

Synthesis of polymer - based inverted opal and transformation of its optical properties

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Abstract. We have obtained opal-like photonic crystals based on opals and inverted opals exhibiting a shift of the selective reflection band toward longer and shorter wavelengths with respect to the diffraction band of the initial opal consisting of SiO₂ spheres. The contribution of frames forming three-dimensional periodic structures and that of fillers to the spectral arrangement of the diffraction bands has been determined.

Keywords: opal; inverted opal; polymer ED-20; reflectance spectra

1. Introduction

Opal-like structures attract particular interest owing to their unusual optical properties and feasible technical applications (Sander 1964, Bogomolov 1978, Biswas *et al.* 1996, Bogomolov *et al.* 1997, Krauss 1998). Opal forms an fcc structure with four SiO₂ microspheres in the elementary cell. The developed techniques of producing synthetic opals enable to obtain structures with a period from 100 to 3000 nm. Such structures appear to be photonic crystals with three-dimensional modulation of the refractive index. Due to its spatial periodicity, the light falling on the opal at a certain angle suffers Bragg diffraction which involves spatial and spectral transformation of light. As a rule, opal structures grow in the [111] direction. The (111) growth plane is a densely packed hexagonal structure. Selective reflection wavelength $\lambda = 2d\bar{n}\sin\theta$, at fixed diffraction angle θ is determined by interplanar spacing d and mean (effective) refractive index of opal-like structure \bar{n} . Opal-like structures are attractive due to their optical properties that can be changed to fill intersphere voids with various materials thus changing effective refractive index \bar{n} . It should be noted, however, that the use of conventional materials with refractive index n within 1.3-1.6 allow only limited wavelength rearrangement since the greater part of the opal volume is filled with amorphous silicon dioxide. Yet, voids that can be filled with filling material thereby changing their refractive index \bar{n} , occupy only the smallest part of the total opal volume. Another limitation is conditioned by the fact that, as voids are filled, the mean refractive index increases and the selective reflection wavelength can be shifted only toward longer wavelengths.

In recent years techniques of producing opal-like structures using inverted opal have been

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intensively developed (Míguez *et al.* 2001, Scharrer *et al.* 2005, Aleshyna *et al.* 2007, Kim *et al.* 2012, Golubev *et al.* 2001, Menshikova *et al.* 2011, Ralchenko *et al.* 2011). Inverted opal is a structure with voids filled with organic or inorganic material and serves as a frame for an opal-like structure, SiO₂ microspheres removed. The use of inverted opal enhances considerably the scale of photonic structure modification. Materials with different optical properties can serve as frames for opal-like structures. Voids occupy the greater part of the crystal and, thus, their filling can affect the optical properties to a greater extent. Spectral properties and peculiarities of optical diffraction of inverted opal-like structures have been investigated (Meseguer *et al.* 2002, Scharrer *et al.* 2005, Gajiev *et al.* 2005, Bohn *et al.* 2010). It is shown in particular (Bohn *et al.* 2010) that linear dependence exists between diffraction wavelengths of direct and inverted structure. Multiple peaks were found at oblique light incidence which indicates diffraction on two crystal planes (Gajiev *et al.* 2005).

Photonic crystals are investigated using opal structures in the form of bulk matrices or thin films with one or several tens of densely packed layers of monodisperse spherical SiO₂ particles (Jiang *et al.* 1999, Masalov *et al.* 2001, Prevo and Velez 2004, Denkov *et al.* 1992). Bulk matrices are obtained by natural particle deposition or suspension centrifugation. In both cases precipitates exhibit columnar structure composed of misoriented vertical domains (about 1 mm in diameter) in the matrix volume and a practically single-domain surface structure. Misorientation of domains in the matrix volume leads to a shift of the peak maximum of reflection from different sample regions (different domains) owing to the angular dependence of photonic crystal reflectance spectra. Different methods of producing film opal structures are used to obtain large (up to several square centimeters) single domain regions. Film structures are obtained on glass, quartz, silicon and sapphire substrates. However, formation of film opal structures involves a number of technical problems. As precipitates obtained from suspensions are dried, they are subject to cracking or even peeling from the substrate as a result of significant (up to 5%) structural shrinkage. This problem can be partially solved by means of preliminary particle annealing (Chabanov *et al.* 2004). Yet, further annealing of films required for their hardening, impregnation with liquid solutions also lead to peeling of films from their substrates because of the difference in the thermal expansion coefficients and the influence of the liquid capillary forces acting on the opal structure. In many cases fabrication of inverted opals from substrate films presents difficulties since etching-out of silicon dioxide spheres is performed in hydrofluoric acid which destroys most types of substrate. These problems can be avoided by using a bulk opal matrix as a substrate.

