Synthesis of inverse opals

F. Meseguer a,b,*, A. Blanco a,b, H. Míguez a,b, F. García-Santamaría a,b, M. Ibisate a,b, C. López a,b

a Unidad Asociada CSIC-UPV Edificio de Institutos II, Universidad Politécnica de Valencia, 46022 Valencia, Spain
b Instituto de Ciencia de Materiales de Madrid (CSIC), Campus de Cantoblanco, 28049 Madrid, Spain

Received 18 December 2000; accepted 30 August 2001

Abstract

Here we report different simple and inexpensive approaches to the fabrication of inverse opals originated from silica opal templates with sphere size in the range between 0.2 and 1.3 µm. The opal porous lattice is infiltrated with semiconductors (CdS, Ge, Si) as well as polymers by several methods such as chemical vapour deposition, chemical bath deposition, and hydrolysis. Afterwards the template is removed from the composite by a mild chemical etching method giving rise to an inverse opal. The periodicity of the template is chosen to guarantee that photonic gaps or pseudogaps are in the transparency region of the bulk-infiltrated material, which in the case of silicon and germanium can be easily integrated in the existing microelectronic technology. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Colloids; Inverse opals; Photonic crystals

1. Introduction

In the last half century the microelectronics technology has become one of the most powerful industries over the world permitting the development of integrated circuits at the submicron range. Most of these devices are based on silicon, a semiconductor material in which electrons are allowed to stay in certain energy regions separated by forbidden gaps. However, in the 60s, after the invention of the optical fibre, it was shown that photons could be efficiently used as information carriers as well with an important advantage; they would be much more efficient in the transport of information since they have neither mass nor charge. However, optical devices cannot (so far) process information as electronic devices do.

In the last decade a new material called photonic crystal (PC) has seen the light in the photonic laboratories. Photons' behaviour in PCs is very much like electrons' in semiconductors [1,2]: the photonic band structure may show forbidden gaps in which photons cannot exist, therefore many of the devices and concepts based on the band gap phenomena may be extended to PC. Recently, new and revolutionary devices such as optical transistors have been proposed [3]. If large-scale three-dimensional (3D) PCs working at the visible or near infrared (NIR) regions were achievable, new photonic devices such as sharp
bend optical fibres, photonic transistors, high efficiency lasers would be feasible in a short term. It would open the door to a new technology in which the photonic integrated circuit is the next step, and the all-photonic computer being the main goal.

However, the obstacles to obtain this kind of PCs with a complete gap in the desired spectral region represent a big challenge. PCs can be defined as mesoporous materials with a periodic distribution of submicrometric pores. Mainly, there are two parameters that determine the existence of a photonic gap. First, the refractive index contrast, defined as the ratio between the refractive indices of the material and the surrounding substance; secondly, the filling fraction, defined as the percentage volume occupied by the voids, is a very important parameter. Also, the topology of the structure will be decisive to explain the band structure. The most extended method to fabricate them is the micro-machining of a bulk material by lithographic methods, but this impressive approach is so expensive and time consuming that only a few monolayers are technically achievable so far [4,5].

An alternative route concerns self assembly methods to achieve opal like structures [6–9]. Opals are gemstones formed through the settlement of monodisperse submicrometric silica particles. As a consequence of periodicity they show opalescence colours that come from the Bragg diffraction of the periodic distribution of particles. Bragg diffraction constitutes the fingerprint of photonic band gap (PBG) properties. However, theory predicts that inverse opals would show much better PBG properties than direct opals. For inverse opals that can be regarded as the negative replica of opals, we have a collection of micrometric spherical cavities surrounded by a high refractive index material, in which both the cavities and the high refractive material is connected throughout the structure. Then, the main goal in many laboratories [10–16] is the fabrication of inverse opals.

Our approach lies on the synthesis of semiconductors and insulators within the mesoporous voids of artificial opals. This method is very attractive because it is easy and cheap. Here, we report on the fabrication of inverse opals made of different materials such as polymers, CdS, Ge [15] and silicon [16]. We will summarise the different steps to achieve the inverse matrix.

