Synthesis optimization of photonic crystals based on silicon and vanadium dioxides

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Abstract. The photonic crystal is the material which structure is characterized by periodic distribution of refraction index in the spatial directions, which have the photonic band gaps in a spectrum of own electromagnetic states. There are numerous approaches of the creation of photonic crystals. In the present the optimal conditions of synthesis of photonic crystals based on silicon dioxide as well as the inverse photonic crystals based on vanadium dioxide are investigated. It is known that the synthesis process is influenced by many different factors. We have studied the dependence of the particle size on the concentration of reagents, as well as on the duration of the reaction. These studies are important for the production of samples of photonic crystals with a definite structure.

1. Introduction

One of the most important areas of modern physics is the study of periodic optical nanostructures, known as photonic crystals (PC) in which the dielectric constant varies periodically in space with period allowing Bragg diffraction of light. It is known that crystals of all types can disperse some radiation, provided that the period of the crystal lattice is of the same order as the wavelength of the radiation. Similarly, photonic crystals do not transmit the light with a wavelength comparable to the period of the photonic crystal structure, at the same time PCs are transparent to a wide range of electromagnetic radiation spectrum. These spectral bands are called “photonic band gap” (PBG) [1]. The works on photonic crystals are motivated by a number of promising applications, such as high-performance light emitting diodes, low-threshold lasers, optical waveguides with sharp bends and optical microchips. Nowadays there are numerous approaches to the creation of PC by using the lithography [2], interferential holography [3] and self-assembly of colloidal particles [4]. One of the first materials that have been considered as photonic crystals were synthetic opals, consisting of close-packed spherical particles of silica. Self-assembly techniques are very promising, since they are quite simple in terms of hardware design and have no fundamental restrictions both on the sample size and the number of photonic crystals produced in one cycle of synthesis. However, the synthesis process is influenced by the factors like setting of the concentration ratio of the reactants, reaction temperature, sequence of blending and more. So our purpose is to investigate the effect of concentration ratio of reactant and duration of the reaction on the particle size, making possible creation of PC with predetermined characteristics. Our results are relevant for the experimental verification of the effect predicted by the authors in [5].

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2. Self-assembly method for the preparation of photonic crystals based on silica and vanadium dioxide

The preparation of photonic crystals based on silica (SiO$_2$) particles is carried out in two phases. First, suspension with SiO$_2$ particles was synthesized, in the second phase the particles were deposited in the close-packed structure. Suspension of silica particles was synthesized by the method described in [6]. According to this method, spherical particles are prepared by hydrolysis of tetraethyl orthosilicate (tetraethoxysilane, TEOS, Si(O-C$_2$H$_5$)$_4$) in hydroalcoholic medium with ammonia as a catalyst. The amount of reactants was varied in different ranges (100 - 170 ml of ethanol; 0 - 45 ml of water; 11 - 14 ml of aqueous ammonia; 2.5 - 9 ml of TEOS).

Self-assembly of colloidal particles was performed using a vertical deposition [4]. Glass substrate was immersed vertically into the suspension of the microspheres. This forms a meniscus at the interface "liquid-air-substrate", where the particles are drawn by capillary action. With the evaporation of the liquid meniscus moves down the surface of the glass, leaving a thin film of close-packed microspheres.

Synthetic opals can be used for the producing of inverse opals using template method [7]. To perform this the voids between the particles in synthetic opals are filled with the desired compound, which is transformed into a solid structure as a result of chemical reactions. After that the colloidal particles are removed using the processes of dissolution or thermal decomposition. Thus we synthesized inverse PC based on vanadium dioxide (VO$_2$). In turn, vanadium dioxide is attractive due to the rapid semiconductor-metal phase transition [8], so that the material can be used to create ultra-fast switch.

3. Photonic crystals characterization techniques

Photonic crystals parameters were measured by atomic force microscopy (AFM) (Ntegra Prima, NT-MDT) and by optical spectrophotometry (Lambda-35, Perkin Elmer). Each method has a certain range of applicability.

3.1. Atomic-force microscopy method

AFM produces three-dimensional image of the sample with high resolution, but it makes possible to visualize only the surface layer of the PC. Figure 1 shows AFM image of synthetic opal based on SiO$_2$. As a result of AFM image processing the particle size was determined (560 ± 15 nm).