In this work we report synthesis of opal-like structures of different composition and with different optical properties: “direct” opal composed of SiO₂ spheres, “inverted opal” with a polymer frame, inverted and direct opals filled with material with a refractive index different from that of the supporting frame. The inverted opals were made from the layers deposited on the bulk opal matrix surface. The obtained opal-like materials demonstrated shifts of the peaks of the optical reflectance spectrum over a wide wavelength range toward the long and short wavelengths with respect to the selective reflection of the direct opal from the SiO₂ spheres.

2. Experimental techniques and morphology of synthesized opal-like structures

Monodisperse microspheres of amorphous SiO₂ were obtained by combined synthesis including preparation of seed particles by heterogeneous synthesis using the reaction of tetraethoxysilane hydrolysis in the presence of amino acid (L-arginine concentration 7-7.5 mM, TEOS concentration

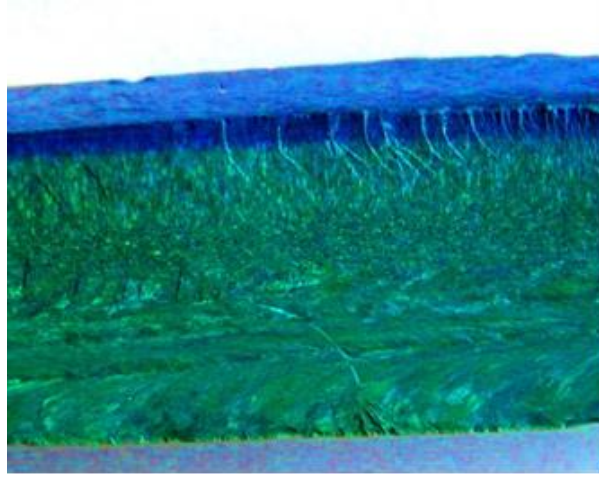


Fig. 1 Photograph of opal matrix cleavage with 1 mm thick monodomain film

0.3-0.4 M, synthesis temperature 50-60°C) followed by their further growth by the modified Stober-Fink-Bohn method in aqueous alcoholic solution in the presence of ammonium hydroxide (50 % vol. ethanol; 1.0 M ammonia) (Stöber *et al.* 1968, Masalov *et al.* 2011). The diameter of the prepared spherical particles was $D=255\pm10$ nm. The initial synthetic opal was obtained by sedimentation of SiO_2 particles in the aqueous medium. The precipitates were hardened in several steps including initial drying at room temperature for several days, drying at 150°C (120 h) and annealing at 600°C (4 h). Drying at 150°C ensures removal of physical water from the opal matrix structure and annealing at 600°C ensures removal of chemically bound water and organic residues without significant changes of the structure porosity providing thereby its partial hardening (Samarov *et al.* 2006).

The films were obtained using the ordering capacity of the upper particle layer on the deposited bulk opal structure realized by way of self-organization owing to the capillary forces acting on the surface solid precipitate in the suspension layer left for this purpose during decantation of the clarified liquid. As a result, an ordered monodomain film several layers to about a millimeter in thickness is formed on the misordered columnar structure of the bulk opal. Fig. 1 presents a photograph of an opal matrix cleavage with a 1 mm monodomain film. After drying and annealing the upper layer of the bulk opal is cut off and then used to create composites and inverted opal matrices.

