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# Atomic layer deposition in porous structures: 3D photonic crystals

J.S. King, D. Heineman, E. Graugnard, C.J. Summers\*

School of Materials Science and Engineering, Georgia Institute of Technology, Atlanta, GA 30306-0245, USA

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#### Abstract

This paper reports recent results from studies of atomic layer deposition for the infiltration of three-dimensional photonic crystals. Infiltration of ZnS:Mn and TiO<sub>2</sub> are reported for SiO<sub>2</sub>-based opal templates. It has been demonstrated that high filling fractions can be achieved and that the infiltrated material can be of high crystalline quality as assessed by photoluminescence measurements. The highly conformal and uniform coatings obtained in these studies are shown to contribute significantly to the photonic band gap properties. These investigations show the advantages of atomic layer deposition (ALD) as a flexible and practical pathway for attaining high performance photonic crystal structures and optical microcavities.  $\bigcirc$  2004 Elsevier B.V. All rights reserved.

Keywords: Three-dimensional photonic crystals; Photoluminescence; Photonic band gap properties; Optical microcavities

## 1. Introduction

A material with a periodic modulation of its dielectric constant is known as a photonic crystal (PC). The possibility of obtaining photon confinement and suppression of the material's natural spontaneous emission rate in a three dimensional (3D) PC was first considered independently by Yablonovitch [1] and John in 1987 [2]. Since this work, much effort has been placed into fabricating photonic crystal devices, with the primary interest being the development of

\* Corresponding author. Tel.: +1 404 894 1275; fax: +1 404 894 1258.

*E-mail address:* chris.summers@mse.gatech.edu (C.J. Summers).

microcavities through a spectral modification of the recombination rate.

Photonic crystals can exhibit a photonic band gap where certain frequencies of light are not allowed to propagate in the material. Numerous methods have been employed to make such PC structures [3–7] and a complete photonic band gap has been demonstrated at millimeter [3,4] and infrared [5,6] wavelengths. At long wavelengths, it is possible to fabricate structures by mechanical means, as demonstrated by "Yablonovitch" [3]. However, devices for near-infrared and optical frequencies present challenges for both microfabrication techniques and selecting materials with a sufficiently high refractive index. For the former, selfassembly techniques offer many potential advantages. Several groups have shown that the most feasible method for fabricating 3D PCs, with the desired

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periodic structure, is by the infiltration of opals to form an inverted synthetic opal structure [6–10]. To create an inverted opal, an opal template is infiltrated with a high dielectric material, thus filling the void spaces. The template is then removed, leaving an inverted lattice of air spheres. However, to exhibit a full (omnidirectional) photonic band gap, the structure must have a high refractive index contrast (>2.8), longrange dielectric periodicity in three directions, and a high filling fraction. For 3D PCs operating in the UV– vis, the sphere size is ~200–400 nm, and void space between the spheres is small (<40 nm), making it difficult to achieve full infiltration of the opal.

Here, we report recent progress on using atomic layer deposition (ALD) to infiltrate ZnS and TiO<sub>2</sub> into SiO<sub>2</sub> opal templates to fabricate inverted opal films with photonic band gaps in the visible spectrum [10-12]. These materials were selected because of their luminescent properties and relatively high refractive index, respectively. ALD is a growth technique that utilizes the sequential application of reactants coupled with substrate temperature optimization to achieve layer-by-layer growth [13]. As a result, growth is surface-controlled instead of source-controlled, enabling highly controllable deposition of conformal films on substrates with complex geometries, [14] such as opals. Using this technique, we have successfully infiltrated SiO2 opals with ZnS and amorphous and crystalline films of TiO2. By optimizing pulse lengths, purge lengths, and temperature, full infiltration was achieved in opals made from spheres as small as 200 nm in diameter.

# 2. Experimental

For this study, silica opal films were formed by selfassembly of monodispersed colloidal silica [15] on silicon or silica substrates, followed by sintering, as described elsewhere [15]. The resulting films were (1 1 1)-oriented with grain sizes of ~100  $\mu$ m [16]. The interstitial volume of the opal was then infiltrated with either ZnS:Mn or TiO<sub>2</sub> using conventional ALD precursors. The silica spheres were next removed by etching in a 2% HF solution, leaving a mechanically stable inverse opal. The structural properties were characterized using scanning electron microscopy (SEM), and their optical properties determined by specular reflectivity and photoluminescence (PL) measurements. To obtain a complete characterization of these structures, and the processes used in their fabrication, sequential measurements were performed on the sintered opal, after infiltration, and after etching. After sintering, the specular reflectivity was measured to confirm the lattice constants of the resulting opals by analysis of the (1 1 1) Bragg peak position. The calculated plane spacing agreed well with the measurements of colloidal silica sphere sizes obtained via TEM. Theoretical calculations were also performed to determine the photonic band structure.

