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Template assisted fabrication technique towards Si-inverse opals with diamond structure

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Abstract

A method to fabricate silicon (Si) inverse opals with diamond structure is introduced. The method is based on the arrangement of silica particles in a template consisting of Si pillars periodically distributed. The profile of the pillars is specially designed to induce the self-organized growth of the particles in a diamond lattice along the (1 1 0) direction. Afterwards, the inverse structure is achieved by infiltrating the opal with Si and subsequently removing the silica by chemical means. Different from a former approach based on robotic manipulation, this method allows the fabrication of large samples available for integration in planar photonic devices.

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The search for fabrication methods of three-dimensional (3D) photonic crystals (PCs) with length scale in the optical regime and with large absolute band gaps is a major target in materials science. From all methods so far reported, lithography [1,2] and colloidal templating [3,4] have demonstrated reliable routes. However, both technologies suffer from certain disadvantages that forbid their technological implementation on a mass scale. On one hand, lithography becomes a very tricky and quite expensive technology when one must to stack the number of monolayers needed to get the full band gap formation. On the other hand, colloidal template produces only face centered cubic (fcc) close-packed structures. These structures have reduced gaps between higher bands and, consequently, a great sensitivity to unwanted intrinsic

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defects in their construction. Other techniques like holographic lithography [5] or nanorobotic manipulation [6], although very promising, are still far to achieve full PC band gap materials.

Vectorial growth with lithographic patterned substrates has shown as a very useful technique to build up fcc colloidal thin films [7,8] and fibers [9] in which the control on the facet orientation as well as the formation of small aggregates is achieved [10,11]. However these methods are restricted to close-packed lattices. Templating growth methods that use either a pattering substrate [12] or the surface of a colloidal crystal as template for the layer-by-layer growth of binary colloidal crystals [13] are suitable to build up non close-packed structures. Still, as the pattering is quasi two-dimensional (i.e. the depth profile is of the order of the particle size), they solely have direct control on the growth of the first layers. Therefore, these methods are only useful for restricted type of lattices. This fact constitutes a drawback when the growth of very open structures, like that of diamond, which could act as a precursor of PCs with full band gaps, is envisaged.

The comments above indicate an enormous interest to find methods to pack colloidal particles in diamond-like crystal lattices. Here, we propose one such method to allow fabrication of opal inverse structures with a diamond lattice. The idea behind the method is quite simple and it is represented in Fig. 1, which gives

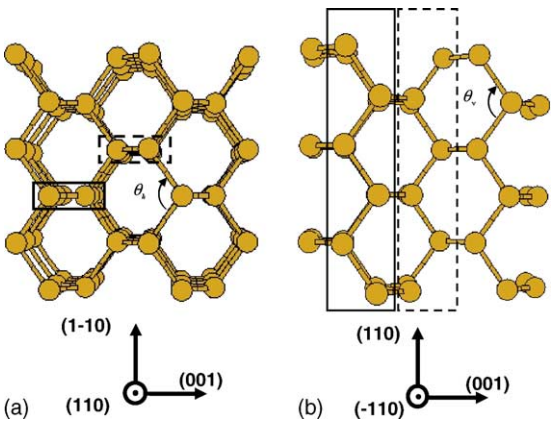

Fig. 1. Schematic view of a diamond lattice along (a) (1 −1 0) and (b) (1 1 0) directions. The circles represent particles and cylinders between particles represent the interparticle contact points. The bond angles are θ_h, θ_v for (1 1 0) and (1 −1 0) directions, respectively. The bonds enclosed by rectangles in (a) correspond to the zigzag string of atoms enclosed in the rectangles of (b).

an ''atomic'' illustration of the diamond structure along the (1 1 0) direction.

The ''atoms'' (spheres in Fig. 1) represent the colloidal particles. The ''bonds'' (cylinders in Fig. 1) define the touching points between particles in the colloidal structure. Two important facts can be extracted from Fig. 1. First, Fig. 1a shows the diamond structure of touching spheres presents, in the [1 0 0] plane, a periodic distribution of channels bounded by the tetrahedral bonds of the lattice. Second, Fig. 1b demonstrates that the diamond structure along the (1 1 0) direction looks like a periodic distribution of strings of spheres distributed in a zigzag manner; the angles between nearest-neighbors spheres, θ_h and θ_v in Fig. 1, being 109.47°. A closer look at the lattice also reveals that two types of zigzag strings can be defined; one with left-hand symmetry, the other with right-hand symmetry. Both are enclosed by continuous and broken rectangles, respectively, in Fig. 1b.

