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Local laser oxidation of porous silicon photonic crystals

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The process of thermal oxidation of porous silicon photonic crystals by laser treatment has been studied experimentally and theoretically. The temperature of laser heating was calculated by solving of the non-stationary thermal conductivity equation. The degree of silicon oxidation was estimated experimentally by measuring the spectral shift of the reflection curve of photonic crystals. We demonstrate the controllable shift of the photonic band gap of porous silicon photonic crystals made by means of laser irradiation.

Keywords: porous silicon, photonic crystals, local laser oxidation, laser surface treatment.

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Porous silicon has long been regarded a promising material for optics and photonics, but its application is hindered by strong optical absorption [1]. Since the diameter of pores in silicon depends monotonically on the etching anode current density, a spatial periodic structure of layers with different porosity forms in silicon if the current density is varied periodically. This provides an opportunity to fabricate photonic crystals (PCs). Porous silicon may be oxidized to silicon oxide in order to reduce optical losses. Its porous structure is retained in the process, and the PC structure also remains unchanged [2]. Being a promising alternative to heating a silicon sample in a furnace [3], oxidation by laser irradiation allows one to specify complex geometries and form photonic structures. However, the process of local laser oxidation (LLO) of PCs prepared from porous silicon has not been examined in detail. In the present study, we investigate the process of LLO of porous silicon PCs.

The model of local laser heating [4] was used to model the distribution of temperature T numerically. This model is based on thermal conductivity equation

$$\frac{\kappa}{\rho c_v}\Delta T(x,y,z,t) + \frac{w}{\rho c_v} e^{-2\frac{x^2+y^2}{R^2}} e^{-\frac{t^2}{2\tau_0^2}} \gamma e^{-\gamma z} = \frac{\partial T(x,y,z,t)}{\partial t},$$

where κ is the thermal conductivity coefficient, ρ is the material density, c_v is the specific thermal capacity, R is the laser beam radius, w is the laser radiation intensity, τ_0 is the laser pulse duration, and γ is the coefficient of radiation absorption in matter. The thermal conductivity equation was solved numerically in MATLAB. The model allows one to set a periodic source function to simulate heating by a pulse laser. Calculations were performed for the following parameters: laser wavelength $\lambda = 1064$ nm, pulse duration $\tau_0 = 120$ ns, a beam radius of 0.3 mm, a pulse repetition rate of 80 kHz, and a beam displacement rate of 20 mm/s relative to the surface; the material constants were $\rho = 1800\,\mathrm{kg/m^3}$, $\kappa = 0.3\,\mathrm{W/(m\cdot K)}$, and $c_v = 900\,\mathrm{J/(kg\cdot K)}$ [5]. Owing to the smallness of the Debye temperature, the thermal capacity and the thermal conductivity do not increase in the course of heating [6].

Calculated data (Fig. 1, *a*) demonstrate that the temperature in the central region reaches a constant level of 1034°C after irradiation with a series of 100 pulses. Since the beam center shifts gradually along the sample surface, the material in the origin of coordinates, which is assumed to coincide with the position of the beam center on the sample surface at zero time, starts to cool. While reaching saturation, the center of the beam shifts by 1/25 of its diameter; therefore, this effect may be neglected. The in-plane temperature distribution (Fig. 1, *b*) has a maximum; the temperature decreases outside of the irradiation region.

Photonic crystals for the experimental examination of oxidation were fabricated in accordance with the procedure detailed in [2]. These PCs featured 100 alternating layers with porosities $p_1 = 0.66$ and $p_2 = 0.74$, anode current densities $j_1 = 40\,\mathrm{mA/cm^2}$ and $j_2 = 160\,\mathrm{mA/cm^2}$, and thicknesses $d_1 = 109.5$ nm and $d_2 = 102.5$ nm. The diameters of pores in each layer have been measured earlier in [7] with a scanning election microscope: $a_1 = 20$ nm, $a_2 = 50$ nm.

