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Optical photonic crystals fabricated from colloidal systems

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Abstract

Photonic crystals of close-packed arrays of air spheres in a dielectric background of titania have been fabricated with a ceramic technique. Unlike previous methods, ordering of the spheres and the formation of the titania network are performed simultaneously. The photonic crystals exhibit a reflectance peak and a uniform color at the position of the first stop band. The wavelength of the reflectance peak scales very well with the sphere size.

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Comments

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Optical photonic crystals fabricated from colloidal systems

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Photonic crystals of close-packed arrays of air spheres in a dielectric background of titania have been fabricated with a ceramic technique. Unlike previous methods, ordering of the spheres and the formation of the titania network are performed simultaneously. The photonic crystals exhibit a reflectance peak and a uniform color at the position of the first stop band. The wavelength of the reflectance peak scales very well with the sphere size. © 1999 American Institute of Physics. [S0003-6951(99)04526-X]

Photonic crystals (PC) are structures in which the dielectric constant varies periodically in space. If the contrast in dielectric constant is large enough, a frequency gap may occur in which light cannot propagate analogous to the electronic band gap in semiconductors.¹⁻³ The emission of light inside a photonic crystal can be strongly manipulated in the region of the photonic band gap, resulting in intense interest in optoelectronics and photocatalysis applications. However, the fabrication of such crystals at visible wavelengths has posed a formidable challenge. Recently, several groups⁴⁻⁸ have successfully fabricated materials in which pores are arranged in periodic arrays on a length scale comparable to optical wavelengths. Such materials are very good candidates for use as photonic crystals. However, in all the previous publications, a definitive signature of the existence of a photonic gap is still missing. We present a ceramic fabrication technique for photonic crystal thin films at visible wavelengths. We show that the reflectance spectra of these crystals shift systematically with the pore size, providing evidence of photonic crystal effects.

Colloidal crystals are very attractive candidates for use in fabrication of optical photonic crystals. Monodisperse colloidal suspensions of silica or polystyrene spheres can self-assemble into close-packed structures at optical length scales, with excellent long-range periodicity. However, to observe photonic gaps requires an inverse structure where lower dielectric spheres (refractive index n_1) are embedded in an interconnected higher dielectric background (refractive index n_2). Optimum photonic effects require a low filling ratio (20%–30%) of the dielectric background.⁹ A major difficulty lies in the introduction of an interconnected dielectric background for the colloidal spheres, and the subsequent removal of the spheres, by calcination or etching, to achieve the desired dielectric contrasts.

We use titania as the background dielectric filling me-

dium which has a refractive index of ~ 2.6 – 2.8 at optical wavelengths, with negligible absorption above 400 nm. In contrast to previous work,^{4,7,8} where the colloidal template is first assembled and the titania is introduced afterwards in a sol-gel process, we start with a slurry of nanocrystalline titania suspension and monodisperse polystyrene spheres. A few drops of this slurry is spread on a glass substrate and allowed to dry slowly over a period of ~ 24 h in a humidity chamber. The samples are then pressed in a cold isostatic press to improve the initial green density of the as-dried samples and to reduce stress cracks during subsequent heat treatment. The sample is slowly heated to 520 °C for 5 h, whereby the polystyrene spheres are burned off leaving behind air spheres in a titania matrix. Thin films with dimensions ~ 10 mm \times 2–3 mm can be reproducibly synthesized in this way in much shorter times (~ 1 day) than with the infiltration technique.^{4,7,8}

Optical inspection of our samples reveals shiny regions with characteristic colors that depends on the size of the polystyrene spheres used. This is especially clear when the samples are viewed under the microscope. Samples fabricated with 395 nm spheres exhibit bright green regions. With larger spheres (479 nm), the color shifts to a salmon-red color. Unlike previous reports,^{4,7,8} our films exhibit uniform color over large regions millimeters in size.

Wide-view scanning electron microscope (SEM) images [Fig. 1(a)] show large domains with excellent order extending from ~ 50 μ m to more than ~ 100 μ m. Also visible [Fig. 1(a)] are single-height steps separating large domains of hexagonally ordered regions. The domains are well ordered across drying cracks in the sample [Fig. 1(a)], indicating that ordering in the samples occurs upon deposition and is not disrupted by the drying and heating process. Our crystals exhibit considerably better short-range and long-range order than the macroporous materials fabricated with sol-gel methods.⁵