![AFM image of a silica-based PC.](image-url)
3.2. Spectrophotometric method

Spectrophotometric method is based on the fact that the spectral position of the band gap obeys the Bragg’s law:

$$\lambda = 2d_{(111)}\sqrt{n_{eff}^2 - \sin^2 \Theta},$$

(1)

where $\lambda$ is the wavelength, $d_{(111)}$ is the period of the structure (the distance between the (111) planes), $n_{eff}$ is the effective refractive index, $\Theta$ is the angle between the normal to the sample surface and the direction of the incident light. Equation 1 is written with the Snell’s law. The effective refractive index $n_{eff}$ of the photonic crystal depends on the refractive index of the SiO$_2$ particles ($n = 1.45$), the refractive index of air ($n_{air} = 1$) and the volume fraction of microspheres ($f = 0.74$):

$$n_{eff} = \sqrt{n^2 \cdot f + n_{air}^2 \cdot (1 - f)}.$$  (2)

Figure 2 shows the transmission and reflection spectra of PC samples based on silica. According to equation 1, the dependence of band gap spectral position ($\lambda$) on the incidence light angle ($\Theta$) is linear in terms of $\lambda^2 - \sin^2 \Theta$ (figure 3). Using a linear least-squares approximation, we have calculated the effective refractive index $n_{eff} = 1.35 \pm 0.02$ for sample A and $n_{eff} = 1.34 \pm 0.03$ for sample B (theoretical value calculated using the equation 2: $n_{eff} = 1.35$), the period of the structure $d_{(111)} = 460 \pm 20$ nm and $470 \pm 20$ for samples A and B respectively, the particle diameter $D_A = 560 \pm 20$ nm and $D_B = 570 \pm 20$ nm, which agrees well with the AFM. These parameters can be determined by the transmission spectra for all layers of photonic crystal unlike the using AFM method.

Figure 2. Transmission (a) and reflection spectra (b) of samples A and B respectively.

For the inverse photonic crystal based on vanadium dioxide reflection spectrum was recorded (figure 4 (a)). Contour width is about of 50 nm, which is 2-3 times less than in the spectra of similar samples from the reference [9] (figure 4 (b)). In this way, the phase transition of vanadium dioxide will be accompanied by an abrupt change of the band structure that is required to create quality femtosecond optical switches.
4. Silica particle size dependence on the concentration of the reactants and the reaction duration

During the synthesis of silica microparticles the selection of the reactants concentration significantly affects on the size of the particles. Therefore it is necessary to know the size of the particles at a certain ratio of the reactants and how the diameter depends on the amount of a particular component.

4.1. The particle size dependence on the water and TEOS concentrations

The water concentration changes during the synthesis can lead to a fairly significant change in the size of the colloidal particles. Figure 5 (a) illustrates the influence of the molar concentration of water on the size of the synthesized microparticles in comparison with data from reference [10]. The concentrations of ammonia and TEOS was 2.3 M and 0.15 M, respectively. According
to the data of [10], these concentrations were 1.0 M and 0.17 M. Similarly, the dependence of the silica particles diameter on the amount of TEOS was obtained (figure 5 (b)). As the authors of [11], an important advantage of the variation of tetraethoxysilane amount is the monotony of this dependence, which is convenient for predicting the size of the particles obtained under certain conditions.

Figure 5. a) Dependence of silica particle size on the water concentration: 1) according to our data, 2) according to the reference [10]; b) Dependence of the particle diameter on the amount of TEOS: 1) according to our work, 2-3) according to data published in [11].

4.2. The particle size dependence on the reaction duration
It is also important to know how fast the particles grow during the reaction, or how soon their size reaches its maximum. To this end, the colloidal solution was prepared using the following amounts of reagents: ethanol - 162.8 ml, water - 4 ml, aqueous ammonia - 14 ml, TEOS - 8.9 ml. After reaction starts the particle sizes were measured at certain intervals of time. As can be seen from the figure 6, for 180 minutes (3 hours) the particles grow significantly and the average diameter increases to 800 nm. When the duration of the reaction $t > 180$ min size of microparticles remains virtually unchanged. Thus, the synthesis of SiO$_2$ microparticles with a size of about 800 nm can be completed within three hours.

Figure 6. Dependence of the microparticle size on the reaction duration.
5. Conclusions
The dependence of silica particles diameter on the concentration of water and TEOS was investigated, as well as the influence of the reaction duration. We have shown that the experimental dependence is in agreement with the reference data, and allows to achieve a determined size of microparticles under appropriate conditions. Synthesized inverse photonic crystal based on vanadium dioxide has a pronounced band gap, which is important for the creating a high-quality ultra-fast optical switches.

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