Methods for improving the structural 3D ordering of self-assembled photonic crystal coatings obtained by electrophoresis deposition

E V Panfilova¹ and D A Ezenkova¹
¹ Bauman Moscow State Technical University, 105005, Moscow, Russia

E-mail: panfilova.e.v@bmstu.ru

Abstract. The article describes the main properties of self-assembled colloidal photonic crystal coatings. A comparison of coating deposition methods is presented. Electrophoresis deposition method has gained great interest because of its possibility of conditions variation. The main factors affecting the quality of the colloidal opal films during electrophoresis deposition are studied. The results of experimental research on increasing the ordering of photonic crystal coatings are presented. It was found that the voltage range of 0.7 - 2.7 V and pH of 7 allows one to obtain thick films with a pronounced PBG.

1. Introduction
Self-assembled photonic crystal (PhC) coatings are a class of materials that are most promising for modern science and technology. Interest in these coatings is due to the refractive index periodic changes in one, two or three dimensions and a photonic band gap (PBG). PhC films and coatings are widely used in electronics [1], optoelectronics [2], power electronics [3], solar power [4], spintronics [5], medicine [6], military and aerospace industries [7] and power engineering (supercapacitors) [8] on their own and as a part of multilayer structures. The structure of opal PhC is a matrix with highly ordered three dimensionally periodic cubic lattice of closely packed microspheres with a equal diameter of 50 … 1000 nm [9]. Self-assembly of polymer or silica (SiO₂) colloidal particles is one of the most simple and low-cost methods for the formation of photonic crystals (PhCs) [10]. Opal matrices are used to obtain PhCs, inverse structures and 3D nanocomposites as it shown in figure 1.

Figure 1. The structure of self-assembled PhC coatings: photonic crystal (A), inverse structure (B), 3D nanocomposite (C)

Interest in 3D - nanocomposites is due to a combination of ordering and matrix geometry, as well as properties of the implementation material [11]. By varying the diameter of the matrix microspheres
one can change the voids size (10…600 nm), which in turn affects the properties of the implementation material. Due to the ordering of the structure, it is possible to create periodic nanoparticle arrays.

While various strategies have been developed to direct the self-assembly of colloidal particles, fabrication of 3D ordering transferrable colloidal coating with controllable PhC structure still remains a major challenge. In this study we determine the electrophoresis deposition process modes to make possible deposition of qualitative PhC coating.

2. Method description
At that moment, there are a number of widely used methods [10,12,13] for creating self–assembled PhC coatings. These technologies are presented in the table 1.

| Table 1. PhC coatings forming methods |
|-------------------------------------|
| Method | Process time | Film thickness | Nanocomposite forming | Disadvantages |
| Sedimentation | Weeks, month | Not limited | 2 stage process | Long process time |
| Vertical deposition | Hours | <10 layers | 2 stage process | Low repeatability |
| Electrophoresis deposition | Minutes, hours | up to hundred μm | Simultaneous deposition | Particle surface must be charged |

It was revealed that the electrophoresis deposition method allow to form well-ordered structure in a wide range of thickness at high speed, and this method is also suitable for the formation of 3D – nanocomposites in one iteration. The essence of this method is described below.

The electrophoresis deposition method combines the self–assembly of microspheres from a colloidal system under the action of gravity with the application of external electric fields. The scheme of the process is shown in figure 2. The advantage of this method is a wide range of variation parameters, which makes it possible to obtain highly ordered coatings. The main parameter is potential difference supplied to the interelectrode space. It allows varying the microspheres deposition rate. Matrix formation is based on the self-assembly in an open dissipative system. The main driving force of the process is the evaporation of the solvent and, as a consequence, the change in the volume of the system. The main driving force depends on the temperature and vapor pressure of the solvent in the environment. The application of external electric fields allows to control and influence self-assembly process. Thus we get better quality of the coating structure.
Figure 2. The schematic diagram of the electrophoresis deposition.

