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Self-assembly approach to optical metamaterials

J F Galisteo, F García-Santamaría, D Golmayo, B H Juárez, C López and E Palacios

Instituto de Ciencia de Materiales de Madrid, Consejo Superior de Investigaciones Científicas (CSIC), C/Sor Juana Inés de la Cruz 3, 28049 Madrid, Spain

E-mail: cefe@icmm.csic.es (C López)

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Abstract

Photonic crystals can be viewed just as a subclass of a larger family of material systems called metamaterials in which the properties largely derive from the structure rather than from the material itself. Opals have only a relatively recent history as photonic bandgap materials and have received a strong thrust from their adequacy as scaffoldings for further templating other materials with photonic applications for instance. The tortuous route from materials to devices might perhaps find reward in the ease and low cost of fabrication of these materials. In this paper we present a review of recent work and work under way in our laboratory tending towards synthesis based on self-assembly to realize metamaterials in the optical range. This comprises the formation of the templates (opals) and subsequent synthesis of guest materials such as semiconductors, metals and insulators. The possibility of further processing allows additional two-dimensional and quasi-two-dimensional patterning for the design of new structures. In this paper we show how the raw matter can be checked for quality and learn how to use its optical properties to evaluate application potential. Issues relating to the optical properties (such as crystalline quality, finite size effects and infiltration with other materials) are examined. We show some examples where opals are used to pattern the growth of other materials with photonic applications (such as metals and semiconductors) and developments leading to both vertical and lateral engineering are shown.

Keywords: opal, opal infiltration, templating, photonic bandgap, photonic crystal, diffraction, spectroscopy

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Artificial opals as photonic crystals (PCs) are cheaper alternatives to other more sophisticated PCs fabricated by using techniques such as photolithography or holographic lithography [1]. Methods for opal preparation are usually based on the natural tendency of microscopic colloidal particles of silica, polystyrene (PS) or polymethylmethacrylate (PMMA) to self-assemble in an ordered face centred cubic (fcc) structure. However, the main problem found in the preparation of artificial opals is the unavoidable presence of some sort of disorder generated by both the polydispersity of the microspheres used and the inherent stacking defects developed during the growing process. Many efforts have been devoted to improving the quality of the opaline samples in the last few years, by using different methods of preparation, such as sedimentation [2], electrophoresis [3], confinement in special cells [4], vertical deposition [5] or some others introducing small modifications of these methods [6, 7]. These optical systems are ideal references for studying the intrinsic properties of a PC, such as the density of states inside the crystal [8] or gap formation [9], or to confirm theoretical predictions, such as the super-prism effect [10] or high transmission through sharp bends [11] in waveguides. An additional advantage is that their optical properties can be modified continuously in a controlled way, allowing the preparation of more sophisticated systems. One of the most usual methods is void infiltration with different materials. If a high refractive index material is used in the infiltration, the PC obtained may exhibit full photonic bandgaps (PBGs) in the near infrared and visible range [12, 13]. Infiltration with polymers or other organic compounds is a suitable method for fabrication of photonic inks [14] or sensors [15]. Recent work has shown that 'band engineering' can be achieved by multilayer infiltration with different materials [16, 17] or by obtaining new inverse structures through morphological changes of the material filling the voids [18]. Silica and PS spheres containing a metallic or magnetic core can be prepared [19, 20], allowing us to couple the metallic and/or magnetic properties, Using patterned respectively, with the photonic ones. surfaces as substrates, the fabrication of prisms [21] and microfibres [22] made of PCs has been possible. Another possibility is the introduction of controlled defects in colloidal crystals by the use of two-photon polymerization [23] or laser micro-annealing [24]. By combining spheres of two different sizes, ordered superlattices [25] or structures containing planar defects [26] have recently been obtained.

This work is divided into several parts. Firstly, we present a study of the effects induced by the introduction of controlled numbers of spheres with larger diameters and with refractive index different from the host's in thin artificial opals. These systems are grown by the vertical deposition method [5], the most widespread and easiest procedure to build high quality self-assembled colloidal systems. For this purpose, PS and PMMA spheres can be mixed. The PMMA beads were used as the host colloids and the PS ones as dopants.

Finite size effects have been thoroughly studied prior to comparing the optical response of the samples with calculated band structures¹. The latter is done along high symmetry directions in reciprocal space once the sample is properly oriented by means of optical diffraction.

