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► **To cite this version:**

Patrick Ferrand, M. Egen, R. Zentel, J. Seekamp, S. G. Romanov, et al.. Structuring of self-assembled three-dimensional photonic crystals by electron-beam lithography. *Applied Physics Letters*, 2003, 83 (25), pp.5289-5291. 10.1063/1.1636271 . hal-00272373

HAL Id: hal-00272373

<https://hal.science/hal-00272373v1>

Submitted on 15 Apr 2015

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Structuring of self-assembled three-dimensional photonic crystals by direct electron-beam lithography

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(Received 11 August 2003; accepted 31 October 2003)

An electron-beam lithography technique is described capable of structuring three-dimensional self-assembled photonic crystals. It is shown that the control of the writing depth can be achieved by varying the electron acceleration voltage. Microscopic structures with a depth from 0.4 up to 2 μm are fabricated with a typical lateral resolution of 0.4 μm . The relevance of this technique for the fabrication of deterministic defects sites in opal photonic crystals is discussed and its extension towards buried structures is suggested. © 2003 American Institute of Physics.

[DOI: 10.1063/1.1636271]

Periodic refractive index materials allow the manipulation of photons in analogy to the manipulation of electrons by the periodic potential of semiconductors.¹ Due to the potential to control light emission, routing, and filtering, these photonic crystals (PhCs) constitute a promising approach towards a future generation of optoelectronic devices, combining high integration and high-speed processing. In this context, research on self-assembled PhCs (e.g., opals), gained much attention since this approach allows the realization of genuine three-dimensional (3D) PhCs.² It is probably the only approach able to provide a full control of light emission and propagation, with submicron feature sizes required by optical wavelengths. Compared to competing techniques involving micromanipulation³ or layer-by-layer growth,⁴ self-assembly is significantly more cost effective and compatible with very-large-scale integration technologies.

With the crystal growth established, the next step is to explore fabrication techniques to fashion, assemble, and structure these PhCs, in order to build complex architectures. Dramatic progress has been achieved recently by using deep structured silicon substrates as a container, in order to grow high-quality PhCs of controlled size and shape on a technology-relevant platform.^{5,6} Furthermore, it is desirable to create intentional microscopic defects, to provide light confinement and guiding. Indeed, these structures constitute the building blocks of light circuits, and they are expected to benefit from reduced losses when they are embedded within a 3D PhC.⁷ The introduction of a small proportion of spheres of different size during the crystallization has been recently proposed as a possible way towards this goal.⁸ Nevertheless the positioning of such defect remains to be controlled. A

method using two-photon polymerization has been demonstrated,⁹ but the volume of the smallest structure is limited by optical diffraction to λ^3 , where λ is the laser wavelength.¹⁰ In this letter, we describe a technique which allows fabrication of deterministic structures in 3D PhCs using direct electron-beam lithography (EBL).

Colloidal monodisperse poly(methyl methacrylate) (PMMA) microspheres were synthesized via surfactant-free emulsion polymerization, using the routine described elsewhere.¹¹ The polymer colloids had the measured molecular weight of 200 000 g/mol with a measured polydispersity index of 2.4. The (100) silicon substrates were cleaned by a standard process, hydrophilized in a $\text{H}_2\text{O}_2(35\%):\text{NH}_3(25%):\text{H}_2\text{O}(1:1:5)$ bath for 3 h and rinsed in deionized water. The sedimentation was performed by drawing up the substrate in a vertical position¹² at a velocity of about 300 nm/s from a 3 wt % suspension of spheres of diameter 325 or 400 nm. With these parameters, the opal films were about 10 μm thick. All these processes were carried out at ambient conditions. Sintering was performed at 80 °C for 2 h in air. EBL was carried out using a Philips XL30-SFEG scanning electron microscope (SEM) equipped with a Raith Elphy Plus EBL control unit at accelerating voltages V_{acc} between 2 and 30 kV and a free working distance of 5 mm. The exposure dose was 400 $\mu\text{C}/\text{cm}^2$. Fine tuning of the beam focusing, writing location, and orientation was possible by a preliminary 5 s scan of the whole writing field for imaging, with a dose lower than 100 nC/cm^2 , which is insufficient to expose the material. After exposure, the samples were developed for 20 s in a solution of methyl isobutyl ketone (MIBK) and then placed in a solution of isopropanol to stop the development process for 20 s. The samples were dried in a flow of nitrogen. Prior to imaging with a Philips XL30-TMP SEM, the samples were sputtered with a 10 nm thin film of gold.