The transfer matrix method [8] was used to calculate optical reflectance spectra of PCs. A three-component model tested in [7] and based on the Bruggeman approximation [9] was used to calculate refraction indices n_1 and n_2 of porous silicon layers. Pores in silicon are approximated in this model by elongated ellipsoids. The walls of pores are coated by an oxide layer of a given thickness. The oxide thickness increases in the course of oxidation. while the volume fractions of air and silicon decrease in proportion corresponding to the stoichiometric ratio of the oxidation reaction. The oxide layer thickness is the only approximation parameter in this model. A Raycus P20QB laser adjusted so as to match the parameters of

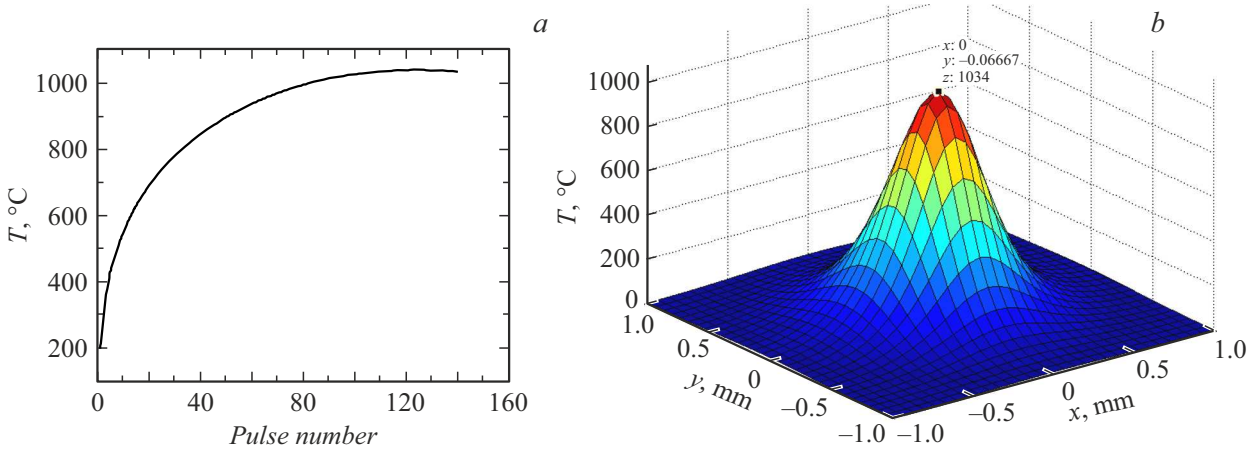

Figure 1. Result of calculation of temperature of porous silicon irradiated by a series of laser pulses. *a* — Dependence of the temperature at the beam center on the pulse number; *b* — temperature distribution in the substrate plane after irradiation with a sequence of 150 pulses.

