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Optical study of the full photonic band gap in silicon inverse opals

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An optical study of the band structure of both silicon–silica composite and silicon inverse opals is presented. The study is aimed at demonstrating the development of a full photonic band gap for a system already revealed as paradigmatic. The characterization is based on the comparison between the band structure calculations and optical reflectance spectroscopy experiments. This study is carried out for various symmetry points in the Brillouin zone, some never explored before as K, (110) and W, (210). The results show that, in accordance with the band structure, there is a certain frequency range that produces a reflectance peak regardless of orientation and can be assigned to the band gap. Similarly all other reflectance peaks can be accounted for by other band structure features.
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Since the introduction of the concept of a photonic crystal (PC),[1,2] much effort has been targeted at producing and characterizing three-dimensional (3D) photonic crystals working in the optical wavelength range. These materials have a dielectric nature and possess a periodic modulation of the dielectric function. Consequently, their optical properties are determined by strong scattering effects and the propagation of electromagnetic waves within a certain range of frequencies may not be allowed. Stop bands may exist that prevent propagation along different crystal directions depending on energy. These are referred to as pseudogaps to be differentiated from the case where, for certain energy ranges, light propagation is forbidden regardless of direction in the crystal. In the latter case the material is said to have a full photonic band gap (PBG).

Three-dimensional (3D) photonic structures are manufactured by using, among others, lithographic techniques,[3] holographic lithography,[4] or nanorobotic manipulation.[5] The large scale fabrication of this sort of materials is, to a certain extent, limited by the use of sophisticated technology and high economic cost. The use of ‘‘synthetic opals’’[6] has been proposed as a cheap and easy alternative. Colloidal spheres of different dielectric materials (e.g., silica or latex) exhibit a strong tendency to self-assemble spontaneously into a face centered cubic (fcc) crystal lattice.[7] Infiltration of the interparticle voids with materials of appropriate refractive index, followed by removal of the spheres by dissolution, leads to the formation of close-packed spherical air cavities embedded in a high dielectric background. This new structure is called an inverse opal. If the refractive index of the remaining material is high enough (>2.85), a full PBG, located between the eighth and ninth bands, is expected according to theoretical calculations.[8,9] Several reports have shown the fabrication of inverted opals that nearly[10] or fully[11,12] satisfy the requirements for the opening of a band gap.

No matter how demanded, obtaining experimental proof of the existence of a full PBG is a difficult task. Furthermore, defining what constitutes hard evidence remains controversial. Using the suppression of luminescence of an impurity dye embedded in the PC, has been proposed as a means to detect the existence of a full PBG.[1,2] The local photonic density of states will have to go to zero if a true PBG exists in the PC structure. To date, this remains a challenge. Another option would be the acquisition of transmission or reflection spectra along high symmetry directions[13] of the first Brillouin zone, namely ΓL (111), ΓX (100), ΓK (110), and ΓW (210). If a range of frequencies were found where the stop band overlaps for all directions, if not a proof, a strong evidence of a full PBG would be given. In this respect the only direction, other than (111),[11] from which reflectance has been obtained is, to the best of our knowledge, the (100) direction reported for silicon inverted opals.[14]

In this work, we report on the optical characterization of silicon infiltrated opals. Reflection measurements have been recorded from (111), (100), and (110) faces in the silica–silicon composite opal. In order to study the opening of the PBG, the same kind of measurements have been performed after the structure was inverted. We have found that, common to all these directions, there exists an energy band of intense reflectance. Comparison of this result with band structure calculations, leads to the association of this reflectance peak with a full PBG. In addition, we have carried out optical reflectance measurements for the (210) facet finding again good agreement with the theoretical predictions.

The samples studied were prepared by using the same methods described previously.[11] The opal spheres are 0.97 μm in diameter and the infiltration with silicon was carried out to a filling fraction of 90% of the pore. If templated growth is not used,[15] opals grow spontaneously along the denser (111) direction by stacking hexagonal planes. In order to expose facets in other crystal directions, sample cleavage is necessary. Upon cracking, samples tend to show cleft

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edges of the most compact faces. Thus, the size of the created facets and frequency of appearance increases from (110) to (100) to (111), with large sample areas showing (111) and seldom presenting (110) oriented planes. The sample was then placed on a spherical holder sitting on a washer that allows aligning the facet normal with optical axis of the spectrometer.