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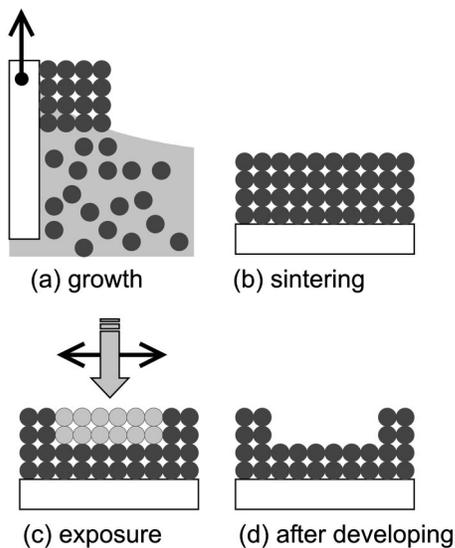


FIG. 1. Scheme of the complete process, from opal growth to defect generation by direct EBL.

EBL is a standard lithography technique widely used to create two-dimensional patterns when high resolution (smaller than 10 nm) and high versatility are required.¹³ Our approach consists in replacing the usual resist layer by an opal film built of microspheres tailored in the same material. The photonic crystal structuring is schematically represented in Fig. 1. After the crystal is grown on the substrate in a vertical position, the structuring is a two-step process. First, the opal film is locally exposed to an electron beam, followed by a development in a solvent to remove selectively the exposed material.

In conventional EBL, the resist is usually deposited on the substrate as a very thin layer (typically below 300 nm). In this nearly two-dimensional geometry, the processed material is basically defined by the area that has been exposed to the scanning electron beam. Since in the case of an opal film, the thickness is typically 5 to 10 μm , this description is no longer valid. In fact, the volume of processed material depends on the 3D distribution of the electrons within the film. Thus, by controlling the electron accelerating voltage V_{acc} (i.e., the penetration depth of electrons),¹³ it becomes possible to control the depth of the written structure.

Thus, compared to other exposure parameters (magnification, spot size, step size, etc.), which affect the in-plane resolution and the writing time, V_{acc} is the most relevant one for 3D structuring purposes. Several values were tested and the dependance upon V_{acc} is plotted in Fig. 2. In order to have a working definition of lateral resolution in opal films, we have considered here the sharpness of the corners compared with the sphere diameters, expressed in radius of curvature. SEM micrographs of various structures obtained for different V_{acc} are shown in Fig. 3. Although high V_{acc} provide the best in-plane resolution, it is not possible to distinguish the bottom surface by SEM due to shadowing [Fig. 3(a)]. Optical microscopy observations (not presented here) show that the patterning becomes as deep as the film and the film itself is melted by the process. On the contrary, low V_{acc} result in a very shallow depth of writing, but a worse lateral resolution [Fig. 3(c)]. With our material molecular weight,

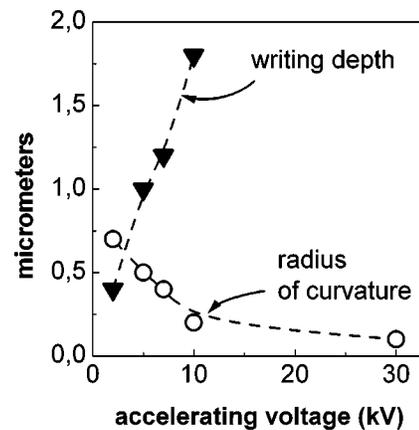


FIG. 2. Dependence of writing depth and lateral resolution upon the accelerating voltage V_{acc} . Dashed lines are guides for the eyes.

the best working conditions, which are the trade-off between writing depth and resolution, were found to be the 2 to 10 kV range, giving rise to a range of controllable writing depths from 0.4 up to 2 μm .