The proposal concerns the use of templates with a quasi-3D profile wherein the particles are arranged. In brief, the method is as follows. First, a template is carefully designed to address the growth of the diamond lattice along the (1 1 0) direction. The template consists of a periodic distribution of large aspect ratio Si pillars in air. Second, a colloidal suspension of monodispersed silica particles is infiltrated in the free space of the pillars of the template. After the spheres settlement, a diamond lattice of silica particles embedded in a lattice of Si pillars is obtained. Third, the remaining structure is then infiltrated by Si and, finally, the removal of silica spheres produces the inverse opal. Below, we explain step-by-step the overall process.

Regarding the template, it would be made of pillars that fill up the channels of the diamond structure along the (1 1 0) direction. Fig. 2 shows a schematic plot of the cross sectional view of the template on the [1 1 0] plane (Fig. 2a) as well as details of a Si-pillar (Fig. 2b). In order to settle the silica particles in the correct manner, the parameters of the template must be properly chosen. If ϕ defines the sphere diameter, the first layer is deposited on the square region defined by $d_1 = d_2 = \phi$ (Fig. 2a). The others parameters of the template are the distances $d_3 = \phi/\sqrt{3}$ and $d_4 = \phi[1 - \sqrt{(2/3)}]$. White zones in Fig. 2a represent the kinks at the bottom of the pillars (see Fig. 2b). The purpose of these kinks is to address the settlement of the first layer

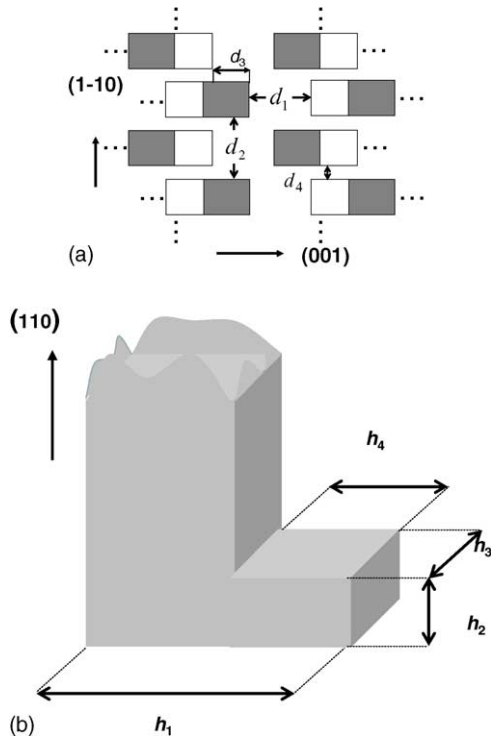

Fig. 2. (a) Top view of the template. The section of each pillar has a rectangular shape, where the dashed zone represents the taller part of the pillar and the white region defines the kink at the bottom of each pillar. (b) The distances d_1, d_2, d_3, and d_4 are given in the text. Detail of a pillar with the parameters value given by: $h_1 = \phi[(4/\sqrt{3}) - 1]$; $h_2 \leq \phi/\sqrt{(2/3)}$; $h_3 = \phi[\sqrt{(8/3)} - 1]$, $h_4 = \phi/\sqrt{3}$. ϕ represents the sphere diameter.

of spheres in such a manner to induce the growth of the zigzag strings along the (1 1 0) direction as it occurs in the diamond lattice. The position of the kink with respect to the pillar induces the hand symmetry (left or right) of the sphere string along the (1 1 0) direction. As the orientation of kinks with respect to the pillars alternates periodically along the (1 −1 0) direction, the zigzag orientation of strings would also change periodically along the (1 −1 0) direction. Fig. 3 shows a detailed schematic representation of the diamond lattice growth in this template, where the two types of zigzag strings along the (1 1 0)-direction are clearly illustrated. The appropriate distribution of pillars, as well as the relative position of their associated kinks, would induce colloidal particles to self-assemble in a diamond lattice. The template we are proposing could be constructed by available lithographic techniques. The main drawback in these techniques is the depth profile that in standard silicon processing technology achieves values around 10:1 [14]; i.e., the depth is ten times larger than the base of the pillar. Recently, submicron size pillars with aspect ratio values as large as 25:1 have been obtained by combining e-beam lithography and anisotropic attack [15]. An accurate control of the arrangement of pillars is critical for a proper particle ordering. However, the pillar shape is not so important. Small modifications of the shape of the pillars, unavoidable in the etching process, would probably give reasonable results in the template-assisted sedimentation process.

