Mesoporous anodic aluminum oxide photonic crystalline films and its applications

V S Gorelik\textsuperscript{1,2}, A V Pudovkin\textsuperscript{1}, Y P Voinov\textsuperscript{1}, V V Filatov\textsuperscript{2}, Dongxue Bi\textsuperscript{2}, Guo Liang Shang\textsuperscript{3} and Guang Tao Fei\textsuperscript{3}

\textsuperscript{1} Lebedev Physical Institute of the Russian Academy of Sciences, Moscow, 119991, Russia
\textsuperscript{2} Bauman Moscow State Technical University, Moscow, 105005, Russia
\textsuperscript{3} Key Laboratory of Materials Physics and Anhui Key Laboratory of Nanomaterials and Nanotechnology, Institute of Solid State Physics, Hefei Institutes of Physical Science, Chinese Academy of Sciences, Hefei, China

E-mail: gorelik@sci.lebedev.ru

Abstract. We have calculated the optical characteristics of mesoporous photonic crystalline film of aluminum oxide. We obtained the dispersion relation for electromagnetic waves in the film, calculated an effective refractive index of photonic crystal, worked out group velocities and effective masses of photons and polaritons in mesoporous medium. The results of theoretical analysis are in the good agreement with the measured reflection spectrum. It is shown that the mesoporous photonic crystalline films are good as the radiation amplifiers and highly efficient selective mirrors and filters.

1. Introduction
New gain medium, high efficient selective mirrors, narrow-band filters developments are actual issues in laser science now [1]. Photonic crystals and photonic crystalline films may be used to resolve such issues [2]. Applications of mesoporous globular photonic crystals (based on amorphous SiO\textsubscript{2}) as optical resonator mirrors for different laser types were analyzed [3]. Mesoporous photonic crystalline films (based on Al\textsubscript{2}O\textsubscript{3}) manufacturing technology was announced [4].

Reflection coefficient of photonic crystal film is very high in photonic stop band region. Our tasks were: to analyze optical properties of anodic mesoporous photonic crystalline films based on Al\textsubscript{2}O\textsubscript{3}, to perform experimental measurement of these properties and compare our calculations with experimental data. The possibilities of such films usage in laser science and spectroscopy were analyzed.

2. Experimental part
Photic crystalline films of anodic aluminum oxide with thickness about 20 µm were the object of research. These films were produced from aluminum (see figure 1) in electrolyte with acid [5].

In the process of electrolysis the electric current was changing periodically in electrolyte (see figure 2). As a result the periodical crystalline structure was produced. This crystalline structure is formed from two kinds of dielectric layers with refractive indexes $n_1$ and $n_2$.

Photographs of the film produced out of aluminum substrate are shown in figure 3 (a, b, c). Film
color depends on observation angle: this property is consistent with Bragg’s law. The film is transparent in wide frequency region: in ultraviolet, visible and infrared.

Figure 1. Photonic crystalline film production plant layout: 1 – dielectric cuvette, 2 – dielectric holder, 3 – Al₂O₃ film, 4 – cathode, 5 – anode, 6 – ammeter, 7 – current source, 8 – electrolyte with acid, 9 – resistance.

Figure 2. Current-time dependence is periodical: electric current with higher density $j_1$ exposure film with shorter duration $t_1$ and then electric current with lower density $j_2$ exposure film with longer duration $t_2$. 
Figure 3. Photonic crystalline film surface photo taken from different observation angles.

Schematic view of aluminum oxide photonic crystalline film structure is shown in figure 4. We can see, that Al₂O₃ photonic crystalline film (1) consists of two kinds of layers with different refractive indexes: this film is surrounded by aluminum frame (2) which was not affected by acid. The lattice constant of fabricated anodic aluminum oxide mesoporous crystalline films may be changed at 200-500 nm range.

Figure 4. Photonic anodic aluminum oxide mesoporous crystalline film nanostructure: 1 – Al₂O₃ photonic crystalline film, 2 – aluminum substrate.

Figure 5. Photonic crystalline film transmission spectra for zero angle of registration: (a), (b), (c) – three types of anodic aluminum oxide crystalline films.

Vertical light transmission spectra of incandescent light through film surface for three samples are presented on figure 5 (a, b, c). There are three stop bands in the spectrum of these films. Spectral position of the first stop band is in infrared area, the second stop band is located in visible region and
the third one – in near UV.