First, we will report on the synthesis of bare opals, based on silica, that are used as templates to fabricate inverted structures. Also, we will report on both the various infiltration methods and the fabrication of the inverse photonic lattice. The reflectance and transmission properties of these templates that will not be reported here, can be well accounted for by calculations based on transfer matrix algorithm and/or by an analysis of the photonic band structure [17–19].

2. Bare opals

Template fabrication must accomplish several conditions: a high quality of opals is required since uncontrolled defects drastically reduce the gap width and the intensity of the reflectance peaks. Another point is that photonic properties must appear in the transparency region of the material that will form the inverse structure. For instance, the gaps of silicon inverse opals should appear at a wavelength larger than 1.1 μm, the absorption edge for bulk silicon. The position, in terms of frequency, for optical gaps can be controlled by the inverse opal periodicity tuned through the size of the silica particle of templates. In the case of silicon (germanium) inverse opals, the diameter of the silica sphere must be above 0.85 (1.2) μm.

The fabrication method for silica FCC templates of small lattice parameter (between 0.2 and 0.6 μm) has been reported in the literature [20–22]. Here, we have focussed on the method of fabrication of larger lattice parameter (between 0.6 and 1.3 μm) that is of paramount importance in the fabrication of semiconductor inverse opals such as Ge and Si.

The fabrication method involves several steps.

2.1. Synthesis of monodisperse silica particles

We have used a modified Stöber method in which we make the synthesis process in a suspen-
sion of smaller silica particles (around 500 nm in size) that act as seeds in the synthesis process. If needed, the synthesis process is repeated several times and the spheres homogeneously increase in size to values of 1.3 µm, monodispersity being better than 5%.

2.2. Settlement processes

Small particles (below 600 nm) are settled by natural sedimentation, thanks to gravity. The entropy of the system is such that the minimum energy positions correspond to those of an FCC arrangement. However, this process fails with suspensions of larger particles (above 600 nm) and there is no order. Two methods have been developed to slow down the settling process and therefore, favour FCC ordering. The first one, useful for particles up to 900 nm, relies on the use of electrophoretical deposition [23] in which sedimentation velocity was controlled through the application of a reverse electric field. In the second one we use mixtures of water and other solvents and co-solvents such as ethyleneglycol, glycerol and acetone to increase the viscosity.

After sedimentation, the opal is dried at different temperatures ranging from 60 to 120 °C. Temperature plays an important role in the crystallisation process because it influences the particle diffusion in the suspension.

2.3. Sintering process

The sintering process endows the opals with mechanical stability and connects every sphere with its neighbours; the success of the inverse opal fabrication strongly depends on the connectivity between silica particles provided by the sintering process [24]. Such treatment also permits to control the opal void volume, a crucial parameter in the search for optimal semiconductor infilling and, therefore, the maximum gap width. Fig. 1 shows a scanning electron microscope (SEM) image of the cleaved edge of an opal with silica particles of 1.3 µm. It has been settled in a suspension with a mixture of co-solvents (water and ethyleneglycol). Different terraces with (111) facets can be observed.

Uncontrolled defects can reduce gap widths as has been recently calculated by Li and Zhang [25].

Fig. 1. SEM image of the cleft edge of a bare opal with silica particles of 1.3 µm. One can see different terraces with (111) facets.
Although the study of uncontrolled defects in our structure and their influence on the optical properties of opals is out of the goal of this paper, we would like to comment some general aspects of defects control. The number of defects depends on two main parameters: particle monodispersity and the size of particles. Larger monodispersity implies lesser number of defects. Also when particles are large in size, the probability to have misplacements in the particle settlement increases. Recently, several groups have shown various methods to fabricate opal thin films with very limited number of defects [26 – 28]. Although these methods concern small silica opals, it can be a route to the control of the number of defects in the structures.

3. Polymer inverse opals

The inverse polymer opal, made of epoxy resin, is achieved in a manner similar to those previously reported by Park and Xia [29]. The polymer infiltrated was obtained by the polymerisation of an epoxy resin (bisphenol-A–epichlorhydrin, Struers) in the presence of a catalyst (tri-ethylenetetramine, Struers). In this way a viscous fluid is obtained in which the opals is immersed. The liquid soaks the opal and when the diffusion is total the opal turns transparent as a consequence of partial index matching between silica and polymer. In about 12 h the polymerisation is completed and the shrinkage between the liquid and the solid is less than 5%. This allows a good filling and a very good connection of the infiltrated material. The polymer refractive index was measured by the prism’s minimum deviation angle and resulted to be $n = 1.609 \pm 0.005$.