The potential of semiconductors as materials for photonic applications has been well stated since the appearance of two works published by Blanco [12] and by Míguez [28] respectively. For the first time they presented crystals (based on opals) accomplishing all the requirements to present a complete PBG in the NIR. Apart from their high refractive indices, both materials have a long established technological tradition. In this paper we describe the accurate control of the synthesis of these semiconductors, amorphous silicon and germanium, within thin silica opals. Growth of semiconductor layers or even multiple layers combining air, Si and Ge is shown. Accurate design and control of the materials composing an fcc crystal is a tool for band engineering. The super-prism effect, all angle negative refraction [29], high group velocity dispersion [30] or the improvement of non-linear optic effects are all consequences of what can happen when light couples with the appropriate bands. Thus, smart engineering on the band structure becomes an important discipline. The use of high refractive index

semiconductors importantly affects band structure. Also, varying the topography would involve changes, and therefore is another tool to be considered. On the other hand, it is well known that large PBGs are predicted for periodic metallic structures, opening up new alternatives in the development of potential photonic applications [31–34]. Measuring and interpreting the optical response of metallic photonic crystals has become a challenging task [35–38]. Due to the large refractive index, complete PBGs can be opened in regions where the metal absorption is negligible. In thin periodic metallic structures new interesting phenomena can be expected from the interaction of light with plasmon resonances [39]. In this work, we present zinc inverted opals obtained by means of electrochemical methods.

Photonic slab heterostructures based on artificial opals are an example of the vertical engineering that can be done on this sort of materials. A method that combines high quality thin film opal growth and silica infiltration through a multi-step process is also presented. By varying structure parameters, such as lattice constant, sample thickness or refractive index, different heterostructures can be obtained to tailor the optical response of these systems. The proposed method allows a full control of the structure parameters involved, opening the possibility of tuning their photonic behaviour. Special attention in the optical response of these materials has been paid to the study of planar defects embedded in opals. An important aspect of photonic crystal engineering is the possibility of incorporating well defined point, linear or 3D features in an exact placement of the crystal body. Electronbeam lithography (EBL) can be used for structuring PMMA sphere opals and providing lateral structure. To conclude the work we present a method that combines the SiO₂ infiltration of thin PMMA opals with the EBL process, obtaining selective inverted opals. This demonstrates the possibility of horizontal engineering in this class of materials.

2. Colloidal crystals: optical characterization

The optical response of photonic crystals is closely related to the quality of the structures. The growth in confined environments and the development of new procedures have improved the quality of colloidal crystal films [6]. Although many efforts are being made to optimize the optical response, there is only a little work studying the role of defects in these structures in detail [40-44]. Colloidal crystals have been used to obtain stoichiometric binary crystalline phases by combination of controlled size-ratio and concentration of different colloids [45, 46]. The control over electrostatic interactions between spheres has yielded controlled crystallizations of binary colloidal crystals [47]. To study the influence of defects in self-assembled structures, the existence of impurities can be simulated by doping highly monodispersed 3D lattices with spheres of different size. Previous work by Xia [48] shows the negative influence on the stop-band response of PS colloidal crystal lattices doped with different concentrations of PS spheres of diameter smaller than the host's.

By using the vertical deposition method [5], good quality single-crystalline samples are obtained with lateral dimension in the order of cm^2 and up to 55 layers. In order to introduce

¹ Photonic band structures are computed using a plane wave basis in an iterative implementation as described in [27].



Figure 1. (a) Reflectance spectra of a PMMA opal (sphere diameter 270 nm) doped with different concentrations of 700 nm PS spheres. (b) Reflectance responses for three opals doped with the same concentration of guest spheres (0.1%) but different dopant/host ratios.

structural disorder, controlled amounts of dopant spheres of sizes different from those of the host were added. 270 nm monodisperse PMMA spheres and 700, 450 and 360 nm monodisperse PS spheres as the host and dopant particles respectively were synthesized by surfactant-free emulsion polymerization methods [49, 50]. The size of the spheres can be controlled through several reaction parameters and reactive concentrations.

The reflectance spectra of PMMA thin film opals of 270 nm spheres doped with different concentrations of 700 nm PS spheres are shown in figure 1(a). As expected, the Bragg peak intensity decreases as the PS sphere concentration increases, in agreement with previous results [48].

In figure 1(b), the detrimental effect on the intensity of the Bragg peak when different sizes of impurities are added to the lattice in the same concentration (0.1%) is shown. In the case in which the host and guest spheres are closer in size ($d_{PS} = 360$ nm), the reflectance intensity of the Bragg peak is nearly the same as in a 'defect-free' sample. In this case, the disorder provoked by the presence of the impurities is negligible. For larger impurity spheres ($d_{PS} = 450, 700$ nm) the effects of disorder strongly reduce the intensity of the peak.

