonard, S. W., van Driel, H. M., Bimer, A., gosele, U., & Villeneuve, P. R. (2000). *Opt. Lett.*, *25*, 1330.
[9] Kuebler, S. M., Braun, K. L., Zhou, W., Cammack, J. K., Yu, T., Ober, C. K., Marder, S. R., Perry, J. W. (2003). *J. Photochem. Photobio. A: Chemistry*, *158*, 163.
[10] Campbell, M., sharp, D. N., Harrison, M. T., Denning, R. G., & Tuberfield, A. J. (2000). *Nature*, *404*, 53.
[11] Vlasov, Y. A., Yao, N., & Norris, D. J. (1999). *Adv. Mater.*, *11*, 165.
[12] Vlasov, Y. A., Bo, X. Z., Strum, J. C., & Norris, D. J. (2001). *Nature*, *414*, 289.
[13] Stober, W., Fink, A., & Bohn, J. (1968). *J. Colloid Interface.*, *26*, 62.
[14] Jiang, P., Bertone, J. F., Hwang, K. S., & Colvin, V. L. (1999). *Chem. Mater.*, *11*, 2132.
[15] Rogach, A. L., Kotov, N. A., Koktysh, D. S., Ostrander, J. W., & Rogoisha, G. A. (2000). *Chem. Mater.*, *12*, 2721.