The reflection spectra were acquired using a Fourier transform infrared spectrometer. It is well known that the high energy bands are highly affected by the existence of lattice disorder and that even the PBG can be closed.[16] In order to avoid these problems, an optical microscope with a Cassegrain 36× reflection objective was attached to the spectrometer. At this magnification, single spheres can be clearly seen with a 10× eye piece in silicon infiltrated opals of around 1 μm lattice parameter. At the wavelengths used in these experiments ($\lambda \sim 2.5$ μm at the center of the spectra, $a/\lambda \sim 0.56$) the diffraction-limited lateral resolution is ~ 3.3 μm. By the use of the appropriate apertures, this arrangement, allows taking spectra from a single crystal domain of a few tens of microns in size with a high surface quality. Optical microscopy images of the measured areas were saved along with the spectra. Due to the Cassegrain objectives design, there is a light collection cone centered on the optical axis that remains blocked. Because of this, measurements are not performed at exact normal incidence but integrate directions comprised between two limiting angles. In our case these angles are 15° and 30°. This imposes a selection of the light **k** vectors that actually impinge on the sample. When a pseudogap is probed along a given direction of the Brillouin zone the position of the experimental reflectance peak can be acceptably explained[17] assuming that the **k** vector inside the PC follows Snell's law. The effective dielectric function within the PC is obtained from a filling fraction weighed average. The limiting angles within the sample are 7° and 13° for the composite and 8° and 15° for the inverse opal. Thus, in the photonic band diagrams, we have shaded those regions that are excluded from being probed by geometrical constraints. Theoretical calculations were performed using the plane wave expansion method.[18] For Si we have used a value of 11.9 for the dielectric function.[19]

Faces in the SiO_2-Si composite were investigated first. Although the refractive index contrast ($n_{\mathrm{silicon}}/n_{\mathrm{silica}} \sim 2.41$) is not high enough to open a full PBG, there is a very interesting variety of pseudogaps that appear along different directions of propagation in the crystal.

Reflectance spectra recorded along the (111), (100), and (110) directions and the corresponding theoretical bands calculated for a silicon infiltration of 90% of the pore are shown in Fig. 1.

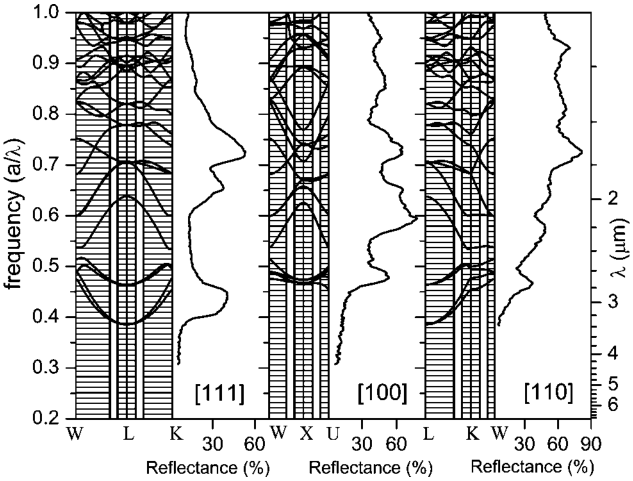

FIG. 1. Calculated photonic band diagrams and measured reflectance spectra for propagation configurations close to the three principal directions (L, X, and K points) in a silicon–silica composite.

The experimental reflectance peaks match well with the pseudogaps predicted by the theory. The appearance of intense reflection peaks at high energy reveals a good crystallographic quality of the studied faces. The lowest energy stop band in the (111) direction appears very broad corresponding to the first pseudogap region, generating a strong reflectance peak. In other directions, however, the corresponding peak appears much narrower as expected from the band structure. The gap between fifth and sixth bands gives rise to a second reflectance peak in all directions not only in the composite but also in the inverse system as will be seen. These two nonintersecting bands always give rise to a reflectance peak at different energy depending on incidence orientation. In all three directions, a peak can be seen as evidence of the seed of the full eighth to ninth band gap. The crossing of these bands in the vicinity of the W point frustrates the opening of this gap. Eventually, this will be prevented by the increase of the refractive index contrast in the inverted structure. For the (110) direction a complex pattern of bands around the K point produces a complicated reflectance at high energies.

In order to investigate changes in the spectra after the inversion, silica spheres were removed by chemical etching with a 1 wt % solution of HF in doubly distilled water for 7 h. Reflectance measurements performed in the same faces are shown in Fig. 2.

