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Optimization of electrochemical etching parameters improves the quality factor of porous silicon microcavities

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Porous silicon is a promising and versatile material for modern technologies with a wide range of potential applications. Here we demonstrate a two-fold increase in the quality factor of porous silicon microcavities by gradient change of electrochemical etching times for each layer of microcavity, which compensates for the gradual decrease in the etching rate during sample fabrication. The results of this work will improve the performance of nanophotonic devices based on porous silicon for applications in optical communications and sensors for diagnostics and environmental monitoring.

Keywords: porous silicon, porosity, etching rate, electrochemical etching, quality factor.

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Porous silicon (PS) and various functional structures based on it have been widely studied in recent decades due to their unique properties and application prospects in areas such as biomedicine, microelectronics, and nanotechnology [1]. One of the most common and inexpensive methods of PS manufacture is electrochemical etching of monocrystalline silicon, which results in a material with a porous structure that has novel optical, electronic, and mechanical properties [2]. The morphology of pores, i.e. their size and shape, is influenced by a number of factors during the process of electrochemical etching the concentration of etching solution, etching current density and mode of its supply (continuous or pulse), the resistivity of the original material, etching time, etc. In addition, porosity parameters can also change under the influence of external factors such as light irradiation, temperature changes or mechanical stresses. If the etching parameters can be precisely controlled, the fabrication of multilayer PS structures with different morphologies becomes possible. Microcavities (MC) based on this material [3] attract great interest of researchers. Such structures are Fabry-Perot MCs consisting of two reflecting surfaces — distributed Bragg reflectors (DBR) [4], and a porous layer between them, called the cavity [5]. Various materials can be embedded into the MC, which allows creating integrated nanophotonic structures [6,7] that can be used to control light at the nanoscale and improve the interaction between light and matter in devices for a variety of applications such as sensing, lasers, optical communications, and photonics.

The quality of MCs is evaluated by the quality (Q) factor parameter. This parameter characterizes the quality of the resonance: it is proportional to the retention time of light in the MC, also called photon lifetime. In order to increase the Q-factor of the PS-based MC, first of all, it is necessary to increase DBR reflectivity, which can be accomplished by increasing the contrast of refractive indices between layers [8] or the number of alternating pairs of DBR layers [9], as well as to ensure the maximum periodicity of the MC layers. However, in real PS-based MCs, periodicity disturbance in the lower MC layers is often observed due to the depletion of the etching solution and increased variation in the silicon etching rate. In this paper, a twofold increase in the Q-factor of PS-based MCs was demonstrated due to gradient increase in etching time during their manufacturing process, resulting in improved homogeneity of the MC structure by achieving stable thicknesses of the porous layers.

The MCs were manufactured by electrochemical etching according to the method described in [7]. MCs were produced at room temperature using boron-dopedp^+-type silicon wafers with crystallographic orientation (100) and resistivity $0.001-0.005\,\Omega\cdot$cm (JSC Telecom-STV/grqq). The electrolyte was a mixture of HF (48%) and ethanol in a volume ratio of 3:7. The current density was controlled automatically using a Keithley 2635A programmable power supply. Calibration curves for porosity dependencies on etching current density were obtained using a hybrid gravimetric method. The PS layers of fixed porosity (so-called monolayers) were used for this purpose. Immediately before and after fabrication of the monolayers, the silicon substrates were weighed with ug precision to determine the mass of etched silicon. Scanning electron microscope (SEM) images of the cross-section of the monolayers were then obtained. From the SEM images, the thicknesses (etch depths) of the porous silicon monolayers were determined using ImageJ software. Taking into account the density of