Finally, the silica is removed from the composite material by means of a 1% HF aqueous solution. It was found that 12 h in this solution completely dissolves the silica leaving a neat inverse polymer opal. The polymer is not affected by the silica etching. The necks connecting the silica spheres (resulting from the sintering process) act as channels through which the etchant flows. Also, the good connectivity provided by the sintering allows it to reach the whole structure and fully etch away the silica skeleton. Fig. 2 shows SEM images of the cleft edge of both polymer–opal composite (Fig. 2(A)) and polymer inverse opal (Fig. 2(B)) that results from an opal template of 850 nm particles. The inset of Fig. 2(A) shows some polymer voids where the silica spheres are removed. It allows seeing the small windows connecting different layers. The number of windows...
(four in the case of (100) face) gives a clue to the symmetry of the crystallographic facet. One can conclude that polymer penetrates easily throughout the void lattice, and it fills completely the empty space between silica spheres. The infiltration process is such that the inverted lattice can be regarded as the negative replica of the bare opal. This is due to the fact that the specific volume change on polymerisation (\(< 5\%\)) allows a good replica of the template. Fig. 2(B) shows an example of the resulting structure after the etching has been performed. The (111) planes are identified by the symmetry and the quality of the replica can be appreciated. The inset displays the structure of these channels for the (111) facet that are three in number connecting the layer underneath plus six connecting the surrounding spheres. Of course, the latter six can only be seen in sections through the equatorial plane of the spheres.

The study of the bare opal along with the opal-composite and the inverse opal allows us to make a comparison between different opal-like structures with the same structure and the lattice constant but different refractive index contrast [30].

4. CdS inverse opals

CdS has very often been infiltrated in opals due to its lucent properties in the visible range, showing very exciting results in optical gain and spontaneous emission inhibition [31,32]. Although CdS inverted opals do not have a full PBG, their high refractive index contrast (2.5, the contrast threshold for gap opening being 2.8) should increase those interesting effects.

CdS is grown by means of a chemical bath deposition (CBD), the method in which the opaline sample is immersed in different solutions. The process consists of two stages which are repeated several times. During the first stage, the opal is immersed in a 2.5 \(\times\) 10\(^{-2}\) M CdSO\(_4\) aqueous solution. After that, the opal/CdSO\(_4\) is placed in a 3.5 \(\times\) 10\(^{-2}\) M \(\text{S-C(NH}_2\text{)}_2\) aqueous solution. The time for each stage depends on the particular experimental requirements. Both stages take place at 60 °C and are catalysed by ammonia. Employing these growth conditions, the amount of CdS inside the opal is controlled as well as the growth on the external sample surface, thus preventing the eventual blocking of the growth inside the opaline structure. The CdS amount inside the opal matrix can be followed and controlled by optical measurements. After some repeated cycles, nearly 100% CdS infilled opals can be obtained. Once the full infiltration is achieved, a soft etching process, by dipping the sample into a 1% diluted HF solution, allows removing the silica spheres. Fig. 3 shows an SEM image of the internal (111) facet of CdS inverse opal with 385 nm diameter hollow spheres. As can be directly seen in the inset of Fig. 3, CdS grows in the form of grains which cover the silica spheres occupying all the free space available, and more important, the FCC ordered structure is conserved.