At still lower magnification, the scan periodicity of the

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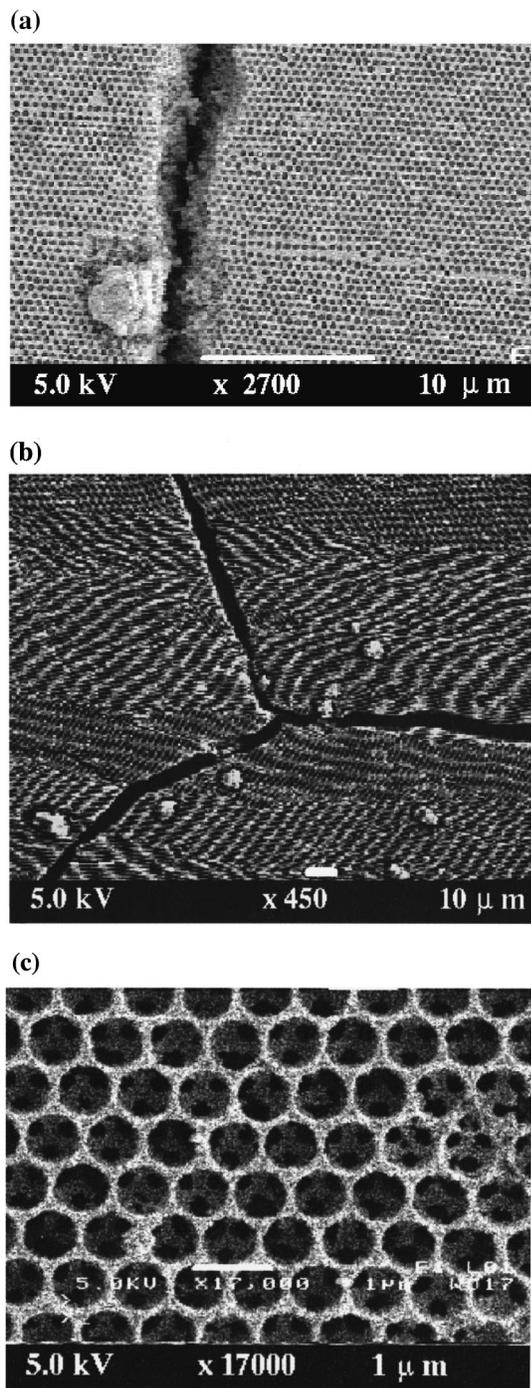


FIG. 1. (a) SEM micrograph of a PC made using 556 nm polystyrene spheres showing excellent long-range order. The bar denotes 10μ . (b) Low-magnification ($\times 450$) SEM image showing the moiré pattern illustrating the domain orientation and strain within the domain. The bar represents 10μ . (c) A high-magnification ($\times 17\,000$) SEM image showing the close packing of the air spheres. The PC was fabricated from 770 nm polystyrene spheres. The bar represents 1μ . The dark regions inside each hollow region correspond to the position of the spheres in the next layer.

cathode-ray tube display and the object periodicity interact, producing fringes or a moiré pattern.¹⁰ This pattern [Fig. 1(b)] illustrates well the domain orientation and strain within the individual domains.

Higher-magnification SEM images [Fig. 1(c)] reveal hollow regions of air spheres that are very well ordered in a triangular lattice. There are three dark regions inside each hollow region corresponding to the air spheres of the under-

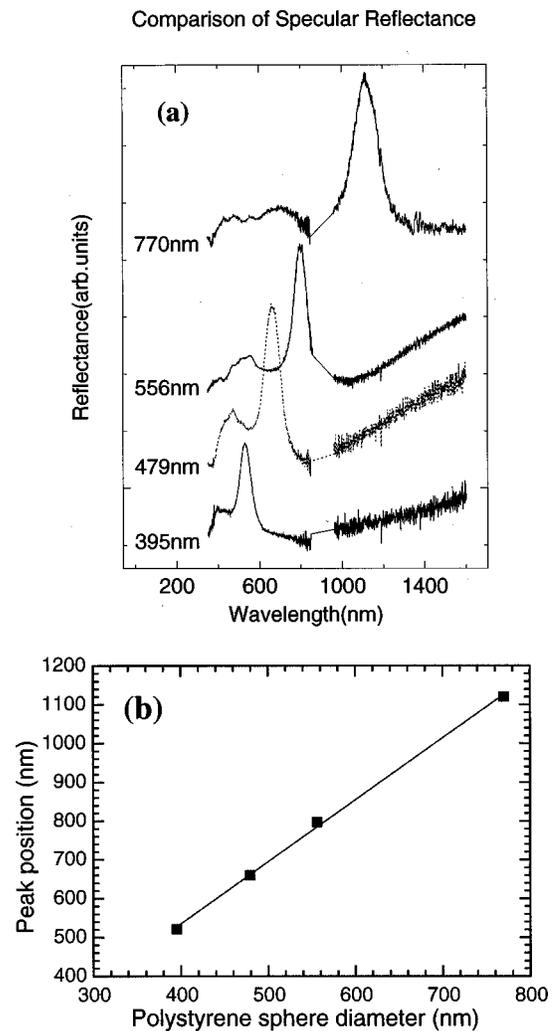


FIG. 2. (a) Specular reflectivity measurements from photonic crystals, fabricated from spheres of varying diameter listed in the legend. The systematic shift in the reflectivity of the first peak is a true optical signature of the photonic crystals. (b) Wavelength of the primary reflectivity peak as a function of the diameter of the polystyrene sphere templates. The straight line is a linear fit to the peak wavelengths. Very good scaling is observed with sphere diameter.

lying layer, indicating that the spheres are indeed close packed. The SEM images indicate that the crystalline grains in the film are highly oriented with the close-packed planes parallel to the substrate. Preferential orientation also exists in the close-packed plane probably due to stresses developing during the drying process. This alignment of crystal grains may prove very useful for applications and measurements especially in cases where a full photonic band gap does not exist in all directions of propagation in the crystal. Determination of the lattice constant indicates a small shrinkage of $\leq 5\%$ in the lateral direction of the film due to the heat treatment and densification of the titania network. Experimental thickness measurements, before and after the pressing and heating process, indicate a larger shrinkage in the direction perpendicular to the film.