3. Theoretical analysis

One-dimensional plane-layered medium model \([6]\) was used to render optical characteristics of the photonic crystalline film. According to this approximation, the propagation of electromagnetic waves in such structure satisfies to dispersion relation \([7]\):

\[
\cos ka = \cos k_1 a_1 \cdot \cos k_2 a_2 - \frac{1}{2} \left( \frac{n_1}{n_2} + \frac{n_2}{n_1} \right) \sin k_1 a_1 \cdot \sin k_2 a_2 .
\] (1)

Here \(n_1\) and \(n_2\) – refractive indexes of layers with thicknesses \(a_1\) and \(a_2\) correspondingly; structure period \(a=a_1+a_2;\) \(k_1=(\omega/c)\cdot n_1,\) \(k_2=(\omega/c)\cdot n_2;\) \(c=3\cdot10^8\) m/sec – speed of light in vacuum. Film transmittance spectrum is inverse to its reflectance spectrum \(T(\omega)=1-R(\omega).\) Film reflectance spectrum is determined by Fresnel condition \([8]\). For normal incidence we have:

\[
R(\omega) = \left[ \left( \frac{ck(\omega)}{\omega} - 1 \right) / \left( \frac{ck(\omega)}{\omega} + 1 \right) \right]^2 .
\] (2)

In the case of thin film (which contains \(N\) layers), it is more accurate to use the following relation \([7]\):

\[
R_s(\omega) = \left[ 1 + \left( \sin ka / \sin Nka \right) / \left( \frac{1}{2} \left( \frac{k_1}{k_2} + \frac{k_2}{k_1} \right) \sin k_2 a_2 \right) \right]^{-1} .
\] (3)

On the basis of dispersion relation (1) we can calculate electromagnetic wave parameters in photonic crystalline film: group velocity \(V(\omega)=\frac{\partial \omega}{\partial k},\) (4); photon effective mass

\[
m(\omega)=\left( \frac{\partial^2 E}{\partial \omega^2} \right)^{-1} = \hbar \left( V(\omega) \frac{dV(\omega)}{d\omega} \right)^{-1} ,
\] (5);

and effective refractive index \(n(\omega)=\pm \frac{c \cdot k(\omega)}{\omega},\) (6), here plus or minus signs match with signs of electromagnetic wave group velocity (4).

So, it is necessary to know thicknesses and refractive indexes of layers \((a_1, a_2, n_1\) and \(n_2)\) to calculate optical properties of the film. In our case the thicknesses of the layers are equal \(a_1=a_2,\) and period \(a=a_1+a_2\) and porosity of the layers are unknown. According to Bragg relation, the spectral positions of stop bands satisfy the condition

\[
2a n_{\text{gf}} = m \lambda_m , \tag{7a}
\]

Here \(m – \) peak sequential number, \(\lambda_m – \) reflectance peak spectral position, \(n_{\text{gf}} = \sqrt{\frac{1}{2} n_1^2 + \frac{1}{2} n_2^2} -\) film effective refractive index. At different incident angles instead of relation (7a) we have:

\[
2a \sqrt{n_{\text{gf}}^2 - \sin^2 \theta} = m \lambda_m , \tag{7b}
\]

On the other hand, spectral line width depends on refractive indexes contrast of layers:

\[
\frac{\Delta \lambda}{\lambda_m} = \frac{2}{\pi} \frac{\Delta n}{n_{\text{gf}}} . \tag{8}
\]

Reflectance peak spectral position \((\lambda_m = 575\) nm\) and full width at half maximum \((\Delta \lambda = 25\) nm\) are known from experiment, see figure 4(c). So, it is possible to calculate film parameters: \(a_1 = 95\) nm, \(a_2 = 95\) nm, \(n_1 = 1.43, n_2 = 1.58\) (and layers porosity is 52% and 31% respectively).

Dispersion relation (1) for given parameters is shown in figure 6. Wave vector tends to zero with frequency decreasing. There are several branches; breaks between them on frequency axis are stop bands. Odd \((2m-1)\) numbers of stop bands are wider than even \((2m)\) ones. Light group velocity in the area of the 2-nd stop band (and other even stop bands) is close to zero according to (4).

Comparison of calculated transmittance spectra (based on equations (2) and (3)) with experimental data (see figure 5c) is shown in figure 7. We can see quite accurate match of stop band spectral
positions, their widths and decreasing of transmittance with wavelength decrease. Experimental transmittance is lower than theoretically rendered one especially in UV area, supposedly because of unaccounted absorption.