5. Ge inverse opals

Ge is transparent to infrared radiation (below 0.67 eV at room temperature) and it presents an extremely high refractive index contrast (\(n = 4\)). This makes Ge inverse opals one of the most promising PBG material made of a semiconductor. We have used two different infiltration methods: the first one that involves a hydrolysis and then a reduction process at high temperatures (above 500 °C). In this case we have used opal templates with silica particles of 870 nm. We take advantage of the high thermal and the mechanical stability of the template lattice to achieve the inverse Ge matrix. It involves several stages [15]. First, a germanium precursor (Ge(OCH\(_3\))\(_4\)) is infiltrated in the opal voids. The alkoxide is allowed to completely infill the template. Secondly, through a hydrolysis process we obtain GeO\(_2\). Fig. 4 (left) shows opal voids in filled with small (100 nm) GeO\(_2\) microcrystallites. Ge is obtained by the reduction process at 550 °C. As a consequence of the different reactions and also because of the Ge aggregation process, Ge does not completely fill the opal voids. In order to increase the infiltration percentage and, also, to give connectivity to the Ge macro-lattice, opals are subjected to several rounds of GeO\(_2\) and Ge formation.
processes as described above. After five cycles, Ge shows connectivity in ranges larger than the single crystal domain of the bare templates (see Fig. 4, centre). Finally, Ge infiltrated opals are chemically etched to remove silica particles with the same method used for the other inverse opals. In this way, we seek to remove the SiO$_2$ spheres from the composite and to obtain Ge inverse opals. Fig. 4 (right) shows SEM images of the cleft edge of a Ge inverse lattice. At variance with the case of the polymer inverse opal (where polymer forms spherical shells around the air voids that are interconnected through small windows), Ge forms an interconnected grain mesh. This is very clearly shown in the right image of Fig. 4. Here a (100) facet as well as the layer underneath can clearly be seen through the large windows of the spherical holes of the upper layer. It can be established that the repeated cycle synthesis, with the aggregation of crystals during the reduction process, furnishes the germanium that is formed within the bare opal with a high connectivity. This provided, the germanium lattice does not collapse on dilution of the silica matrix in spite of being a highly open structure. Therefore, the long range FCC order inherited from the template is preserved in the Ge inverse opals. After etching, samples maintain the same overall volume of the starting bare opal. Defects such as vacancies and dislocations do not disturb the mechanical stability of the system since Ge is also filling them.

A new method, based on chemical vapour deposition (CVD) technique has been developed to increase the homogeneity of Ge layer [33]. It guarantees that no additional disorder comes from Ge growth. This step is crucial in the inverse opal fabrication because, as the refractive index contrast of the inverted structure is enormous, any residual disorder from the infiltration method can diminish dramatically PBG properties. We have used templates of larger spheres (1200 nm) to allow for a full gap to appear at a frequency below the absorption edge of bulk Ge ($\lambda \geq 1850$ nm at room temperature). Germanium is infiltrated by CVD. We have used digermane (Ge$_2$H$_6$) as precursor. First, the germanium pre-

Fig. 3. SEM image of a 385 nm sphere size inverse opal of CdS. A (111) internal facet is shown. The inset is a detail of the structure where small windows connecting the removed spheres can be seen as well.
cursor, $\text{Ge}_2\text{H}_6$ gas is infiltrated into the template placed in a high vacuum cell ($5 \times 10^{-6}$ torr), and then, the sample cell is cooled by using liquid nitrogen. The low temperature of the reactor gives rise to the condensation of the precursor into the opal void volume, the gas pressure being varied between 300 and 1000 torr. Secondly, the reactor is heated up to a temperature at which the decomposition of $\text{Ge}_2\text{H}_6$ takes place to give Ge and $\text{H}_2$. The range of temperatures employed was $473 \text{ K} < T < 623 \text{ K}$. Finally, we submit the sample to an annealing process at 770 K to obtain microcrystalline germanium. Raman experiments show a narrow peak (bandwidth of 13 cm$^{-1}$) at 298 cm$^{-1}$. This is the fingerprint of the microcrystalline quality of the Ge infiltrated, and it is consistent with the information obtained from X-ray diffraction experiments.

A structural analysis of the sample performed by SEM reveals that the growth takes place layer by layer, which gives rise to a uniform shell coating of the silica spheres. This treatment also allows a uniform infiltration along the whole silica template, as was checked by observing the fractured edges of the samples (see Fig. 5(A)). From these cleft edges we can measure the germanium coating thickness and the degree of sintering of the template. Thus, we can estimate the percentage of infiltration, which can be controlled by varying the $\text{Ge}_2\text{H}_6$ pressure and the deposition temperature. In general, through this method we can control the Ge filling fraction up to values near 100% of the template pore volume.