Since the ordered films are thick ($\geq 10\mu$), their transmission is small and the major optical signature is found in reflectance measurements. The specular reflectance at near-normal incidence from our nanostructured films is shown [Fig. 2(a)] for different sizes of polystyrene spheres as tem-

plates. The initial sphere sizes [Fig. 2(a), legend] were measured directly from SEM images of ordered arrays of polystyrene spheres.

The prominent feature is a specular reflectivity peak for each structure, that systematically shifts from 1120 to 521 nm over the range of photonic crystals. The wavelength of the specular peak corresponds very well to the visual color of the samples. The larger pore samples have reflectivity peaks in the near infrared. In addition, there is a gradual but featureless increase in reflectivity at longer wavelengths (above 1000 nm) in several samples [Fig. 2(a)]. This is due to the rough surface of the PC's appearing smoother when probed at longer wavelengths. This increases the specular reflectivity, with an accompanying decrease of the diffuse reflectance at longer wavelengths, which is also observed.

The position of the observed reflectivity peak scales remarkably well with the diameter of the spheres [Fig. 2(b)], indicating that it is an intrinsic feature of the photonic crystals. This is an observation of the optical signature of a photonic crystal together with the required scaling with sphere size, that has not been seen in previous work⁴⁻⁸ on such templated PC's.

We performed photonic band calculations and calculated reflectivities from transfer matrix simulations,¹¹ and find that the peak arises from the wide stop band in the stacking direction for close-packed structures. For the fcc structure this corresponds to the stop band between the lowest bands 2 and 3. Our calculations find that the existence and position of the stop band in the stacking directions are insensitive to the stacking sequence of the spheres [fcc (*ABC*) or hcp (*ABAB*)].¹¹ The stop band corresponds to the known pseudogap in the photonic densities of states, and persists even for lower $n \sim 2$ over a large range of filling fractions. Such a refractive index for titania may be expected from the considerably lower density of the solid titania matrix, as would be expected from these processing conditions and from earlier sintering studies of nanocrystalline titania.¹² Further porosimetry measurements, will be performed to es-

timate the density of the titania matrix. The refractive index of the background skeletal titania may be improved by sintering at higher temperatures.¹² Quantitative calculations of peak wavelengths will be presented later, when accurate interlayer spacings are determined from optical diffraction measurements, but preliminary estimates indicate that the observed peak frequencies are consistent with what we know about the geometry and filling fraction of the films.

The success in the fabrication of large-area optical photonic crystals using rapid, economical, and reproducible ceramic techniques will open the way towards the experimental observation of many interesting effects involving the control of light emission and propagation in these materials.

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¹E. Yablonovitch, Phys. Rev. Lett. **58**, 2059 (1987).

²S. John, Phys. Rev. Lett. **58**, 2486 (1987).

³For a review, see *Photonic Band Gap Materials*, Proceedings of NATO Advanced Study Institute, edited by C. M. Soukoulis (Kluwer, Dordrecht, 1996).

⁴J. E. G. Wijnhoven and W. L. Vos, Science **281**, 802 (1998).

⁵A. Imhof and D. J. Pine, Nature (London) **389**, 948 (1997).

⁶A. Velev, T. A. Jede, R. F. Lobo, and A. M. Lenhoff, Nature (London) **389**, 447 (1997).

⁷A. Zakhidov, R. H. Baughman, Z. Iqbal, C. Cui, I. Khayrullin, S. Dantas, J. Marti, and V. G. Ralchenko, Science **282**, 897 (1998).

⁸B. T. Holland, C. F. Blanford, and A. Stein, Science **281**, 538 (1998).

⁹R. Biswas, M. Sigalas, G. Subramania, and K.-M. Ho, Phys. Rev. B **57**, 3701 (1998); H. S. Souzuer, J. W. Haus, and R. Inguva, *ibid.* **45**, 13962 (1992); T. Suzuki and P. K. L. Wu, J. Opt. Soc. Am. B **12**, 13962 (1995); K. Busch and S. John, Phys. Rev. E **55**, 3896 (1998).

¹⁰*Practical Scanning Electron Microscopy*, edited by J. I. Goldstein and H. Yakowitz (Plenum, New York, 1975).

¹¹R. Biswas, M. M. Sigalas, G. Subramania, C. M. Soukoulis, and K.-M. Ho (unpublished).

¹²H. Hahn, L. Logas, and R. S. Averback, J. Mater. Res. **5**, 609 (1990).