Figure 6. Dispersion relation $\omega = \omega(k)$ for photonic crystalline film (thin line is the dispersion relation for light in vacuum $\omega = c \cdot k$).

Group velocity of light (see figure 8) may be negative or positive in some ranges and may be close to zero near to the 2nd stop band. This property may be used for coherent light generation when photons turn into the state of Bose–Einstein condensate. Convenient conditions for such effect observation are the using of laser emission, with frequency value close to the $\Gamma$- point ($k=0$) of the second stop band (see figure 6: higher branch). The temperature of Bose-Einstein condensation is given by the known relation:

$$T_{B-E} = \frac{3.31h^2}{k_B m_r} \left( \frac{N}{\nu^2} \right)^{\frac{2}{3}}. \tag{9}$$

The effective film refractive index of investigated photonic crystalline films is shown in figure 9. Refractive index can be positive or negative. In the recent case the photonic crystalline film is left-handed material in some wavelengths ranges.

Areas corresponding to the stop bands of photonic crystalline film are confined by vertical lines (see figures 8, 9).

Figure 7. Comparison of theory (grey curves) with experiment (black dots).
Effective photon mass $m(\lambda)$ depends on corresponding wavelength and this corresponding dependence is illustrated in figure 10. The mass meaning may be positive or negative and its value changes in wide frequency region. The rest mass $m_r$, corresponding to the edge of the second stop band, is about 2 eV, i.e. essentially lower than the electron rest mass.

4. Applications of mesoporous anodic aluminum oxide photonic crystalline films
Mesoporous anodic aluminum oxide photonic crystalline films have specific reflection spectrum with distinct stop band. Reflection coefficient in stop band area is very high (up to 99.9%). Such properties are usable in selective optical filters and for splitting of multimode laser emission lines (see figure 11).

Total reflection of chosen emission line can be realized in three different methods: it’s possible to
specify crystalline period while anodization (by changing current-time periods); stop band area may be moved by adjusting of angle of incidence/reflection; stop band area may be transformed [9] by injection of dielectric material inside photonic crystalline film pores.

Another probable application is to improve conditions of Raman scattering spectrum registration. See scheme in figure 12: incident photons are filtered by photonic crystalline film but scattered ones pass through it. Sensor sensitivity may be increased because exciting line doesn’t interrupt to measure Stokes and anti-Stokes components.

Photonic crystalline films may be used as detectors of molecular structures. Molecular structure may be injected in photonic crystalline film pores using different techniques: in form of wetting solution, in form of alloy, etc. Raman scattering cross section increases anomalously when spontaneous Raman scattering spectra are registered under conditions of an anomalous increase in the density of the corresponding photon states [10]. When pores of photonic crystal film are filled with Stimulated Raman Scattering active media, it is possible to generate low-threshold Stimulated Raman Scattering due to an anomalous increase in the density of photonic states [10] in the case when the frequencies of the exciting or generated radiation fall on the edge of the corresponding stop bands. The value of the angle \( \theta \) at which the Wulff-Bragg’s condition is satisfied is given by the well-known relation:

\[
2a\sqrt{n^2 - \sin^2 \theta} = m\lambda_{B}, \quad m = 1, 2, 3...
\]

Here \( \lambda_{B} = \lambda_{0} \) - the values of exciting or Stimulated Raman Scattering radiation wavelengths falling into the edge of the corresponding stop band.

Group light velocity is significantly reduced in this case (see figure 8). This leads to increase of photon density. Similar effect can be used to analyze thin dielectric molecular layers deposited on a photonic-crystalline film.

Photonic crystalline films are usable for filtering of laser generation. In figure 11 radiation from multimode laser (1) is filtered by photonic crystalline films (2). One film reflects 532 nm part and transmits 266 and 1064 nm parts, another film reflects 1064 nm part and only 266 nm band is in output. It is possible to modify optical cavity construction from figure 11 to allow only one frequency mode generation. Such scheme is illustrated by figure 12. In this case one of the cavity mirrors is replaced by photonic crystalline film (5). This film reflects only one frequency radiation (based on incident angle). So the single frequency emission will be in output although there are some other allowed modes of the cavity.