From the above results, it may be concluded that in mixtures of two populations of spheres possessing very similar or the same size no morphological defects are apparent. In this case, the two different material spheres are randomly distributed through the lattice, forming an alloy. In order to illustrate the properties of these compound crystals, samples made by mixing PMMA and PS spheres of 242 and 252 nm, respectively, are shown in figure 2. The relative concentrations of PS spheres in the PMMA matrix were 0%, 25%, 50%, 75% and 100%, the 0% and 100% samples being the pure PMMA and PS opals respectively. Under the assumption that no morphological defects are produced, no strong variations in the reflectance intensity are expected or found. The continuous



Figure 2. Optical images of samples prepared by mixing varying numbers of PS and PMMA spheres of the same size from pure PMMA (left) to pure PS (right).

variation of the colour can be appreciated as a response to the continuous variation of average refractive index.

With real crystals the question arises of how to decide whether the crystal has achieved infinite crystal behaviour. Here we have assumed the well known criterion of comparing the full width at half maximum (FWHM) of the reflectivity peak with the gap width as the number of layers increases. A number of parameters which can also be employed to describe the reflectivity peak, such as its centre frequency or the edges, were taken into account in order to gain further insight into the finite size effects present in our system. We also considered the influence of the optical environment on the optical properties of the crystals by using samples which were grown on silica and silicon substrates.

We found that finite size effects disappear, independent of the parameter considered to describe the Bragg peak, only for samples thicker than 35 layers [9]. Further, it can be appreciated that if we describe the Bragg peak in terms of its edges or central frequency, finite size effects are manifest in a different way depending on the substrate on which the sample is grown. Therefore, these two parameters are not only dependent on the finiteness of the sample alone, but also on the optical environment that surrounds it. The FWHM, however, depends only on the sample thickness and can thus be used as representative of electromagnetic radiation interaction with the photonic crystal alone, and not its optical environment. In figure 3 we present a comparison between theoretical predictions and experimental results for the FWHM. The horizontal line represents the width of the Lgap extracted from band structure calculations [27]. The solid curve represents predictions obtained with the scalar wave approximation (SWA) for the finite system [51]. It can be seen that experimental results converge to the behaviour of the infinite crystal predicted by the exact calculations. Results from the SWA overestimate experimental data. This difference is surely originated by the limitations of the approximated SWA [9].

Diffraction patterns obtained with visible light are often used to obtain information on the order present in the volume of the crystal. This pattern is usually modelled [52, 53] in a single scattering configuration as a superposition of diffraction from 2D arrays of spheres which are stacked in a certain order. Depending on the geometry of the 2D array, as well as the stacking sequence, the diffraction pattern will vary. For close packed crystals with hexagonal planes parallel to the surface, hexagonal or triangular patterns are expected



Figure 3. FWHM of the reflectance for samples grown on silicon (+) and on silica (\times) . Theoretical data extracted from band calculations appear as a continuous curve. The horizontal line shows the infinite crystal limit.

depending on the stacking sequence. For pure fcc crystals (ABCABC or CBACBA sequences) a triangular pattern is expected. Hexagonal diffraction patterns are obtained for hexagonal closed packed (hcp), random closed packed (rcp) or twinned fcc structures.

We have studied the diffraction obtained when impinging with lightly focused laser beams perpendicular to the sample surface. The wavelength used was the 476 nm line of an argon laser, and the samples consisted of spheres having a 695 nm diameter. They were recorded on a screen placed 5 cm away from the sample for clarity.

The diffraction pattern can be considered as the Fourier transform of the periodic array present in the surface, so that diffraction spots are assigned to reciprocal lattice points. Therefore by rotating it 30° we obtain the arrangement of spheres in direct space, that is, on the crystal surface. This indicates that the way spheres are ordered into a periodic array by the moving meniscus is in the form of rows parallel to the direction in which the meniscus is displaced. This was further confirmed by observation of the samples under SEM. Further, since the diffraction spots are to be considered as reciprocal lattice points, the Brillouin zone of the surface (being an image of the hexagonal facet of the 3D structure) may be extracted from this pattern. This allows us to orient the crystal when probing the optical properties of the crystal along high symmetry directions in angle resolved experiments. For the particular case of the patterns shown in figure 4, the sample is vertically oriented (that is, parallel to the growth direction) so that the U/K points in reciprocal space may be reached by rotating the sample around that axis. Similarly, the W point may be reached if rotation takes place around an axis perpendicular to the growth direction. Attention was mainly concentrated on the optical behaviour of the samples in the frequency region where first order Bragg diffraction (associated with the $\{111\}$ planes) takes place.