Once the template is reached, the infiltration and the ordering of particles in the silicon template could be solved by using capillary-like techniques recently developed to induce colloidal crystallization in structures of arbitrary shape and geometry [16]. Therefore, at variance to former methods, in this case the template directs the ordering of the whole diamond structure. The full infiltration and deposition of silica spheres in a Si template results in a structure consisting of a diamond lattice of spheres embedded in a lattice of Si pillars. In other words, a vectorial growth of the colloidal crystal would be achieved. Within the huge aspect ratio templates [15], diamond colloidal crystals of about 50 layers should be possible. It is important to emphasize that although the shape of meniscus may be affected by the presence of the substrates (composed by pillars), it would affect homogeneously the entire system because the distance between pillars is much smaller than the meniscus length scale (several hundred micrometers).

Now, a photonic crystal with a complete band gap could be obtained by creating the corresponding inverse opal structure. First, a chemical vapor deposition (CVD) method [3] could be employed to infiltrate the entire structure (silica spheres plus silicon template) with Si. Next, silica particles could selectively be removed with an HF acid attack.

Since the ultimate goal is to obtain a structure with a complete band gap as large as possible, it would be necessary to optimise the air filling fraction value of the inverse structure to obtain the tailored gap [17]. A diamond lattice of touching silica spheres has a small filling fraction (34%) to be used as a template for inverse structures with a sizable photonic gap. For instance, for a Si-inverse diamond opal having a void

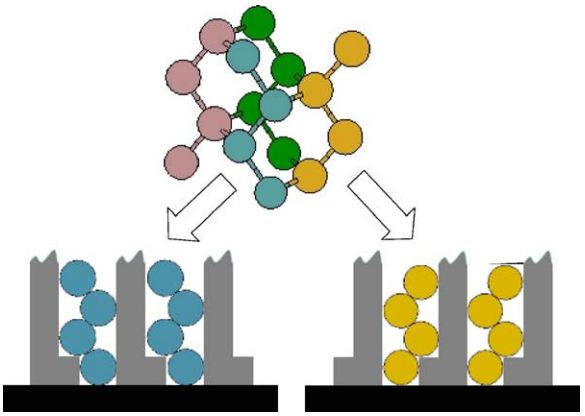

Fig. 3. Schematic view of structure made of a diamond colloidal crystal inside the Si template. The two types of zigzag strings forming the diamond lattice along the (1 1 0)-growth direction are shown.

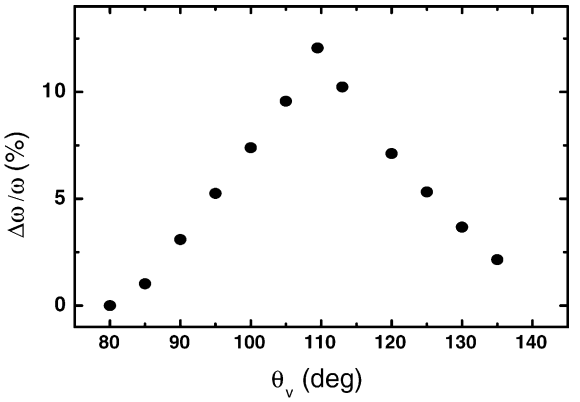

Fig. 4. Gap to midgap ratio ($\Delta\omega/\omega$) for different values of the bonding angle θ_v (see Fig. 1) of the diamond lattice. Filling fraction of the air voids is kept constant to 50%. Maximum value (12%) corresponds to the perfect lattice: θ_v =109.47°.

volume of 50%, a complete band gap as high as 12% is predicted [18]. This can be achieved in the second step of the process by increasing the filling fraction of silica lattice. It can be performed through a CVD silica infiltration process [19] after the particle settlement.

An important issue to be considered is the influence of the particle size in the bonding angles; i.e., θ_h and θ_v defined in Fig. 1. In other words, the particles in a colloid suspension actually are not completely monodispersed and, therefore, defects in the angles of the zigzag strings are expected when particles of different sizes are in contact inside the template. The angles between neighbor particles would vary around 109.47°, the common angle in the perfect diamond lattice. This would distort the original diamond lattice and change the value of the PC gaps. Therefore, it is very important to study the influence of the full gap formation on the distortion of the bonding angle.