Compact analyzer for Raman spectroscopy may be constructed by using photonic crystalline films (figure 13). Laser radiation (6) incidents at an angle \( \theta \) on the sample (1). Sample is placed in the pores of photonic crystalline film (2). Lens (4) converge scattered radiation which goes to refocusator (7) via optical fiber (5). Another photonic crystalline film is placed inside the refocusator at an angle \( \theta \) to the beam. Laser component is reflected by this film while Stokes and anti-Stokes components pass through.

Another Raman spectroscopy analyzer is depicted in figure 14. For this case laser radiation is reflected by film (1), filled by substance for Raman spectra recording. Raman emission goes to tip (4) and then to spectrometer (7) via optical fiber (5). Halogen lamp (6) is needed for spectrometer calibration.

Figure 15 illustrates the setup for generation of the second optical harmonics emission (\( \lambda' = \lambda_{0}/2 \)) by using of mesoporous photonic crystalline film (3), filled by nonlinear optical substances (LiIO\(_3\), NaBrO\(_3\), BaTiO\(_3\)) and rotated at an angle \( \theta \) to the beam (see figure15) for coinciding of exciting line (\( \lambda_{0} \)) or the second harmonic emission (\( \lambda' = \lambda_{0}/2 \)) wavelengths with the edges of the photonic stop band wavelength. There is possible also to observe the opposite phenomenon: the subharmonic transformations of exciting laser emission (see figure 16), when frequency doubling (\( \omega' = \omega_{0}/2; \lambda' = 2\lambda_{0} \)) by photonic crystalline film takes place.
Figure 13. Compact analyzer for Raman spectroscopy: 1 – sample, 2 – photonic crystalline film, 3 – substrate, 4 – lens, 5 – optical fibers, 6 – laser, 7 – refocusator, 8 – mini-spectrometer with multielement radiation receiver, 9 – computer.

Figure 14. Raman spectroscopy analyzer: 1 – photonic crystalline film, 2 – Al₂O₃ base, 3 – fluoropolymeric bracket, 4 – optical fiber probe, 5 – optical fibers, 6 – tungsten halogen, 7 – spectrometer, 8 – computer, 9 – laser, 10 – mirror, 11 – lens, 12 – sample.
Figure 15. Setup for exciting laser wavelength doubling (the second optical generation) by photonic crystalline film: 1 – laser, 2 – lens, 3 – photonic crystalline film, embedded by nonlinear substance, 4 – spectrometer, 5 – computer.

Figure 16. Setup for exciting laser frequency doubling (subharmonic generation) by photonic crystalline film: 1 – laser, 2 – converging lens, 3 – photonic crystalline film, embedded by nonlinear substance, 4 – spectrometer, 5 – computer.

Stimulated Raman Scattering analyzers scheme is shown in figures 17. The same photonic crystalline mesoporous film 3, filled by Raman active media, is used both for Stokes light amplification and for laser beam filtration. Laser beam incidents at an angle $\theta$ to the film surface under the condition $(10)$, providing an density increase of the photonic states. The film 3 in figures 17 reflects laser beam while Stimulated Raman Scattering is generated inside of this film.

Figure 17. Stimulated Raman Scattering with mesoporous anodic aluminum oxide photonic crystalline films, filled by Raman active medium: 1 – laser, 2 – converging lens, 3 – photonic crystalline film, 4 – spectrometer, 5 – computer.

Figure 18. Experimental setup for generation of entangled photonic states during two-photon subharmonic emission excitation: 1 – laser, 2, 4, 5 – lenses, 3, 6 – photonic crystalline films, embedded by nonlinear substance, 7 – spectrometers, 8 – computer.

In figure 18 the experimental scheme for entangled photonic states generation and its recording with the help of mesoporous anodic aluminum oxide photonic crystalline film 3, embedded by nonlinear optics media, is presented. Photonic crystalline film surface is turned at such angle $\theta$ so the wavelength of exciting light emission from laser 1 is close to the edge the second stop band of photonic crystal at wave vector $q=0$. In this case the efficiency of subharmonic generation increases and subharmonic waves with opposite wave vectors ($k_1 = -k_2$) may be detected with the help of two spectrometers 4.