If the sample is rotated around an axis perpendicular to the growth direction (parallel to the meniscus) the incident and reflected wavevectors are contained in the ΓLW plane in reciprocal space and should therefore be compared with bands calculated along the LW direction. Experimental results present an avoided crossing behaviour [54, 55] taking place at the W point in reciprocal space where the incident wavevector fulfils simultaneously the Bragg condition for the {111}, {111] and {200} families of planes, and strong mode coupling takes



Figure 4. Diffraction patterns obtained in transmission with a 476.5 nm laser line for different samples. (a)–(d) correspond to samples having one, two, three and six layers respectively. (e) and (f) are obtained from different regions for samples six layers thick filled with ethanol. (g) and (h) correspond to a sample 20 layers thick before and after being filled with ethanol. (i) Disordered region in a six-layer-thick sample.



Figure 5. Experimental reflectance peaks (obtained at two sample positions separated by a rotation of 60° with respect to its normal) and theoretical (curves) bands when scanning the Γ LW region in reciprocal space.

place. If the centre frequency of these peaks is compared with calculated bands (see figure 5) a good agreement is found. Similar experiments carried out when the rotation axis is parallel to the growth direction may be compared with calculated bands along the Γ LU direction as would be expected due to the threefold symmetry of the hexagonal facet of the Brillouin zone.

While the optical response of opal-based PCs is well known in the frequency region where first order Bragg diffraction by the {111} family of planes takes place, for higher frequencies the situation becomes more complex. The appearance of bands arising from wavevectors originally not parallel to the Γ L direction, but folded back into the first Brillouin zone by translational symmetry, introduces anticrossings between bands of the same energy and symmetry [56]. Higher order Bragg diffractions by the {111}



Figure 6. Left, band structure calculated along the Γ -L direction in reciprocal space for an artificial opal consisting of PS spheres. Reflection (centre) and transmission (right) measured at normal incidence. The arrows point at the peaks originating in anticrossings.

planes are also expected. This complicates the band structure, making the comparison between experimental spectra and calculated bands non-trivial. The above can be appreciated in figure 6, where transmission and reflection spectra at normal incidence are plotted together with the calculated band structure. Most features in reflectance spectra find correspondence in transmittance ones. It can be observed that reflection peaks/transmission dips may be associated with perturbations (such as gaps and anticrossings) found in those bands reminiscent of the free photon behaviour for wavevectors parallel to the ΓL direction. For regions where these perturbations are absent, the crystal presents a low reflectance and high transmittance. This represents a first approach to the understanding of the optical properties of photonic crystals in this utterly interesting, though not yet explored, spectral region.

Finally we must take into account the fact that light is being scattered out of the normal direction, as evidenced by the optical diffraction results presented above. Due to the geometry of the experiment, this light will not be detected, and will certainly affect the experimental spectra. By examining the correlation between reflectance and transmittance with the bands it can be seen that some features correspond to gaps open in the bands, some to diffractions out of the direction of the detector and some to anticrossings in the bands (marked with arrows in figure 6).

3. Growth of silicon and germanium by CVD

Semiconductors such as silicon and germanium can be synthesized by chemical vapour deposition (CVD) performing slight modifications to already published methods [12, 28]. In this system, basically, the sample is placed in a cell where the precursor gas is condensed with liquid nitrogen. Disilane (Si_2H_6) and germane (GeH₄) can be used as precursors for Si and Ge. Once the precursor gas is condensed, the cell is isolated and placed in a furnace at the selected decomposition temperature.

Under these conditions both semiconductors grow amorphous and can be crystallized by a later annealing.



Figure 7. Diagram showing the formation of multilayer systems. Beginning with a bare opal, subsequent growth of semiconductor layers and final selective removal of Ge may give rise to air gaps (a) between the silica spheres and Si or (b) between two Si layers.

Two parameters govern the growth of the semiconductor: the precursor gas pressure and the reaction temperature. Decomposition temperature plays a very important role in two aspects: growth velocity and the presence of undesired particles. The higher the temperature, the faster the precursor decompositions. It has also been observed that high temperatures induce the growth of undesired particles. In the case of Si the precursor gas decomposition temperature selected was $375 \,^{\circ}$ C while for Ge it was set at $270 \,^{\circ}$ C. Lower temperatures resulted in very slow synthesis rates while higher ones allowed little control.