ZnS:Mn was first used as a prototype material because it is highly luminescent and its ALD processes have been well studied [13]. The infiltration method is described elsewhere [10,11]. Its refractive index is too low ( $\sim$ 2.3) for the formation of a full pseudo-band gap (PBG), but high enough to produce a pseudo-band gap at the Brillouin zone edge. TiO<sub>2</sub> was studied because of its high transparency throughout the visible and higher refractive index (>2.8 for <425 nm for the anatase phase) [17].

The deposition of TiO<sub>2</sub> was accomplished in a custom ALD reactor, using TiCl<sub>4</sub> and H<sub>2</sub>O as precursors. As reported by Graugnard et al. the pulse and purge times were increased to optimize the depth of the infiltration [18]. The deposition of  $TiO_2$  was found to present a new range of challenges, due to its allotropic nature and the dependence of the refractive index on crystallographic phase. At low deposition temperatures (<100 °C) highly conformal coverage was obtained, but the films were amorphous, with a refractive index of 2.35. At high temperatures, both anatase and rutile films were obtained, with indices of 2.65 and 2.9, respectively. Thus, a two-step, growth and anneal process was developed, where TiO2 was first grown at 100 °C and then annealed at 400 °C to convert to the anatase phase, resulting in good coverage and high index.

# 3. Results and discussion

The resulting structures were cleaved and examined in an SEM. Fig. 1 shows cross-sections of several ZnS:Mn and TiO<sub>2</sub> infiltrated opals, and inverted structures. Fig. 1a clearly shows the presence of the silica spheres and surrounding ZnS infiltrate on the



Fig. 1. SEM image of (a) 220 nm ZnS:Mn infiltrated opal,  $\sim$ 80% infiltration; (b) ion milled surface of a 433 nm TiO<sub>2</sub> infiltrated; (c) ion milled TiO<sub>2</sub> inverse opal cross-section. TiO<sub>2</sub> estimated infiltration of 40 nm (±3–4 nm).

fractured surface of a ZnS:Mn/SiO<sub>2</sub> opal. In Fig. 1b and c, the images show a cross-section of a  $TiO_2/SiO_2$  opal and an inverse  $TiO_2$  opal. For amorphous  $TiO_2$  growth, the presence of the small central void space, as indicated in Fig. 1c, is consistent with surface limited growth and clearly demonstrates the finesse possible by this technique.

The ZnS:Mn and TiO<sub>2</sub> infiltrated and inverse opals were observed to exhibit uniform angular dependent colors that arise from Bragg diffraction from the (1 1 1) planes. The position of the Bragg peak at normal incidence was determined from specular reflectance measurements taken before and after infiltration, and after etching, and was used to calculate the filling fraction of the interstitial volume. The peak corresponds to the first stop band at the Lpoint in the photonic band structure and using bulk values for the refractive indices, enables calculation of the filling fraction. To ensure that ALD-deposited films exhibit the bulk refractive index, thick films of ZnS:Mn and  $TiO_2$  were grown and their refractive indices were measured using a Filmetrics F20 thin film analysis tool. These measurements were in good agreement with published data [17,19].

Fig. 2A shows typical reflectance spectra for 200 nm sintered, ZnS:Mn infiltrated, and etched ZnS:Mn inverse opals. After infiltration, the peak shifts to longer wavelengths, from 434 to 535 nm, due to an increase in the average refractive index, and the gap-to-midgap ratio increases significantly. This is in agreement with the photonic band structures that were calculated using a plane-wave expansion software package [20]. After etching to form the inverse opal, the reflectance peak shifted to 451 nm, a significantly shorter wavelength, corresponding to the consequent decrease in the average refractive index. The gap-tomidgap ratio further increased, from 9% to 15.5%, due to the increase in the refractive index contrast resulting from the removal of the silica spheres. This behavior was also well described by the calculated band



Fig. 2. (A) Reflectivity for 200 nm (a) sintered silica (b) ZnS:Mn infiltrated silica and (c) inverse opals. (B) Reflectivity for 330 nm (a) sintered silica (b)  $TiO_2$  infiltrated silica, and (c) inverse opals.



Fig. 3. Reflectivity and *I*-*L* band diagram for (a) sintered 330 nm silica opal; (b) TiO<sub>2</sub> infiltrated silica opal; (c) TiO<sub>2</sub> inverse opal.

structures, which predicted a shift of the photonic band gap to higher frequencies for the inverse opal structure. The reflectivity peaks were found to correspond to the mid-gap frequency of the pseudogap in the  $\Gamma$ -L direction. Also these calculations showed that the width of the pseudo-gap increases in the inverted opal structure, reinforcing the widening of the reflectivity peak seen in the spectrum.