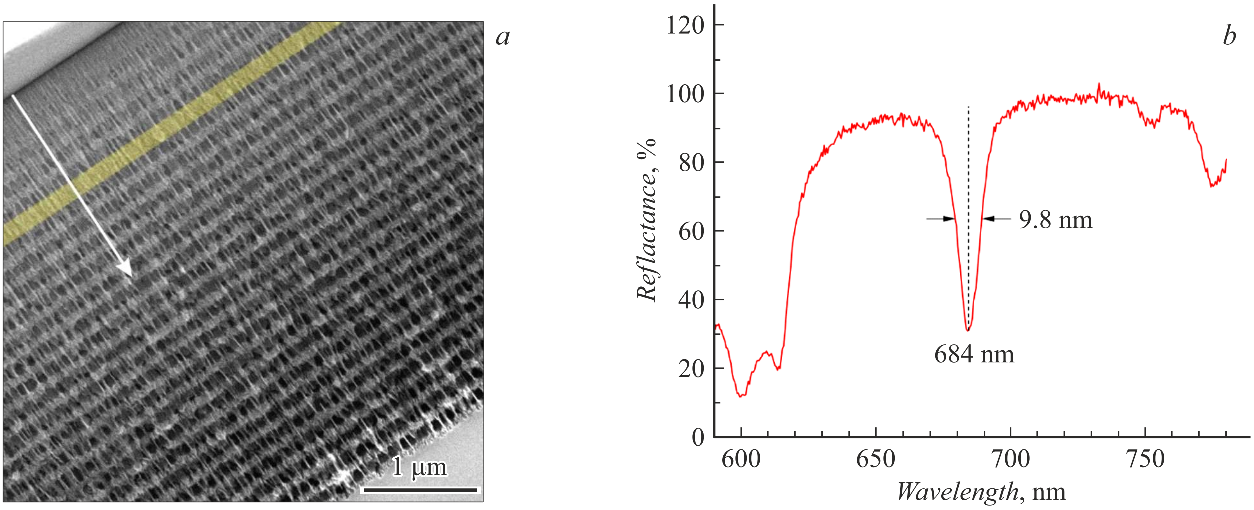

Figure 1. *a* — SEM image of the MC cross section. The arrow shows the direction of etching, the MC cavity is highlighted in yellow. *b* — reflectance spectrum of the unoptimized PS-based MC. A color version of the figure is provided in the online version of the paper.

monocrystalline silicon, the diameter of the etching area, and the mass of etched silicon, porosity values for individual monolayers were calculated.

MCs were manufactured by alternating low and high etching currents (3.5 and 26.8 mA, etching area diameter 9.7 mm) so that the layers were quarter-wavelength. MC reflectance spectra were recorded using an OceanOptics USB2000+ spectrometer. Surface and cross-sectional images of the PS structures were acquired using a MAIA3 Tescan SEM (OXFORD Instruments), and the images were analyzed using ImageJ software.

Unoptimized PS-based MCs were fabricated by periodic exposure to low and high etching currents in the absence of pauses after each layer. Such MCs consisted of a top and bottom DBRs with 5 and 20 pairs of alternating layers, respectively, separated by a double-thickness layer forming a cavity (Fig. 1, *a*). The large number of layer pairs in the lower DBR made it possible to increase the Q-factor of the MC and, in the case of its application as a base for hybrid systems with embedded luminophores, to create a preferred direction of photoluminescent signal propagation, thus increasing the efficiency of its acquisition. On the other hand, the MC was asymmetric due to a smaller number of layer pairs in the top DBR, which increased its transmittance and allowed efficient excitation of the MC eigenmode.

The reflectance spectrum of the unoptimized MC (Fig. 1, *b*) has a typical shape for this type of resonant cavity and contains a pronounced eigenmode at 684 nm. The eigenmode width is 9.8 nm. It follows that the Q-factor of this MC has a value of 69.8. SEM images of the MC cross-section were obtained (Fig. 1, *a*), from which the average thickness of each MC layer was determined. It was found that during the etching process, the thicknesses of the layers gradually decreased in the direction away from the sample surface, which is due to the depletion of the electrolyte caused by the silicon etching process as well as the blocking of the silicon surface by hydrogen bubbles [10]. Fig. 2 shows the dynamics of change in the thicknesses of high porosity layers in the structure (a similar result was obtained for low porosity layers).

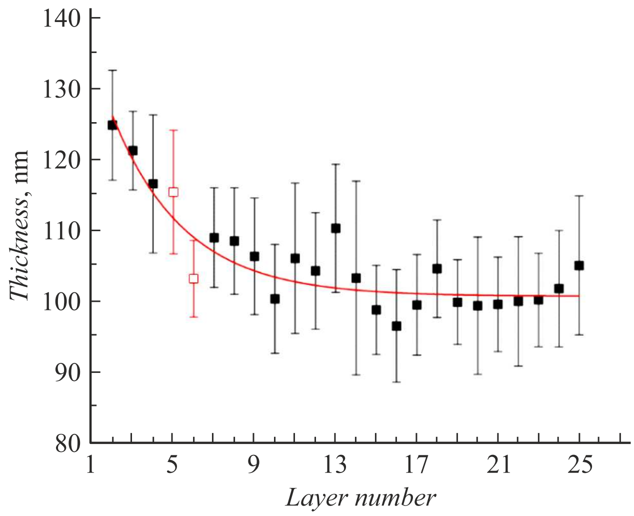

Figure 2. Dynamics of change in the thicknesses of high porosity layers in MC. The light-colored dots indicate the layers adjacent to the MC cavity layer.