The accuracy of the process can be evaluated in Fig. 3(b). The orientation of the rectangular structure matches the orientation of the PhC lattice. The sharpness of the edges as well as the small radius of curvature at the corners demonstrates that the lateral resolution is of the order of magnitude

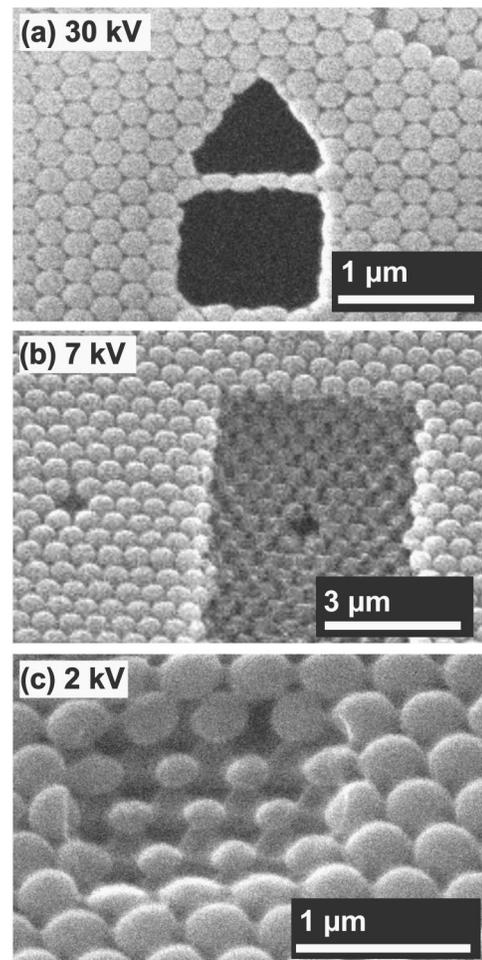


FIG. 3. SEM micrographs of intentional defects created in opal films, for different values of the accelerating voltage V_{acc} : (a) 30 kV, (b) 7 kV, and (c) 2 kV.

of one sphere diameter or better. The bottom surface of the structure is clearly flat on the scale of one sphere diameter, but it is covered by small particles. These are probably residues of incompletely dissolved spheres, indicating that the exposure parameters and that the developing conditions need better tuning. Nevertheless, in the present case, the remarkable size uniformity of these particles constitutes unambiguous evidence that the bottom surface of the cavity follows the PhC lattice.

As such, this technique allows the writing of structures with a size from a few spheres up to several 100 μm . We have shown that EBL affects preferably the upper layer of the opal film, however this technique could be extended towards the fabrication of deterministic buried defect structures, by taking advantage of two specific properties of opal films; namely, the possibility of growth interruption¹⁴ and the open porosity of the film. For example, buried defects could be fabricated by the following three-step process: (i) definition of defect structures by EBL, (ii) subsequent growth of another film on the first one, and (iii) development of the exposed and buried spheres, within reach of the developing solvent thanks to the porous nature of the material.

In addition, in order to fulfill the conditions for a complete photonic bandgap, the infilling of the opal structure with a high refractive index material is necessary. This issue has been addressed recently by several groups. In the case of a polymer template, various techniques, such as sol-gel hydrolysis,¹⁵ infilling with nanoparticles,¹⁶ or chemical vapor deposition,¹⁷ have been investigated. Although the filling factor f still needs to be improved, results obtained using TiO_2 (f up to 12% in Ref. 16) and SnS_2 (f up to 14% in Ref. 17) are encouraging.¹⁸ This approach would offer a unique way to create genuine 3D optical microstructures, from highly confined 3D resonators to single-mode light guides.

In summary, a technique has been described that is capable of structuring 3D PhCs using EBL. We have shown that the control of the writing depth can be achieved by varying the electron acceleration voltage. Controlled structures with a depth from 0.4 up to 2 μm have been fabricated with a typical lateral resolution of 0.4 μm . The relevance of this technique for the fabrication of deterministic defects in photonic crystals has been discussed, and its extension towards buried structures has been suggested.

The authors acknowledge the support of the German Research Council (DFG) Priority Program SPP 1113 "Photonic Crystals" and of the EU-IST Project PHOBOS Grant No. 19009.

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- ¹⁸Note that the volume fraction of voids for an ideal compact fcc packing is $f=26\%$.