Similar effects were also obtained for a 330 nm silica opal when infiltrated with TiO<sub>2</sub>, as shown in Fig. 2B. As expected for this larger opal structure, the  $\Gamma$ -L reflectivity peak moves to 710 nm as a result of the larger sphere size. Fig. 3a shows that good agreement is found with theory and the high quality of the opal film is confirmed by the fringe spectra at long wavelengths. With TiO<sub>2</sub> infiltration, the higher index not only shifts and broadens the spectra features in the

expected manner, but also introduces a strong peak at shorter wavelengths, ~440 nm, as shown in Fig. 3b. This feature can be explained from the photonic band structure calculations as arising from the large number of energy bands at the energy corresponding to this wavelength, and which shows small energy dispersion, that is they are "flat" over this region of the Brillouin zone. Consequently, the photon group velocity is low and the density of states is large, leading to high absorption and strong reflectance. For the inverse opal (Fig. 3c) the same behavior was observed after accounting for the change in refractive index contrast after the silica was removed. Again, good agreement was obtained between experiment and theory. Comparisons of the photonic band structures shown in Fig. 3, with those calculated for ZnS:Mn infiltration, using a similar opal sized



Fig. 4. (a) SEM of TiO<sub>2</sub>/ZnS:Mn/TiO<sub>2</sub> inverse opal; (b) high magnification of multi-layered region.

structure, show that the predicted pseudo-photonic band gaps (PPBGs) are narrower for the lower index ZnS:Mn infiltrate. Again this was confirmed by experiment. Thus, good agreement was found between these two measurements and theory.

Using the technologies developed for ZnS:Mn and TiO<sub>2</sub>, a multi-layered TiO<sub>2</sub>/ZnS:Mn/TiO<sub>2</sub> structure was studied to investigate the potential of combining the luminescent properties of ZnS:Mn with the higher refractive index of TiO<sub>2</sub>. For this investigation, 10 nm of ZnS:Mn was deposited in a sintered opal, followed by a TiO<sub>2</sub> layer that filled the remaining interstitial volume. An ion mill was then used to expose the SiO<sub>2</sub> spheres, which were next removed by HF etch, thus, forming an inverse opal. A third infiltration step was used to back-fill the inverse opal with 10 nm of TiO<sub>2</sub>, yielding a 3-layer structure, as shown in the SEM in Fig. 4. This image shows conformal coverage for all three-infiltration steps.

The photoluminescence properties of the threelayer structure are shown in Fig. 5 as a function of the "construction" of the opal. For only a 10 nm deposition of ZnS:Mn, luminescence comparable in intensity with the emission from a thin film of ZnS:Mn was measured with the two peaks at 450 and 585 nm representing self-activated (Cl<sup>-</sup> defects) and Mn<sup>2+</sup> donor–acceptor emission, respectively. The PL spectra measured from a TiO<sub>2</sub>/ZnS:Mn inverse opal made from the same sample shows similar features, but also reveals modifications; a slightly shifted Cl<sup>-</sup> emission



Fig. 5. Photoluminescence data excited by pulsed 337 nm  $N_2$  laser from (a) 10 nm ZnS:Mn infiltrated silica opal; (b) TiO<sub>2</sub>/ZnS:Mn inverse opal; (c) TiO<sub>2</sub>/ZnS:Mn/TiO<sub>2</sub> inverse opal.

and an enhanced  $Mn^{2+}$  emission intensity. The further infiltration of an additional 10 nm TiO<sub>2</sub> layer, deposited on the inside surface of the air spheres, at a relatively benign temperature of 100 °C impacts the emission properties significantly as shown: now only a broad band centered at ~560 nm is observed. The modulated PL spectra observed with further infiltrations demonstrates the use of ALD as a tool to investigate the optical properties of opals and inverse opals in great detail and as an effective means to compare theory with experiment.

## 4. Summary

It has been demonstrated that ALD has high potential as a flexible infiltration method for the fabrication of inverse opal and other structures. By the successful optimization of the growth parameters for ZnS:Mn and TiO<sub>2</sub>, ALD has been used to infiltrate highly porous opal structures for photonic crystal fabrication. The technique has been shown to produce infiltrations with filling fractions as high as 100% of the available interstitial volume: ideally for highly conformal films, 86% of the pore volume in an opal. The material deposited exhibits high crystalline quality, as is shown by the attainment of the full refractive index of the infiltrate, and the strong photoluminescence observed. These studies have provided clear confirmation of the modulation of visible light expected in high index 3D photonic crystals. Since ALD can be used for the deposition of all classes of materials, it holds great potential for the growth of highly luminescent materials, high refractive index materials, for multilayered materials and as a tool to fabricate and investigate the properties of complex three-dimensional photonic crystal structures.

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