Fig. 2 shows that the thickness difference between the upper and lower high porosity layers is 24 nm, which is up to $\sim 25\,\%$ of the planned layer thickness, while for the low porosity layers this value was found to be close to 9 nm. The increase in pore diameter, etch depth, and silicon porosity is mainly determined by the current density. After critical current values are reached, the thickness of the layers decreases due to diffusion control of the electrochemical etching reactions: at high reaction rates, the acid is consumed rapidly and the local HF concentration

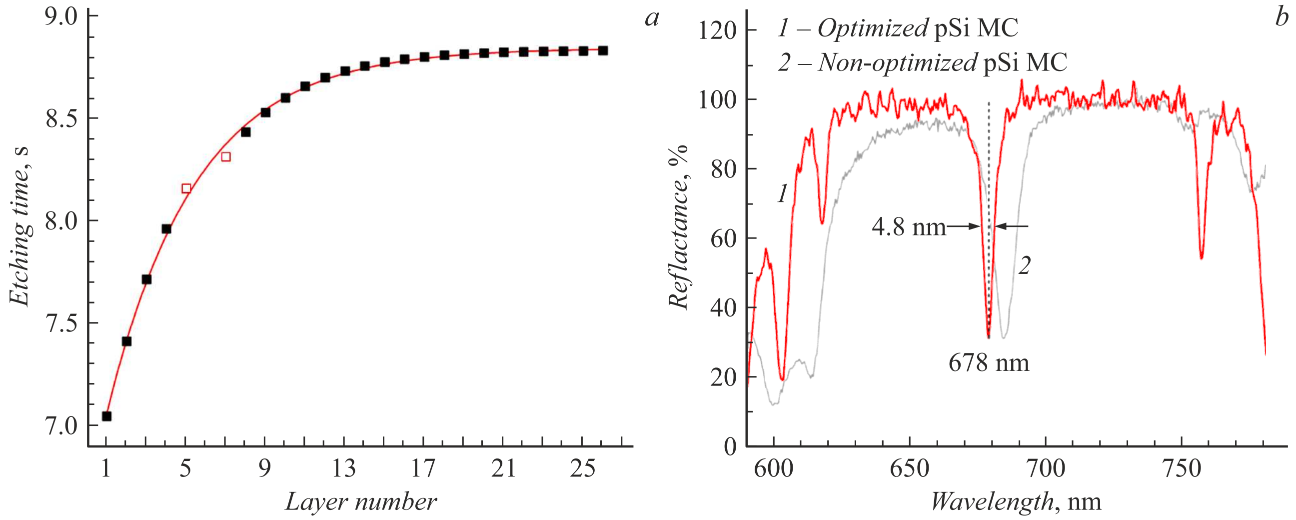

Figure 3. *a* — curve illustrating the corrections for etching times during fabrication of optimized MCs (light dots indicate the same as in Fig. 2). *b* — experimental reflectance spectrum of the optimized MC (*1*) compared with that of the unoptimized MC (*2*).

decreases. At the PS/monocrystalline silicon interface, a lack of F^- ions occurs, which leads to an increase in local porosity, a decrease in the etching rate in deep layers, and shifts the reaction to the electropolishing mode [1]. Based on the analysis of SEM images, correction factors for the etching time of each layer were determined to equalize the observed gradient of MC layer thicknesses. The corrections were chosen to bring the thicknesses of the top and bottom layers of the structure to values corresponding to the layers in the middle. Thus, a shorter etching time was chosen for the upper layers having a larger thickness. A monoexponential function was chosen to approximate the dependence describing the etching time gradient (Fig. 3, *a*), and pauses of 5 s after etching each MC layer were added to the etching program to prevent silicon passivation due to hydrogen accumulation. The pauses allowed the H_2 bubbles to move away from the surface without interfering with the etching process and allowed the HF molecules to react with the substrate. Fig. 3, *b* shows the reflection spectrum of a MC fabricated using the optimized technique with pauses and etching time gradient. Te eigenmode wavelength of this MC is 678 nm, and its full width at half maximum is 4.8 nm; thus, the Q-factor of the MC is 141.3.

Thus, including pauses after each layer and a gradient of etching times in the etching program allowed a twofold increase in the Q-factor of the PS-based MC compared to the unoptimized MC. As a result, we show that fine-tuning the of the etching parameters by taking into account the emerging changes during this process is essential for manufacturing MCs with high Q-factor. The introduction of pauses in the etching process also improves the quality of PS structures by restoring the local concentration of fluoride ions in the electrolyte. Therefore, the modification of etching parameters has been demonstrated to provide a significant improvement in the optical performance of PS-based MCs, which opens up prospects for the optimization of devices used in the fields of nanophotonics and sensorics.

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Conflict of interest

The authors declare that they have no conflict of interest.

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