The density and porosity of the samples were studied by hydrostatic weighing and the mass of the dry sample (m), the mass of the air-weighed liquid saturated sample (m_1) and that of the sample weighed in the same liquid (m_2) were determined. The effective density (ρ_{ef}), apinitia density (ρ_{ap}) and open porosity (P_o) of the opal matrices were calculated by the formulas:

$$\rho_{ef} = m\rho_L/(m - m_2); \quad \rho_{ap} = m\rho_L/(m_1 - m_2); \quad P_o = (m_1 - m)/(m_1 - m_2) \cdot 100\%,$$

where ρ_L is the liquid density. Water and butanol were used as pycnometric liquids. The level of liquid filling of the opal matrix was determined by the changes of the matrix weight as a function of impregnation time and the value of ρ_{ef} , calculated by the above formula. The achievement of constant weight and approach of ρ_{ef} to the true value of the matrix frame density ($\sim 2.22 \text{ g/cm}^3$ for amorphous silica and 1.23 g/cm^3 for ED-20 oligomer) was the criterion of the level of liquid filling

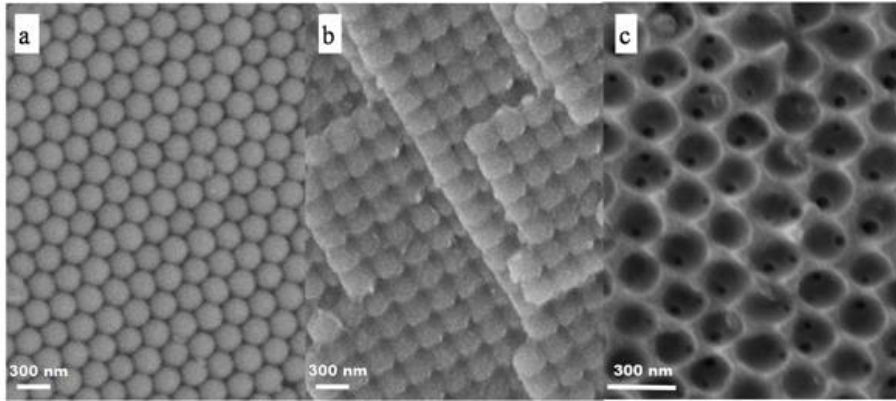


Fig. 2 SEM image of initial opal matrix formed by silica spheres with diameter $D=255\pm10$ nm (a) ((111) surface orientation)), cleavage of ED-20 polymer-opal composite with (100) orientation (b) and that of inverted ED-20 polymer opal (c) ((111) surface orientation))

of the opal matrix and the absence of foreign phases in the matrix structure.

Opal wafers 1-8 mm thick were used in the experiments. The wafer surface was parallel to the (111) plane of the cubic opal structure. Most perfect opal structure was achieved near the wafer surface. Inverted opal was prepared by filling the initial lattice with ED-20 epoxy resin (diglycidyl ether- and diphenylolpropane-based oligomer) containing isomethyl tetrahydrophthal anhydride (iso-MTHPA) as a polymerization initiator. In order to reduce the viscosity, a hardening agent was added to the resin pre-heated to 100°C and the mixture obtained was used for impregnation the opal matrix. The epoxy resin was polymerized by the following regime: 2 hours at $T=100^\circ\text{C}$, then 10 hours at $T=150^\circ\text{C}$. The resulting ED-20 polymer had refractive index $n=1.55$. To produce inverted opal, the polymer excess on the sample surface was removed by dissolution in dichlorethane followed by rinsing in ethanol and removal of the silica particles from the opal-polymer composite by holding the samples in hydrofluoric acid in an ultrasound bath for 24 h. The effective density (ρ_{ef}) of the inverted opal samples was 1.232 g/cm^3 which corresponds to the true density of ED-20 polymer ($1.2\text{-}1.25\text{ g/cm}^3$) and is indicative of complete removal of silica from the composite. The apinitia density (ρ_{ap}) of the inverted opal was 0.335 g/cm^3 , its porosity 72.8 %, accordingly, which appeared to be close to the volume fraction occupied by the spheres (74 in the initial opal matrix). It should be noted that ED-20 oligomer does not penetrate into porous silica spheres since its molecule sizes exceed the characteristic sizes of particle pores (Bardyshev *et al.* 2006).