The process of electrophoresis deposition is possible due to the presence of a double electric layer (DEL) of microspheres. DEL causes uncontrolled behavior of microspheres during the deposition process. The density of DEL is determined by the value of $\zeta$ - potential, which can be set by changing the pH of the colloidal system as it shown in figure 3.

Figure 3. Microspheres $\zeta$ – potential vs pH of the colloidal system.

However, if pH significantly different from neutral, the formation of an ordered matrix frame is difficult. For a pH range of 3 ... 5, the value of $\zeta$ - potential and the density of DEL become insufficient to prevent coagulation of particles in solution. At pH = 9 ... 11, the formation of an ordered coating is difficult, due to the presence of repulsive forces, therefore, pH = 7 was chosen for further studies [14].

The study was carried out on copper substrates. In order to remove fats, dust and oxides from the surface of the substrate before the experiment they were purified in acetone for 2 min, isopropyl alcohol - for 2 min. In order to remove products from the previous purification stage - in deionized water for 30 s.

The photonic properties of the obtained coatings were monitored as an output parameter by measuring the reflection coefficient of PBG by means Epsilon spectrophotometer (IZOVAC, Belarus).

3. Results and discussion

Colloidal polystyrene monodisperse latex and silica SiO$_2$ particles with a microsphere diameter of 520 nm were used as a material for the formation of opal matrix. A preliminary experiment was performed using pH of 7, the applied potential difference of 0.5 V, colloids concentration of 2 %, interelectrode distance of 15 mm and the deposition time of 5 min. 10% colloidal solution with particles diameter 220 nm at a lifting velocities of 1 mm/min and 0.8 mm/min. Figure 4 presents the reflection spectrum of the polystyrene and silica structures obtained during the preliminary experiment.

The similarity of the reflection spectra between the samples indicates a similar behavior of the silica and polystyrene microspheres under electrophoresis conditions. The structures were defected and many empty plots of substrate were seen. It was revealed that the use of polystyrene particles as a matrix material increases the reflection coefficient, which indicates an increasing of the structures ordering. This can be justified by the small heterogeneity of the sizes of polystyrene microspheres (~5%), while the heterogeneity of silica microspheres can reach 30%.

The film’s areal density is proportional to the deposition velocity. In order to increase it a voltage range from 0.3 V to 2.7 V was chosen.
Figure 4. Spectrophotometric analysis of samples of silica (left) and polystyrene (right), obtained under certain conditions. For all samples reflection spectra obtained at three points on the surface of the substrate were obtained.

It was revealed that the deposited films were formed mainly on the anode and they covered the entire surface of the substrate. As a consequence of obtained periodicity obtained films showed opalescence: reflected colors that came from the Bragg diffractions in the periodic distribution of microspheres. Spectrophotometric analysis showed that all structures possessed a PBG in the wavelength range of 460 - 480 nm. A color-shift from green to red was found. The reflectance spectrums of such structures demonstrate a defined Bragg stop band at every sample as shown in figure 5. A similar position of the PBG indicates the identical behavior of microspheres under electrophoresis at the different values of the applied voltage. However, obtained in the voltage range of 2.7… 0.9 V coatings were characterized by brittleness, poor adhesion to the substrate surface due to significant residual stresses in the structure and appearance of large clusters of particles on the substrate.

Figure 5. Reflection spectrum for samples obtained with a potential difference of 2.7 V, 0.9 and 0.3 V. For all samples reflection spectra obtained at three points on the surface of the substrate were obtained.

