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Influence of annealing temperature on optical properties of the photonic-crystal structures obtained by self-organization of colloidal microspheres of polystyrene and silica

L.V. Mikhnev, E.A. Bondarenko, O.M. Chapura*, A.A. Skomorokhov, A.A. Kravtsov

North-Caucasus Federal University, Pushkin Street 1, Stavropol, 355009, Russian Federation

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ABSTRACT

The influence of annealing temperature on the transmission spectra of photonic crystals composed of polystyrene and silicon dioxide microspheres was studied. It was found that annealing of photonic crystals based on polystyrene and silica leads to a shift in the photonic band gap to the short-wavelength region. Based on the results of optical studies, the dependences of the structural parameters of the obtained opal-like crystals on annealing temperature were obtained. In the case of polystyrene photonic crystals, the displacement of the photonic band gap is observed in a narrow temperature range above the glass transition temperature. For SiO_2 photonic crystals, it was found that the process of microspheres sintering is complex and involves three stages of structural modification.

1. Introduction

Photonic crystal structures (PCs) now attract the attention of many researchers specializing in the field of optics of low-dimensional structures. Optical effects characteristic for PC will allow to create high-efficiency reflective coatings [1], low-threshold lasers [2], high-efficiency LEDs with coefficient of efficiency close to the theoretically possible maximum [3,4], light flux control devices [5], optical sensors [6] and solar cells [7].

In general, PCs is a material whose structure is characterized by a strictly periodic change in the permittivity. Periodic modulation of the permittivity in such structures leads to the prohibition of the propagation of radiation in one direction (stop-band) or in all directions (photonic band gap) of the radiation propagation. Thus, the parameters of the photon energy spectrum are influenced, in the first place, by such structural properties as the period of modulation of the dielectric constant, the ratio of the volumes of the phases in the photonic crystal [8].

Spherical microparticles of SiO_2 or polystyrene (synthetic opals) are often used to form the PCs. In this case, the initial microspheres are ordered into a face-centered cubic (fcc) structure, usually in the shape of thin layers and films. To harden and modify the structure of a photonic crystal, such opal-like structures are subjected to thermal annealing [9,10]. The study of regularities of the change in the PCs structure caused by the temperature treatment makes possible to control change in its optical properties. Thus, in Ref. [11] in opals obtained from modified silica microspheres, by means of thermal treatment it was possible to achieve a shift of the photonic band gap by more than 25% from the initial position.

To visualize the structure of the PCs, scanning electron microscopy (SEM) [12] and atomic force microscopy (AFM) methods [13,14] are usually used, which give information on the particle size and defect concentration on the surface layer only. For this reason, they do not allow to evaluate objectively the state of the whole PC, which is significantly influenced by heat treatment.

In Ref. [15], a structural modification of synthetic opals based on silicon dioxide under thermal treatment was carried out. The results obtained have allowed establishing the dependence of porosity of the PC on the annealing temperature. However, attention to the effect of the change in the morphology of the PC during heat treatment on the effects of light transmission associated with the presence of a photonic stop-band is not paid. In Ref. [16], the dependence of the photonic band gap (PBG) displacement on the

* Corresponding author.
E-mail address: ChapurOL-7@mail.ru (O.M. Chapura).

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refractive index of the impregnating liquid was investigated. However, as noted earlier, annealing of the PC can lead to changes in the structure that significantly affect the pore volume (the degree of their filling in the case of impregnation), and hence the effective refractive index of the PC can change. Consequently, the study of the effect of the annealing temperature on the position of the PBG does not allow one to uniquely determine the parameters of the crystal lattice of the colloidal crystal.

In the present work, the influence of heat treatment in a wide temperature range (including the temperature of disappearance of the photonic stop band) on some structural parameters of polystyrene and silicon dioxide based PCs was studied. The investigations are based on the analysis of the spectral distributions of the light transmission of PC matrices, the spaces in which are filled with liquids, in comparison with the distributions of light transmission of the original (without filling) matrices.

2. Materials and methods

Reagent grade chemicals, grade A glassware and distilled water with 1.5–5 μS/cm conductivity were used.

2.1. Preparation of PC samples based on polystyrene microspheres

PCs based on polystyrene microspheres were prepared from 1% w/v aqueous suspensions of spherical microparticles of carboxylated polystyrene with a diameter of 270 nm and polydispersity of 2%. Monodisperse polystyrene microspheres were obtained by emulsifier-free emulsion copolymerization of styrene with methacrylic acid [17]. Thin glass plates 20 × 20 mm, previously cleaned in a chromium mixture were placed vertically in a cuvette with an aqueous suspension and held at room temperature until the water evaporated completely. This led to the ejection of microspheres on the meniscus border with the substrate under the action of capillary forces. As a result of the evaporation of water, the microspheres on the border of the meniscus and the substrate self-organized into the closest sphere packing configuration.