5. Conclusion
Thus we have shown that the high reflection coefficient in narrow stop band range may be realized in mesoporous anodic aluminum oxide photonic crystalline films for wide frequency region: in UV, visible and infrared. Stop band spectral position and its width may be optimized with the help of lattice constant and effective refractive index changing. Such properties open the wide field for applications [11-17]. One way for it is the filling of mesoporous film void by different substances, including liquids, ferroelectrics, luminophores etc. Mesoporous anodic aluminum oxide photonic crystalline films may be explored as selective filters in laser resonators and in devices for registration of spontaneous Raman scattering (see figures 10-13). Mesoporous anodic aluminum oxide photonic crystalline films, embedded by nonlinear optics substances (NaNO$_2$, LiIO$_3$, NaBrO$_3$, BaTiO$_3$), may be used as nonlinear optic elements for the second harmonics and subharmonics generation and for observation of Stimulated Raman Scattering.

Acknowledgments
This work was supported by the Russian Foundation for Basic Research (RFBR) (grants 15-02-02882, 16-08-00618, 16-02-00488, 16-52-00026) and China Scholarship Council.

References
[1] Kaiwei Li, Ting Zhang, Nan Zhang, Mengying Zhang, Jing Zhang, Tingting Wu, Shaoyang Ma, Junying Wu, Ming Chen, Yi He and Lei Wei 2016 Integrated liquid crystal photonic bandgap fiber devices Frontiers of Optoelectronics 9 466–481
[2] Svyakashovskiy S E, Maydykovskiy A I, Novikov V B, Kompanets V O, Skorynin A A, Bushuev V A, Chekalin S V, Murzina T V and Mantsyzov B I 2015 Dynamical Bragg Diffraction in the Laue Geometry in 1D Porous Silicon-Based Photonic Crystals Journal of Russian Laser Research 36 588–601
[3] Gorelik V S and Filatov V V 2012 Spectroscopy of stop bands in artificial opals filled with an alcohol solution of potassium iodide Optics and Spectroscopy 113 301–305
[4] Gorelik V S, Klimonsky S O, Napolskii K S and Filatov V V 2016 Optical properties of one-dimensional photonic crystals based on porous films of anodic aluminum oxide Optics and Spectroscopy 120 32–38
[5] Yisen Liu, Yi Chang, Zhiyuan Ling, Xing Hu and Yi Li 2011 Structural coloring of aluminum Electrochemistry Communications 13 1336–39
[6] Rytov S M 1955 Electromagnetic properties of a finely layered medium JETP 2 466–475
[7] Yariv A and Yeh P 1984 Optical waves in crystals. Propagation and control of laser radiation. (New York: Wiley) p 589
[8] Born M and Wolf E 1999 Principles of Optics: Electromagnetic Theory of Propagation, Interference and Diffraction of Light (Cambridge: Cambridge Univ. Press)
[9] Gorelik V S and Pudovkin A V 2013 Resonance Globular Photonic Crystals Filled with Al$_2$O$_3$:(Cr$^{3+}$) Nanoparticles Herald of the Bauman Moscow State Technical university. Natural sciences 49 43–49
[10] Almohamed Y, Barille R, Vodchits A I, Voynov Yu P, Gorelik V S, Kudryavtseva A D, Orloviich V A and Tcherniiega N V 2015 Reduction of the threshold of stimulated Raman scattering in Raman-active media introduced into pores of a globular photonic crystal JETP Letters 101 399–404
[11] Burdanova M G and Gorelik V S 2015 Polariton waves in capillary fibers doped with rare-earth ions Herald of the Bauman Moscow State Technical university. Natural sciences 63 46–51
[12] Gorelik V S 2015 Photon-boson conversion in ferroelectrics and amino acids Herald of the Bauman Moscow State Technical university. Natural sciences 61 23–36
[13] Tappura K, Luomahaara J, Haatainen T, Hassel J and Vehmas T 2016 Influence of Substrate on Plasmon-Induced Absorption Enhancements Plasmonics 11 627–635
[14] Kaniber M, Flässig F, Reithmaier G, Gross R and Finley J J May 2016 Integrated superconducting detectors on semiconductors for quantum optics applications Applied Physics B 122 115:1–10

[15] Gorelik V S, Dovbeshko G I and Pyatyshnev A Yu 2016 Photoluminescence spectra of DNA and ADP in photon traps under ultraviolet excitation Herald of the Bauman Moscow State Technical university. Natural sciences 65 25–33

[16] Gorelik V S, Pudovkin A V and Filatov V V 2016 Mesoporous Photonic-Crystal Films for Amplification and Filtering of Electromagnetic Radiation Journal of Russian Laser Research 37 604–610