The key parameter to control the amount of semiconductor loaded in the opals is reaction time. This is the time the sample remains at a certain temperature at which the decomposition of the precursor gas takes place. The only limitation for complete infillings seems to be a geometrical one related to the closure of the pores in the {111} close packed planes. This happens for a grown layer of thickness equal to 5.47% of the lattice constant (corresponding to an 86% infilling, or 15.47% of the sphere radius). Of course, this upper limit is valid for defect free samples. Polydispersity in sphere diameter, sample cracks and vacancies may lead to this value being exceeded. This explains why filling ratios close to 100% have been reported.

This method allows not only growth of both materials on silica but of either on the other [16]. A further degree of freedom will be provided by the selectivity of different solvents that can be used to remove some of the materials. *Aqua regia* (a [3:1] mixture of hydrochloric and nitric acid) can selectively remove Ge, damaging neither the silica spheres nor the Si layer. Furthermore, Ge can be oxidized at 500 °C without changing the properties of the rest of the materials: silica spheres remain unaffected and higher temperatures are required for a-Si oxidation.

To demonstrate the ability to grow a semiconductor multilayer, a sample with 30% of the pores loaded with Ge is re-grown with Si to 80%. Then, Ge is etched with *aqua regia*. Route (a) in figure 7 shows a diagram with the necessary steps to obtain this structure. The result is shown in figure 8, where an air gap separates the silica opal from the Si filling.



Figure 8. Cleaved edge SEM images of the (100) plane of a Si infiltrated opal. The Si layer is separated from the continuous silica structure by an air shell.

There are many other possibilities available. For example, Ge can be oxidized to obtain germanium dioxide (GeO₂) at 500 °C. For this reason the oxidation of Ge can be regarded as a selective process in these systems. Apart from the materials that can be grown directly or indirectly with a CVD system, other materials that grow in a layered way may be added to increase the number of possibilities. As an example of a compatible method, the direct growth of silica by CVD can be mentioned [57].

4. Growth of metals

Although not commonly used to infiltrate opals, electrodeposition deserves special attention due to its low cost, low temperature working conditions and precise control over the thickness and composition of the electrogenerated material. In fact, it is a suitable method to grow metals, semiconductors, alloys and a large number of different compounds. Braun and Wiltzius [58] used this approach to infill II-VI compounds in silica opals. Bartlett and co-workers [59] have reported several macroporous structures fabricated by electrochemical methods. Many other authors have used the electrochemical approaches to build up III-V compounds [60], metallic structures [61], alloys [62], semiconductor composites [63] and conducting polymers [64] based on artificial opals. Electroless baths [65] have been employed as well to fill the macroporous bare structures with metals. Other approaches such as photolithography and CVD methods were combined to grow oneunit-cell-thickness wood-pile arrangements of tungsten [66].

The metal here reported presents interest not only on its own but also associated with the extraordinary optical properties of its oxide. Since ZnO can be electrochemically grown through colloidal templates [67], ZnO and ZnO/Zn structures derived from Zn opals could be tackled by proper and controlled oxidation of Zn opals in order to study luminescent properties in metallic fcc structures. In this work Zn growth in opals on semiconductor substrates, namely, indium tin oxide (ITO) and n-doped silicon substrates, is presented [68]. Two different electrochemical methods with different growth mechanisms open up the possibility of controlling the fabrication of metallic photonic crystals with different topologies on semiconducting substrates. The growth of periodic metallic zinc on transparent substrates (ITO) and silicon surfaces can be of relevant importance in optoelectronics and other technologies.

Cyclic voltammetry and square wave pulsating potential methods [69] were used to grow and improve the homogeneity and density of zinc deposits on both substrates. Several studies have been reported on the morphology and microstructure of Zn electrodeposits as a function of concentrations and applied voltages [70]. At variance with commercial plating baths that contain additives to improve the final appearance of the deposits, no additives were used in this work. The samples were used as working electrodes without masking so that the whole area was allowed for growth.

PS opals were covered with a thin film of SiO₂ to increase their mechanical strength. The synthesis of SiO₂ in the vapour phase at room temperature [57] shows important advantages over temperature treatments when adding strength to the opal. A mere 8% of the pore volume (2% of the total opal volume or a layer of SiO₂ around 1% of the radius) was revealed to be enough. Although both opals grown on ITO and n-Si substrates were covered with silica, the latter were immersed in diluted HF before acting as working electrodes to remove the native SiO₂. By doing so, the silica shell previously deposited was also partially dissolved. After this process the samples remained mechanically stable. PS spheres were then removed by means of oxygen plasma etching at room temperature.