The infiltrated samples are later etched in a similar manner as in the previous cases. By this procedure, we obtain a germanium inverse opal which has inherited the long range FCC order of the original template. Big windows interconnecting the spherical cavities reflect the penetration of the particles in the template (see Fig. 5(B)). High amplification SEM image of the inverted sample indicates a very homogeneous Ge layer (see Fig. 5(C)).

6. Si inverse opals

Among all materials silicon inverse opals are the most promising in the PBG technology. First, silicon has a high refractive index (3.5) enough to guarantee a sizeable full gap (up to 9% [18]) for frequencies in the transparency region of bulk silicon (below 1.125 eV). Secondly, silicon inverse opals can be easily tailored to work in the frequency ranges of interest for the communication technology. For instance, full gaps at around 1.5 μm have been predicted in silicon inverse opals with 1.2 μm lattice parameter [18]. Thirdly, both silicon–silica and silicon inverse structure can easily be implemented in the present photonic technology. Therefore, the integration of several optical devices can easily be performed.

Here, we report on the method of fabrication of silicon inverse opals in which full gap appears near 1.5 μm [16]. We have used FCC bare opals with 0.87 μm silica particle with a typical single domain value of 100 μm as template. Optical
properties of templates and the comparison with theoretical calculations allow us to determine both periodicity and opal void volume available for a subsequent silicon infiltration.

Silicon is grown inside the voids of the opal template by CVD technique using disilane (Si₂H₆) gas as a precursor [34]. The temperature is varied from 250 °C for low infilling samples to 350 °C for high infilling ones. Theory predicts that the maximum PBG is obtained with a 90–97% infilling of the opal voids in the form of a uniform, thick, wetting layer on the silica surfaces. After the growth of silicon, the samples are heated to 600 °C in order to improve the semiconductor crystallisation and to allow diffusion of silicon inside the void structure. The silica template is subsequently removed in a similar manner as reported above. Templates have been infiltrated with different amounts of silicon ranging from 60% up to 100% and monitored by measuring their optical properties (reflectance and transmission).

Fig. 6 shows SEM images of cleft edges of both silicon–silica template and the inverse lattice. One can see (Fig. 6, left) that silicon grows layer by layer on the silica surface. It forms an interconnected network of shells around the silica particles that is mechanically stable after the etching process (see Fig. 6, right). Silicon inverse opals can be regarded as a mesoporous lattice formed by spherical air cavities. Adjacent cavities are connected through windows (of circular shape in most cases). These windows, as occurring in polymer inverse opals, have their origin in the connection of touching silica spheres after the sintering process of the opal template. Silicon inverse opals put together the two essential conditions for full gap appearance. First, the refractive index contrast (as in the case of Ge inverse opals) is above the threshold value (2.8 for FCC lattice). Secondly, the size of the silica sphere that forms the opal template is above a minimum value to guarantee that full gap appears in the transparency region of bulk silicon, i.e. at a wavelength region larger than 1.1 μm, the absorption edge of silicon at room temperature.

Optical spectra and theoretical calculations of silicon–silica composites and inverted silicon opals have been reported elsewhere [16].

In summary, here, we have shown several examples of inverse opals with different refractive
index contrast ranging from 1.6 (for the inverse polymer opal) up to 4 (for the germanium inverse opal), the largest index inverse opal achieved so far at optical wavelengths. The fabrication methods used here are easy and inexpensive and it constitutes a very promising route in photonic technology. In all cases (CdS, polymer, Ge, and Si) we are able to control the infiltration percentage from 0% to values close to 100%.

Acknowledgements

This work has been partially financed by the Fundación Ramón Areces, the Spanish CICyT project MAT97-0698-C04 and European Community project IST-1999-19009. We would like to acknowledge the fruitful collaboration of several laboratories from whom we have learned different expertises. Professors Ozin, John, and van Driel groups at the University of Toronto made real the silicon infiltration, optical characterisation and theoretical calculations of silicon inverse opals. Also acknowledged the fruitful discussions and theoretical feedback from Professor Sanchez-Dehesa group at the Universidad Autonoma de Madrid.

References