We have theoretically analyzed the robustness of the photonic bandgap against variations of the angles in the tetrahedral coordination of the voids in the inverse Si opal. A plane wave expansion method was employed to obtain the 3D photonic bands [20]. For Si (silica) we have used a value of 11.9 (2.1) for the dielectric function. As θ_v and θ_h are equivalent to each other, we have calculated the influence of θ_v on the gap value. Fig. 4 shows the behavior of the gap to midgap ratio, $\Delta\omega/\omega$, of the full band gap, for different values of the bonding angle θ_v. A 50% for the filling fraction air voids was assumed. As expected, the full band gap that exists between the second and the third bands reaches the maximum value of $\Delta\omega/\omega$ for the perfect structure, that corresponds to a bonding angle of 109.47, when no distortion of the tetrahedral angles exists. Also, notice that slight variations of the ideal angle produce a substantial decrease of $\Delta\omega/\omega$. A simple calculation indicates that the dispersion of the bonding angles is about twice the particle dispersion. Even though with the available monodispersity values of the colloidal particles, one can achieve inverse diamond structures with sizable gaps around 9%. For example, since silica spheres with sizes between 200 and 600 have a typical standard deviation of 3% [21], the expected dispersion of the bonding angle is ±6° around the maximum in Fig. 4. Silica spheres, with very small dispersion values, recently synthesized [22] could help to increase the potentiality of the method proposed here.

Summarizing, we have proposed a method to fabricate large samples of Si inverse opals with a diamond-like structure. This method, based on template-assisted growth of silica particles in a diamond lattice, can be extended to any other semiconductor compound with high dielectric constant, such as germanium, if the fabrication of the template is feasible. Since the template could be developed by planar technologies, the procedure presented here would allow the integration of 3D photonic crystals, based on opals in planar photonic devices.

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References

[1] N. Yamamoto, S. Noda, A. Chutinan, Jpn. J. Appl. Phys. 37 (1998) 1052.
[2] J.G. Fleming, S.-Y. Lin, Opt. Lett. 24 (1999) 49.
[3] A. Blanco, E. Chomski, S. Grabtchak, M. Ibisate, S. John, S.W. Leonard, C. López, F. Meseguer, H. Míguez, J.P. Mondia, G. Ozin, O. Toader, H.M. van Driel, Nature 405 (2000) 437.
[4] Y.A. Vlasov, X. Bo, J.C. Sturm, D. Norris, Nature 414 (2001) 289.
[5] M. Campbell, D.N. Sharp, M.T. Harrison, R.G. Denning, A.J. Turberfield, Nature 404 (2000) 53.
[6] F. García-Santamaría, H.T. Miyazaki, A. Urquía, M. Ibisate, M. Belmonte, N. Shinya, F. Meseguer, C. López, Adv. Mater. 14 (2002) 1144.
[7] Y. Yin, Y. Xia, Adv. Mater. 14 (2002) 605.
[8] P. Jiang, J.F. Bertone, K.S. Hwang, V.L. Colvin, Chem. Mater. 11 (1999) 2132.
[9] S.M. Yang, H. Míguez, G.A. Ozin, Adv. Funct. Mater. 12 (2002) 425.
[10] Y. Lu, Y. Yin, Y. Xia, Adv. Mater. 13 (2001) 405.
[11] G.A. Ozin, S.M. Yang, Adv. Funct. Mater. 11 (2001) 95.
[12] A. van Blaaderen, R. Ruel, P. Wiltzius, Nature 385 (1997) 321.
[13] K.P. Velikov, C.C. Christanova, R.P.A. Dullens, A. van Blaaderen, Science 296 (2002) 106.
[14] G. Sanchez, private communication.
[15] M.J.A. de Dood, L.H. Sloof, T.M. Hensen, D.L.J. Vossen, A. Moroz, T. Zijlstra, E.W.J.M. van der Drift, A. van Blaaderen, A. Polman, Photonic crystals and light localization, in: C.M. Soukoulis (Ed.), in: Proceedings of Nato School, Crete Greece, vol. 563, NATO Science Series, Kluwer Academic Publishers, June 2000, p. 555.
[16] P. Ferrand, M.J. Minty, M. Egen, J. Ahopelto, R. Zentel, S.G. Romanov, C.M. Sotomayor Torres, Nanotechnology 14 (2003) 323.
[17] K.M. Ho, C.T. Chan, C.M. Soukoulis, Phys. Rev. Lett. 65 (1990) 3152.
[18] F. Garcia-Santamaria, C. López, F. Meseguer, F. López-Tejeira, J. Sánchez-Dehesa, H.T. Miyazaki, Appl. Phys. Lett. 79 (2001) 2309.
[19] H. Míguez, N. Tetreault, B. Hatton, S.M. Yang, D. Perovic, G.A. Ozin, Chem. Commun. (2002) 2736.
[20] S.G. Johnson, J.D. Joannopoulos, Opt. Express 8 (2001) 173.
[21] M. Ibisate, Ph.D. Thesis, Universidad Autonoma de Madrid, 2003.
[22] L.H. Sloof, M.J.A. de Dood, A. van Blaaderen, A. Polman, Appl. Phys. Lett. 76 (2000) 3682.