The cyclic voltammetry and pulsing potential electrodeposition approaches are characterized by different ways of infiltration. Feature filling during the Zn deposition under cyclic conditions occurs by growth of an increasingly thicker layer following the spherical geometry of spheres. This approach yields metallic shells around the spheres that become thicker as electrodeposition time evolves. On the other hand, by means of pulsing potential electrodeposition, the electrodeposits nucleate in preferential sites on the substrate around the beads and grow to flood the space between spheres giving rise to smooth deposits in which opals finally become immersed. Figure 9 clarifies both ways of infiltration.

Figure 10 shows a SEM image of a zinc inverted opal grown under pulsing conditions. The image shows that after removing the initial template, highly ordered and hexagonal structures are obtained. Although not shown, similar SEM images are obtained for samples grown on ITO surfaces.

Relevant differences are observed in opals infilled with zinc by means of cyclic voltammetry. Figure 11 shows a (111) area from an opal infiltrated by cyclic voltammetry on an ITO surface (after oxygen plasma inversion). It can be clearly seen that the electrodeposits grow in a conformal way around the beads, replicating the spherical morphology. Thus, in a particular layer, triangular voids between adjacent spheres are usually empty and surrounded by zinc shells. However, further evolution of the electrodeposits with time evidence the complete infilling of pores in underneath layers which is a sign that the thickness of the deposit is larger in layers closer to the electrode (substrate). Since the type of growth is shared by opals grown on n-Si surfaces and those on ITO, the mode of infiltration is cathode independent.

This demonstrates the possibility of fabricating high quality metallic structures on semiconductor substrates.



Figure 9. Schematic description of the modes of infiltration of artificial opals. (a) Cyclic voltammetry and (b) square wave pulsating potential methods.



Figure 10. Cleaved side and surface of a zinc inverted opal on n-Si under optimized pulsing electrodeposition conditions.

Further improvement in the thickness control of the electrodeposits will help us to understand the optical behaviour of metallic opals. Since both ITO and silicon substrates are chemically treated to make them hydrophilic, their conductivities are reduced. By using less damaging treatments the final conductivity of the substrates could lead to more homogeneous deposits. In addition, a finer control over the thickness of the electrodeposits is necessary in order to fully understand the photonic properties of these systems. A thorough study is currently being carried out.

5. Vertical structures

In order to produce more and more complex materials not only the structure in the unit cell may be tackled as is the case when infiltrating the opal templates. Thus, one step further is the creation of a larger scale structure like the inclusion of defects in an otherwise perfect crystal or the lateral patterning in the plane of the sample. The former can be viewed as vertical and the latter as lateral engineering.



Figure 11. Zinc inverted opal obtained by means of cyclic voltammetry on the ITO surface. The scale bar is $2 \mu m$.



Figure 12. Methods for vertical engineering heterostructures. Thin film PS opals growth by convective self-assembly and SiO_2 growth by CVD can be combined in a number of ways with PS removal to render a wide range of vertical structures.

Here, a method which allows the fabrication of complex opal slab heterostructures for vertical engineering is shown. The method includes a multi-step process combining a high quality thickness controlled thin film opal growth by convective colloidal self-assembly [5] and silica growth by CVD [57]. The potential slab heterostructures that can be obtained by using this method are shown in figure 12. This includes the preparation of SiO₂/PS composite opals, inverse SiO₂ opals, heterostructures with different spheres sizes or engineered planar defects. Experimental evidence of the feasibility of the method as well as the optical properties shown by the fabricated structures is given by optical spectroscopy [71].

By using the CVD method, high precision in the filling fraction can be achieved through simple changes in the number of cycles used for each sample preparation. If PS spheres are removed by calcination a silica inverse opal is obtained. Silica grows on PS spheres forming uniform coatings of constant thickness in sample areas about 1 cm². These silica films



Figure 13. Planar defect comprising two silica inverted opals with a thin silica layer in between.

make a faithful replica of the PS spheres topography when eliminated.

A slab heterostructure can be produced in a way analogous to that of semiconductor heterojunctions by deposition of a new thin film opal made of different size spheres on top of a SiO₂/PS composite previously formed. If opal inversion is carried out by chemical etching instead of calcination, the thin silica layer in between the two opal stacks acts as a capping layer that avoids liquid penetration into the bottom opal preventing its inversion. The resulting slab heterostructure consists of SiO₂/PS opal situated at the bottom and an inverse silica opal on top.