In the three directions shown, spectra exhibit a broad peak centered in 0.8 (a/λ) corresponding to the full photonic band gap. Nearly 100% reflectivity is obtained in (111) and

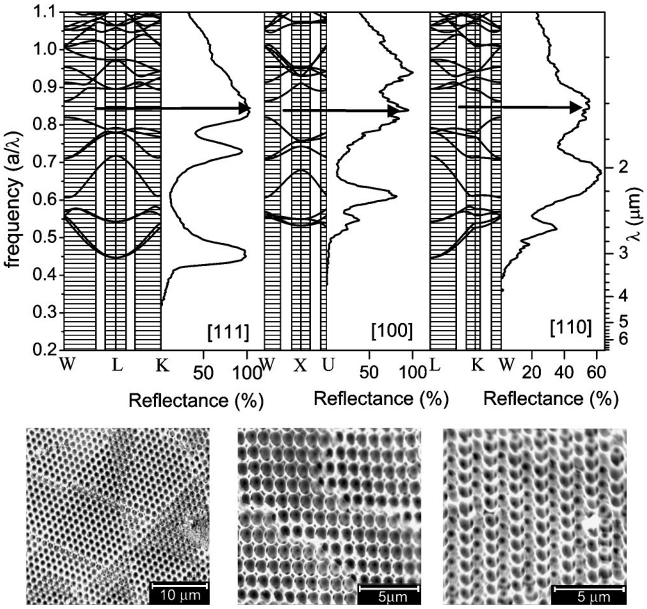

FIG. 2. Calculated photonic bands and measured reflectance spectra for the three principal directions are shown along with the corresponding SEM image of the probed face showing evidence of the crystallographic orientation.

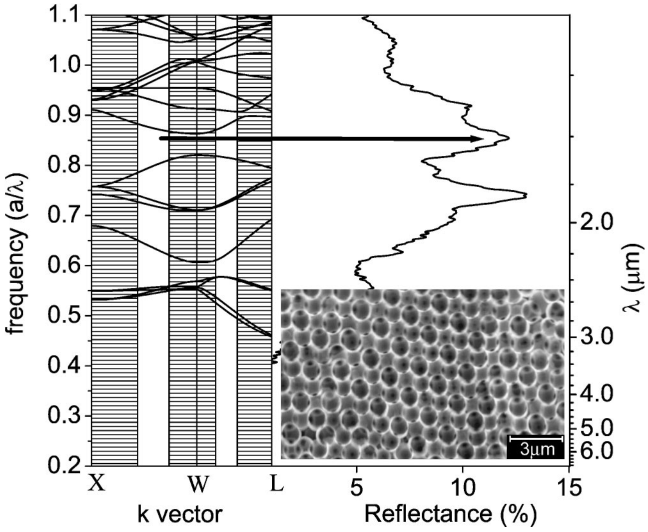

FIG. 3. Band structure compared to the reflectance spectrum for the W (210) orientation shown in the micrograph. Notice the very low density of this facet and the small plane separation make it prone to presenting terraces (inset).

(100) direction and more than 55% in the (110) direction. Scanning electron microscopy (SEM) images were taken in the probed zones to show the faces. The higher refractive index contrast flattens the bands and widens the gaps, for these reasons the eighth to ninth band gaps become a full gap. The pseudogaps observed in the composite still remain in the inverse opal.

Both in the composite and inverse opal, the first energy reflectance peak appears slightly shifted with respect to the theoretical calculations. This may be a result of unavoidable imperfections in our system such as inhomogeneity in silicon infilling or spheres diameter variation. Another possible explanation is the dependence of the dielectric function on wavelength that is taken as a constant to perform band structure calculations.[18] Overall the number of peaks and structure of the spectra is consistent with the calculated band structure.

Among all possible directions to probe, the (210) or ΓW is especially interesting. Here, the width of the PBG is narrower than in other directions. However, this facet is seldom found in cleft edges. First, it is a very low density one, formed by stretched hexagons (Fig. 3 inset). Second, these planes are tightly stacked (spacing 0.63 in units of sphere diameter). In spite of all these problems, a detailed scanning of our sample allowed us to find areas large enough to perform measurements.

Figure 3 shows the reflectance spectrum along (210) direction. Clear peaks are observed and agree with theoretical predictions. Corresponding to the full PBG a peak appears at $0.8\,a/\lambda$. As expected, it is narrower than in the other measured directions. Reflectance is not very intense because the facets obtained tend to be vicinal and present terraces.

In summary, we have carried out a microreflectance study along the main directions of propagation for light of energy around the full photonic band gap in Si–SiO_2 composite and Si inverse opals. In particular, directions such as K (110) and W (210) are probed in this kind of system. The results demonstrate that a peak of reflectance appears at $0.8\,a/\lambda$ irrespective of direction, corresponding to the full gap theoretically predicted.

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