Fig. 2(a) presents a SEM image of the initial opal matrix formed by silica spheres with diameter $D=255\pm10$ nm. Figs. 2(b) and 2(c) present SEM images of the “ED-20 polymer-opal” composite and ED-20 polymer-based inverted opal, respectively.

In order to obtain samples with different positions of selective reflection wavelengths the direct and inverted opals were impregnated with liquid with a refractive index different from that of the frame.

Diffraction measurements were made upon back reflection from the surface parallel to the (111) growth plane, the selective reflection wavelengths being $\lambda=2d\bar{n}$. In the [111] direction the interplanar distance $d=D(2/3)^{1/2}$, and, hence, the selective reflection wavelength is related to the microsphere diameter by the relationship $\lambda=2D(2/3)^{1/2}\bar{n}$. Photon crystal lattice parameter $a=$

$d(3)^{1/2}$. The opal exhibits the most intensive [111] reflection as the highest optical density is in the plane structure perpendicular to the [111] direction and passing through the sphere center, the lower density being in the middle. The quality of the sample surface was controlled in reflected light using an Olympus BX51 microscope. The spectra were measured in the sample regions with lateral dimensions $L \approx 50 \mu\text{m}$ using an Avaspec-2048L spectrometer. The spectra presented are diffraction spectra divided by the lamp spectrum. The spectral resolution was appreciably less than the diffraction band width.

3. Spectral characteristics of opal-like photonic crystals

In the elementary opal cell the fraction of intersphere voids makes up 0.2595 of the total volume. It is known that in the opal SiO_2 spheres have internal substructure composed of finer spherical particles (Darragh *et al.* 1966, Jones and Segnit 1969, Bogomolov *et al.* 1996, Karpov *et al.* 2005, Masalov *et al.* 2011) with voids between them. In this connection the effective refractive index of spheres is less than that of amorphous silica SiO_2 ($n \approx 1.45$). Assuming that finer particles are closely packed (Samarov *et al.* 2006, Masalov *et al.* 2011), the value of opal voids is of the order of 0.452 and that of amorphous silica 0.548. These values will be further used in calculations. Filling of voids can occur not only between spheres forming cubic structure but also by way of filling part of the voids inside large spherical particles. The spectral position of diffractions bands does not depend on the internal structural features of SiO_2 spheres but depends on the values of d and \bar{n} . The average refractive index is dependent on the volume of frame forming three-dimensional structure f , that of the filling compound (filling material) f_2 , and air volume f_3 and their refractive indices

$$\bar{n} = \left(\sum f_i n_i^2 \right)^{1/2} \quad (1)$$

Fig. 3 (curve 1) shows the diffraction spectrum of the initial opal (selective reflection wavelength 545 nm). From relationship (1) and $\lambda = 2d\bar{n}$ we obtain the opal interplanar distance $d \approx 215 \text{ nm}$. This value corresponds to lattice parameter $a = 372 \text{ nm}$ and sphere diameter $D = 263 \text{ nm}$.

Polymer filling of the opal matrix leads to a shift of the diffraction band toward long wavelengths ($\lambda = 611 \text{ nm}$, curve 2 in Fig. 3(a)). The selective reflection band wavelength ratio is proportional to average refractive indices $\lambda_i/\lambda_j = \bar{n}_i/\bar{n}_j$. Using this ratio and Eq. (1), we obtain the volume polymer and void (intraglobular pore) fractions as 0.29 and 0.162, respectively. As the initial opal is filled with ethanol ($n = 1.361$), the selective reflection wavelength shifts toward $\lambda \approx 593 \text{ nm}$ (spectrum 3 in Fig. 3), which corresponds to alcohol and void volume fractions 0.35 and 0.1, respectively. Thus, alcohol fills not only the space between the spheres forming the periodic structure but also partially penetrates into the porous spherical volume.