Breaking of periodicity in a photonic crystal by the presence of defects produces the emergence of localized states for photons within the energy gap. This is analogous to donor or acceptor impurities added by doping in a semiconductor crystal. The spectral position of the localized state depends both on the refractive index and the volume of the defect, as well as the properties of the surrounding PC. It is possible to engineer intentional planar defects inside a photonic crystal, just creating a heterostructure made of two opal slabs of SiO_2/PS with the same sphere size, separated by a silica sheet of desired uniform thickness. An example is shown in figure 13.

A sharp resonance in the Bragg peak associated with the defect state appears in both transmittance and reflectance. Reflectance spectra of samples with the same thickness top and bottom layers (of 311 nm spheres) with varying silica film thickness inserted between them are shown in figure 14. The expected resonance appears at the conduction band edge and shifts across the photonic gap (Bragg peak) towards lower energy as the defect thickness increases. When it reaches the valence band edge the silica film thickness is of the same size as the opal spheres approximately. If the thickness of the silica film is larger than the sphere size the resonance re-enters the gap by the higher energy side. Due to the scale invariance of the Maxwell equations, the peak position in reduced units of the resonant mode relative to the centre of the Bragg peak should be dependent only on the defect thickness/lattice parameter ratio for similar systems.

The structures studied, although lacking a full PBG, could nevertheless be used for conventional light guiding by total internal reflection. Other materials can be explored to form the vertical heterostructures, not only inorganic but also from



Figure 14. Reflectance spectra of engineered defects in 311 nm SiO₂/PS opals. Silica film planar defect of (a) 130 nm (b), 230 nm and (c) 280 nm embedded in the photonic crystal. The defect thickness tunes the peak position across the gap starting at low wavelengths (high energies).



Figure 15. Description of the process. (a) Colloidal PMMA crystal film. (b) PMMA opal film infiltrated with SiO₂. (c) Patterned PMMA/SiO₂ composite performed by EBL. (d) Dissolution of the exposed PMMA.

organic compounds which will expand the possibilities of the system.

6. Lateral patterning by EBL

Self-assembly alone only provides uniform structuring which is apt for the production of 'homogeneous' materials. Should a further degree of complexity be required, other methods need to be explored. Lateral patterning in an otherwise homogeneous (albeit structured) material lends itself as a powerful tool that promises interesting results. Thus, a superperiodicity might be superimposed in a photonic crystal for instance, or a photonic circuit could be recorded. Here we present a technique towards the fabrication of selective inverted opals within a PMMA–SiO₂ composite following the procedure depicted in figure 15 [72]. Thin PMMA artificial opals were infiltrated with SiO₂ by CVD [57]. Patterning of the PMMA/SiO₂ composite is performed by electron beam lithography. After developing the exposed areas, selective inverted opals can be obtained. The PMMA–SiO₂ composites



Figure 16. Optical microscope image of triangles 50 μ m in side patterned on a PMMA opal on glass substrate.

provide better mechanical stability for the colloidal structure to withstand the e-beam lithography process, leading to selective inverted structures. Control of the writing depth by varying the electron acceleration voltage can be achieved [73]. In this work, high electron acceleration voltage has been used for SiO_2 infiltrated PMMA opals, allowing patterning of the whole depth of the opal film. In order to provide vertical confinement successive layered processing can be adopted.

Because of its potential application in creating structures for guiding and confinement of light, the method may find uses in the field of integrated optoelectronic circuits. In addition, the resulting channels combining micro- and nanofeatures may be very useful in the construction of microfluidic architectures [74, 75] for bionanotechnology purposes.

Patterning of the PMMA/SiO2 composite was performed by EBL at an accelerating voltage of 25 kV and exposure doses between 100 and 850 μ C cm⁻². The samples were developed in methyl isobutyl ketone and then placed in isopropanol to stop the developing process. The processing relies on the transparency of the thin SiO₂ layer to the electron beam. Figure 16 shows the optical microscope image (around 1 mm²) of triangular patterns obtained at 200 μ C cm⁻² on a PMMA– SiO₂ composite grown on a glass substrate. The optical contrast is associated with a change in the refractive index due to the EBL process, where SiO₂ inverted structures are laterally surrounded by the PMMA/SiO₂ composite. In order to monitor the recording process we measure reflectance after each step. The evolution in the optical response from bare, composite and patterned inverse opal is shown in figure 17. The sample thickness was estimated to be around 24 layers from Fabry-Perot fringes in reflectance spectra measured at normal incidence on the bare PMMA opal. Figures 17(a) and (b) show the reflectance spectrum from a bare PMMA opal and the red-shifted spectrum for the PMMA-SiO₂ composite after the CVD process respectively. Figure 17(c) shows the experimental reflectance of the opal after being exposed and subsequently developed. In a first approximation, this behaviour can be fairly accounted for by estimating the position of the Bragg peak through an averaged dielectric function.