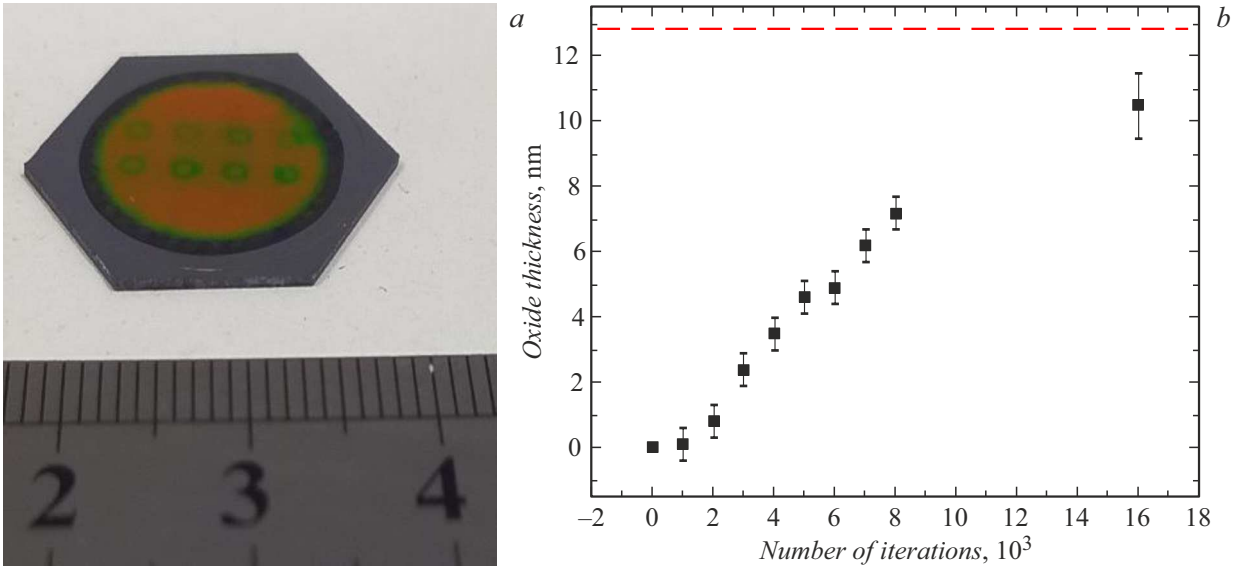

Figure 2. *a* — Photographic image of a photonic crystal irradiated by a laser in eight spots. These irradiation regions differ in the number of iterations, which varies from 1000 to 8000. *b* — Dependence of the oxide layer thickness on the number of iterations. The dashed line denotes the complete oxidation level, which was attained by holding a sample in a furnace at 900°C for 4 h.

numerical modeling was used for irradiation of samples. Irradiation was performed by shifting the focus point of laser radiation along a circular trajectory 2 mm in diameter; the number of iterations varied from 1000 to 8000 with a pitch of 1000. The photographic image of a sample is shown in Fig. 2, *a*. Eight circular regions with different irradiation times are seen in this image. The PC band gap underwent a shift toward shorter waves in each of these regions. The sample was imaged at an angle so as to make the photonic band gap (PBG) shift more noticeable.

The reflectance spectra of each region were measured. Measurements were performed with a white light beam focused to a spot 0.2 mm in diameter. Spectra were measured under normal incidence with an OceanInsight QEPro spectrometer following the procedure outlined in [2,7] at the center of the irradiation line, where the temperature reaches its maximum. An example spectrum for the region with 8000 iterations is shown in Fig. 3, *b*, while the spectrum of unoxidized silicon is presented for comparison in Fig. 3, *a*. It can be seen that the PBG center shifted from 695 to 625 nm. This is indicative of partial oxidation of the material. The results of approximation of spectra by the theoretical model (the oxide layer thickness was set to 0 and 7.2 nm for unoxidized and irradiated samples, respectively) are also shown for illustrative purposes. The oxide layer thicknesses determined by approximating the spectra of other samples are presented in Fig. 2, *b*.