As silica spherical particles have been removed from the inverted opal, its three-dimensional periodic structure is formed by a polymer mesh with a large volume fraction of voids which results in reduction of the total refractive index. Calculation similar to that for direct opal yields the position of the selective reflection band of the inverted opal $\lambda \approx 511 \text{ nm}$, which agrees with the experimental data (spectrum 4 in Fig. 3(b)).

Ethanol filling of inverted opal, as in the case of direct opal, leads to a long wavelength shift of the diffraction band (spectrum 5), though the spectral shift value for inverted opal is larger. The position of the diffraction band ($\lambda \approx 606 \text{ nm}$) allows calculation of alcohol and air volume fractions

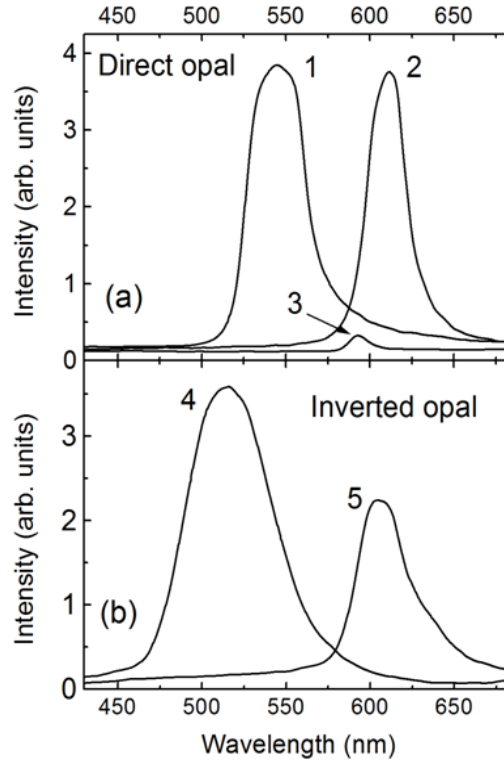


Fig. 3 Diffraction spectrum perpendicular to (111) plane for direct opal-(a) and inverted opal-(b) based structures. Spectrum of initial direct opal (1). Polymer filling (2) of opal or its ethanol impregnation (3) leads to a shift of diffraction bands toward longer wavelengths. Spectrum of inverted polymer opal shifted to short wavelength region (4). Spectrum of ethanol-impregnated inverted opal (5)

(0.67 and 0.04, respectively) in inverted opal by the technique described above. Thus, the volume of inverted volume is practically completely filled with alcohol which enables to achieve a significant shift of the selective reflection band. Infiltration of voids in direct and inverted opals leads not only to a shift of diffraction bands but also to a change in their width (Fig. 3(a)-(b)). The width of the band is determined by the value of the modulus of Fourier harmonics of dielectric permittivity tensor ε_α which is changed upon infiltration of the voids. ε_α depends on the difference in refractive indices of the carcass and the filling Δn . In our case the least value of Δn is for infiltration of the direct opal with ethanol, and the corresponding band (3, Fig. 3(a)) has the least width.

4. Conclusions

Polymer-based inverted opals were synthesized using monodomain SiO_2 - opal films as templates. These films - templates have been prepared on the surface of the bulk opal by self-organization owing to the capillary forces acting during the drying process. The film thickness is

controlled by volume of the suspension of silica particles and their concentration. This approach avoids the problems of substrate selection, cracking and peeling of the film obtained during the chemical and heat treatments, as well as the destruction of the substrate when etching-out the silica spheres in hydrofluoric acid. The synthesized opal-like structures based on direct opal composed of SiO₂ spheres and inverted opal with a polymer frame have allowed changing the spectral characteristics of the photon crystals over a wide range as well as shifting the selective reflection bands with respect to the initial direct opal both toward long and short wavelengths. Liquid filling of inverted opal makes it possible to achieve a shift of the selective reflection band exceeding that of the band in direct opal.

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