In order to assess the power of the writing beam, different doses were used to perform a set of patterns at constant



Figure 17. Reflectance spectra taken from (a) bare PMMA opal, (b) PMMA/SiO₂ composite and (c) an exposed, developed and inverted area.



Figure 18. SEM micrograph of cleft edges of patterns obtained at (a) 600 μ C cm⁻² and (b) 100 μ C cm⁻².

electron acceleration voltage. Reflectance spectra indicate that at low dose (100 μ C cm⁻²) the EBL writing is incomplete and PMMA cores are only partly removed. Higher doses (350, 600 and 850 μ C cm⁻²) are capable of fully removing PMMA cores. Previous work in PMMA opals [73, 76] showed that there is a trade-off between the writing depth and lateral resolution and the control can be achieved by varying the electron acceleration voltage V_{acc}. High V_{acc} (25–30 kV) provides the best in plane resolution (to a fraction of a sphere) and the writing depth becomes as deep as the film. The case of silica infiltrated PMMA opal is much more complex and optimization of exposure parameters still requires further work.

SEM inspections of cleft edges were carried out after the developing process. In figure 18(a) (obtained at 600 μ C cm⁻²) some SiO₂ sphere shells can be observed that were broken upon cleaving. It is worth noting that only after cracking the silica shells is their interior visible, revealing the regions where inversion took place. At doses of 100 μ C cm⁻² (figure 18(b)) SEM observation shows that inverted structures are not achieved as PMMA is not fully dissolved. In this case, structural and optical properties indicate that PMMA is somehow modified by the process but not entirely dissolved.

This technique can be extended to include other materials, other structures and other phenomena. Structures can be fabricated in a first opal layer that can be buried by growing successive layers on top. Thus the perspective to create buried microchannels is enticing because it opens great expectations for microfluidic systems where the optical properties of a channel can be used to detect an analyte transported by biological fluid for instance.

7. Conclusions

In this work we have reviewed some aspects related to the fabrication of optical materials based on opals. Effects of disorder in the photonic response of thin opals have been studied by controlling the amounts of dopants of different sizes incorporated in the lattice.

Finite size effects of the crystal can be identified in several parameters pertaining to the opal systems that can be used to asses the infinite crystal behaviour of actual samples. In particular FWHM can be used to identify the threshold thickness where this behaviour starts.

Optical diffraction enables us to orient the samples, and realize angle resolved reflectivity to probe the optical properties along high symmetry directions. We present preliminary results of high energy optical response of artificial opals. Identification of phenomena responsible for the features appearing in the optical spectra is possible taking into account gaps and anticrossings of the bands. These can lead to explanation of diffractive phenomena that cannot be accounted for by the simple diffraction approach and require further study.

Accurate amounts of silicon, germanium, silica etc can be grown in the interior of opals by CVD. This allows for multilayer systems of semiconductors and insulators to be fabricated. The potential expands with the ability of different solvents to selectively remove different materials, which enlarges the possibilities to engineer the unit cell without changing the lattice and thus modifying the band structure. One further step is provided by the ability to grow metals in opals on semiconductor substrates like Zn, whose oxide presents such interesting properties. Electrodeposition lends itself most useful in this aim and can be used in two forms giving rise to two morphologies in the material grown.

A variety of structures based on vertically engineered artificial opals is presented, such as silica inverse opals and opal slab heterostructures, fabricated with an easy-to-implement multi-step method. This may combine thin film opal growth and CVD growth of silicon, germanium, silica etc with selective removal of the different materials to further expand the possibilities. More complex structures can be built up through the combination of spheres having different chemical nature (silica, PS or PMMA), or size; or by infilling with different materials with higher refractive index or appropriate optical properties as luminescence to use them in laser action. We have fabricated engineered planar defects inside a PC that can act as photonic microcavities. The tuning of the spectral position of the localized state is realized by changing the film thickness.

We have shown the potential of EBL for introduction of micrometre size three-dimensional extrinsic defects in PMMA–SiO₂ composites that can lead to lateral engineering of the photonic structures. These allow further growth and processing, leading to 3D buried structures. The approach proposed has genuine potential because it allows '*a posteriori*' control of a self-assembled structure.

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