In order to eliminate agglomeration of particles in the solution we decreased voltage from to 0.3 V. As a result an increase in the reflection coefficient was noted, which may also indicate an increase in the ordering of the structure. No defects and particles clusters on the structures surface were noted. The coating obtained at a potential difference of 0.3 V possessed a pronounced at a wavelength of 480 nm and good adhesion to the substrate.
4. Conclusions
In the course of the study it was found that the voltage range of 0.7 - 2.7 V allows one to obtain thick films with a pronounced PBG in the wavelength range of 460 - 480 nm. However, the films obtained in this range possessed significant residual stresses, which led to the destruction of the structure. The voltage range of 0.3 - 0.6 V allows one to obtain well-ordered structures with a pronounced PBG in the wavelength range of 460 - 480 nm and the highest values of the reflection coefficient, as well as sufficient adhesion to the surface of the substrate. The authors see the development of the work in the research of the phenomenon of self-assembly in colloids.

References
[1.] Syritskii, A. B., & Panfilova, E. V. (2018, November). Investigation of opal nanostructures using scanning probe microscopy. In IOP Conference Series: Materials Science and Engineering (Vol. 443, No. 1, p. 012035). IOP Publishing.
[2.] Katyba, G. M., Zaytsev, K. I., Chernomyrzidin, N. V., Shikunova, I. A., Komandin, G. A., Anzin, V. B., ... & Reshetov, I. V. (2018). Saphire photonic crystal waveguides for terahertz sensing in aggressive environments. Advanced Optical Materials, 6(22), 1800573.
[3.] DEDE, E. M., & Joshi, S. N. (2019). U.S. Patent Application No. 10/347,601.
[4.] Parchine, M., Kohoutek, T., Bardosova, M., & Pemble, M. E. (2018). Large area colloidal photonic crystals for light trapping in flexible organic photovoltaic modules applied using a roll-to-roll Langmuir-Blodgett method. Solar Energy Materials and Solar Cells, 185, 158-165
[5.] Rinkevich, A. B., Samoilovich, M. I., Klescheva, S. M., Perov, D. V., Burkhanov, A. M., & Kuznetsov, E. A. (2013). Millimeter-wave properties and structure of gradient Co–Ir films deposited on opal matrix. IEEE transactions on nanotechnology, 13(1), 3-9.
[6.] Yu, J., Lei, J., Wang, L., Zhang, J., & Liu, Y. (2018). TiO2 inverse opal photonic crystals: Synthesis, modification, and applications-A review. Journal of Alloys and Compounds, 769, 740-757.
[7.] Gorelik, V. S., & Friman, A. V. (2013). Dispersion of electromagnetic waves in a resonant opal photonic crystal filled with Al2O3: Cr3+. Inorganic Materials, 49(6), 577-580.
[8.] Kim, J. H., Kang, S. H., Zhu, K., Kim, J. Y., Neale, N. R., & Frank, A. J. (2011). Ni–NiO core–shell inverse opal electrodes for supercapacitors. Chemical Communications, 47(18), 5214-5216.
[9.] Gorelik, V. S. (2008). Optics of globular photonic crystals. Laser Physics, 18(12), 1479.
[10.] Kuleshova, V. L., Panfilova, E. V., & Prohorov, E. P. (2018, September). Automated device for vertical deposition of colloidal opal films. In 2018 International Russian Automation Conference (RusAutoCon) (pp. 1-5). IEEE.
[11.] Gorelik, V. S., Kudryavtseva, A. D., Tareeva, M. V., & Tcherniega, N. V. (2014). Stimulated light scattering in synthetic opal filled with dielectrics. Inorganic Materials, 50(12), 1217-1221.
[12.] Bartlett, P. N. (2004). Electrodeposition of Nanostructured Films Using Self-Organizing Templates. Interface-Electrophoresis Society, 13(4), 28-33.
[13.] Hatton, B., Mishchenko, L., Davis, S., Sandhage, K. H., & Aizenberg, J. (2010). Assembly of large-area, highly ordered, crack-free inverse opal films. Proceedings of the National Academy of Sciences, 107(23), 10354-10359.
[14.] Palmer, T. R. (2009). Investigation of electrophoretic deposition as a fabrication technique for high performance composites (Doctoral dissertation, Massachusetts Institute of Technology).