2.2. Preparation of PC samples based on SiO_2 microspheres

To produce PCs based on SiO_2 microspheres, a 1% w/v aqueous suspension of spherical silica microparticles with a diameter of 275 nm and polydispersity of 5% was used. Silicon microspheres were obtained by the Stober method [18]. At the bottom of the cuvette with an aqueous suspension thin plates of fused quartz, previously purified in a chromium mixture, were placed. They were kept until the water evaporated completely. At this time, the processes of deposition of microspheres to the surface of the substrate and the evaporation of water proceeded. As a result, SiO_2 microspheres self-organized into the closest sphere packing configuration.

2.3. Annealing of the photonic crystals samples

Annealing of the polystyrene PCs was carried out for an hour at fixed temperatures in the range of 60–115 °C. Annealing of the PCs based on SiO_2 was carried out for 5 h at fixed temperatures in the range of 100–1000 °C. The annealing was carried out using a laboratory electric furnace SNOL 7,2/1100.

2.4. Research methods

The method of scanning electron microscopy (SEM) was used to characterize the surface of the synthesized samples. SEM images were obtained on a FEI Quanta 3D FEG microscope, the Netherlands.

The transmission spectra of the PC were measured using a device assembled on the basis of a monochromator MDR-23U with the inverse linear dispersion in the visible spectrum of 1.3 nm/mm. The transmission spectra were recorded on a region of the film surface with a size of 3 mm^2 at a 90° incidence angle. The divergence of the incident monochromatic light beam was no more than 2°.

In this work, the transmission spectra of a PCs without filling and saturated with a liquid with a known refractive index were studied. Polystyrene PCs were impregnated with ethyl alcohol ($n = 1.36$), PC based on SiO_2 microspheres were impregnated with water ($n = 1.33$). For this purpose, one half of the sample was placed at a depth of 1–2 mm in an appropriate liquid which filled the PC pores under the action of capillary forces.

3. Results and discussion

SEM images of the growth surface of the PCs samples based on polystyrene and silica microspheres are shown in Fig. 1.

As can be seen, the growth surface of the resulting PC is formed by the (111) plane of the fcc structure, which is characteristic of a PC composed of spherical microparticles [19,20]. In the obtained photonic crystals samples, the presence of vacancies in the lattice is observed, which is due to the rather high polydispersity of the microspheres used. Similar phenomenon is observed for PCs based on SiO_2 microspheres.

The transmission spectra of PC based on polystyrene microspheres without saturating and saturated with ethanol are shown in Fig. 2. On Fig. 3 transmission spectra of PC based on SiO_2 microspheres without saturating and saturated with water are presented.

As can be seen on Figs. 2 and 3, a characteristic dip in the light transmission is observed in all spectra, which is a consequence of the Bragg diffraction of light on the assemblage of (111) planes of the fcc structure, which indicates the presence of a photonic stop-band. The half-width of the dip in the transmission spectra of samples filled with a liquid is less than that of the original PCs without filler. This is due to low dielectric contrast (the dielectric constant of the PC material/dielectric constant of the filling substance) in the impregnated PC as compared to the samples filled with air [21].

As shown by the results of studies, the spectral position of the photonic stop-band in polystyrene PCs is almost independent of the annealing temperature in the range of 25–110 °C. A further increase in the annealing temperature leads to a shift in the transmission minimum to the short-wavelength region. Moreover, in samples impregnated with ethanol, the spectral position of the photonic stop-band displaces greater, and at the annealing temperature of more than 115 °C, the dip in the transmission spectra disappears completely.

In PCs based on SiO_2, an appreciable shift of the spectral dip to the short-wave region is observed starting from 500 °C. In this case, the position of the minimum of the transmission spectrum in water-impregnated samples is shifted to the direction of the short-wave region, as in the PCs based on polystyrene impregnated with ethanol. At temperatures above 960 °C, the photonic stop-band for silica PCs cannot be registered, which is due to the destruction of the periodic structure in the samples by reason of complete sintering of the silica microspheres at this temperature.

The structural features of PC are determined primarily by the period of modulation, as well as by the ratio of the volumes of components of the PC. The modification of the structure of the PC in the heat treatment process can be assessed by the change in the distance between the layers of (111) ordered microspheres, and the