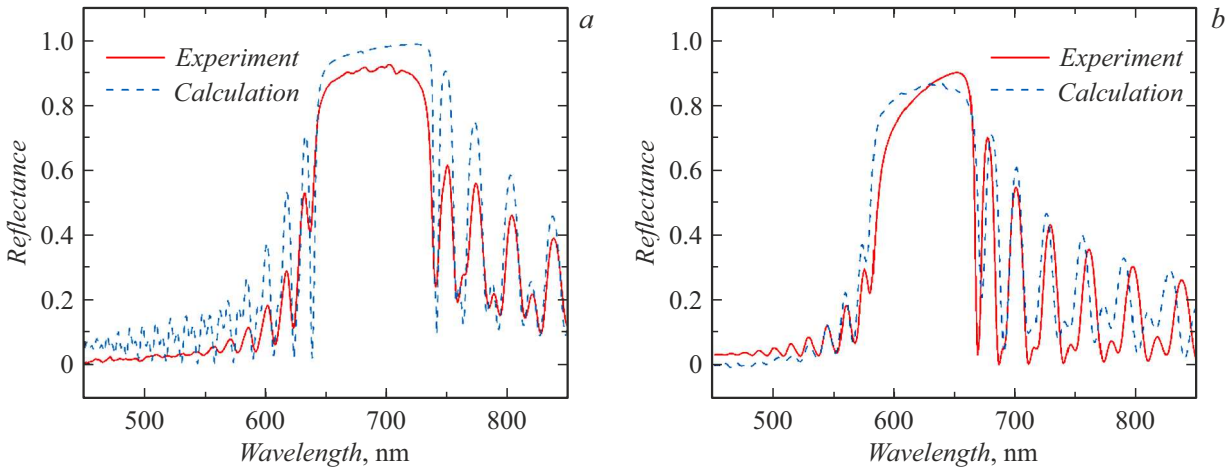

Figure 3. Experimental and calculated reflection spectra of a photonic crystal, which was fabricated from porous silicon, before (*a*) and after (*b*) laser irradiation.

Factoring in the geometric parameters of the beam trajectory and waist in 1000 iterations that had an overall duration of 314 s, one may determine that the sample was subjected to thermal influence for 20 s in total. According to the model of silicon oxidation in the case of thin layers [10], the oxide growth rate at the initial stage is 3 nm/min at a temperature of 1000°C. Therefore, the oxide layer thickness should increase by 1 nm in 20 s, and this agrees with the experimental data: the mean oxide thickness is 0.86 nm per a thousand iterations. According to [10], the rate of growth of the oxide layer thickness at the initial oxidation stage is higher than the one predicted by the diffusion model. This also explains the linear nature of growth.

A method for laser treatment of porous silicon PCs (local laser oxidation) was demonstrated, and a theoretical model of the oxidation process and variation of the spectral PC characteristics was constructed. The model agrees with experimental data. The LLO technique allows one to alter the PBG position locally and in a controllable way, making this technique potentially applicable in the fabrication of various photonic nanostructures.

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Conflict of interest

The authors declare that they have no conflict of interest.

References

[1] A.A. Leonardi, M.J.L. Faro, A. Irrera, Anal. Chim. Acta, **1160**, 338393 (2021). DOI: 10.1016/j.aca.2021.338393
[2] S.E. Svyakhovskiy, A.I. Maydykovsky, T.V. Murzina, J. Appl. Phys., **112** (1), 013106 (2012). DOI: 10.1063/1.4732087
[3] A.M. Rossi, G. Amato, V. Camarchia, L. Boarino, S. Borini, Appl. Phys. Lett., **78**, 3003 (2001). DOI: 10.1063/1.1370536
[4] X. Li, Y. Guan, Nanotechnol. Precis. Eng., **3**, 105 (2020). DOI: 10.1016/j.npe.2020.08.001
[5] A.S. Fedorov, A.S. Teplinskaia, Materials, **15** (23), 8678 (2022). DOI: 10.3390/ma15238678
[6] J. de Boor, D.S. Kim, X. Ao, D. Hagen, A. Cojocaru, H. Föll, V. Schmidt, Europhys. Lett., **96** (1), 16001 (2011). DOI: 10.1209/0295-5075/96/16001
[7] A. Bobrovsky, S. Svyakhovskiy, I. Roslyakov, A. Piryazev, D.A. Ivanov, V. Shibaev, M. Cigl, V. Hamplová, A. Bubnov, ACS Appl. Polym. Mater., **4** (10), 7387 (2022). DOI: 10.1021/acsapm.2c01149
[8] A. Luce, A. Mahdavi, F. Marquardt, H. Wankerl, J. Opt. Soc. Am. A, **39** (6), 1007 (2022). DOI: 10.1364/JOSAA.450928
[9] D.A.G. Bruggeman, Ann. Phys., **416** (7), 636 (1935). DOI: 10.1002/andp.19354160705
[10] H.Z. Massoud, J. Electrochem. Soc., **132** (11), 2685 (1985). DOI: 10.1149/1.jjj2113648

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