Conference Paper

Preparation of Freestanding Porous Silicon Photonic Crystals

I. Kryukova[1], D. Dovzhenko[1], A. Chistyakov[1], and I. Nabiev[1,2]

[1]National Research Nuclear University MEPhI (Moscow Engineering Physics Institute), Kashirskoe shosse 31, Moscow, 115409, Russia
[2]Laboratoire de Recherche en Nanosciences, LRN-EA4682, Université de Reims Champagne-Ardenne, 51100 Reims, France

Corresponding Author:
I. Kryukova
irina.kryukova.mephi@gmail.com

Received: 28 January 2018
Accepted: 15 March 2018
Published: 25 April 2018

Publishing services provided by Knowledge E

Selection and Peer-review under the responsibility of the PhIO Conference Committee.

Abstract

Nowadays, the photonic crystals are of great interest and are widely used in photonics, biosensing, optoelectronics and other fields of research. The one-dimensional photonic crystals manufactured on the basis of porous silicon were proved to be the most suitable for applications due to their high sorption ability, large surface area, easiness of fabrication, and possibility to precisely control porosity and refractive index during electrochemical etching. However, the sensitivity of various kinds of gas and biological sensors as well as the performance of solar cells and other devices on the basis of porous silicon structures may be significantly increased by detaching the structures from the substrate. Here, we have developed and investigated the fabrication procedure of freestanding one-dimensional photonic crystals on the basis of porous silicon with the use of electropolishing method followed stabilization of freestanding porous silicon photonic structures through their oxidation. We have demonstrated that the developed and applied lift-off procedure does not violate the morphology and the photonic properties of the samples.

Keywords: Porous silicon, photonic crystals, microcavity, thin films, freestanding photonic crystals.

1. Introduction

Nowadays, sensor systems on the basis of porous matrices are of great interest for the detection of toxic and dangerous substances as well as for biosensing [1–3]. However, most of the sensors are arranged in such a way that the contact of the medium with the inner surface of porous matrixes is limited by the substrate. A freestanding porous matrix, as the active element of a sensor, significantly increases the detection efficiency due to the possibility of pumping the analyte through the porous structure. The latter is true both for sensors working on the principle of the reflection spectrum shift due to a local change in the refractive index, and for hybrid sensors, based on the registration of the selective fluorescent labels signal [1, 4, 5] or luminescence quenching [6] of luminophores embedded into the porous structure. In addition, freestanding porous matrices are able to increase the efficiency of solar cells [7] and can be used as transmission optical elements: narrowband and edge filters [8, 9].

In our study, we have fabricated freestanding porous silicon microcavities and measured their reflection spectra before and after lifting them off from the substrate. The reflection spectra of the microcavities remain almost unchanged, which allows us to state that the used lift-off technique does not affect the integrity of the samples. Furthermore, we have shown that thermal oxidation could be used to stabilize optical properties of freestanding porous silicon photonic crystals and does not lead to the significant deformation of freestanding porous silicon structure.

2. Materials and methods

We have used electrochemical etching of highly doped monocrystalline silicon wafers in hydroalcoholic solutions of 48% aqueous hydrofluoric acid to produce porous silicon photonic crystals as described in details in [10–12]. Briefly, the etching current density was varied from 3 mA/cm^2 to 30 mA/cm^2 to create a porous silicon microcavity. The process has been carried out in home-built PTFE etching cell with etching surface area around 1 cm^2. Highly boron-doped p-type monocrystalline silicon wafers with (100) orientation and resistivity of 0.003 Ω×cm have been used as a substrate. Once samples of photonic crystals have been fabricated, their reflection spectra were measured with the OceanOptics USB2000+ spectrometer, just before lifting-off from the substrate.

In order to lift-off porous structure from its substrate, we have applied an electropolishing method. During electropolishing, the layers of the silicon atoms were removed, in a layer-by-layer fashion, and the porous silicon was separated from the wafer, i.e. lifted-off. The switching from porous silicon formation to electropolishing was ensured by the increase of the current density to approximately 300 mA/cm^2 (using an electrolyte with the same hydrofluoric acid concentration as that for the porous silicon formation mode) [13]. However it was shown that in order to obtain a higher surface quality, it is more appropriate to use a diluted HF solution rather than HF solution used for porous silicon formation [14]. In fluoride-depleted solution, the electropolishing process leads to the formation of oxygen compounds of silicon at the interface between the porous layer and the silicon substrate, where holes, provided by the substrate, are easily available to promote silicon oxidation. Subsequent attack by fluoride ion in the electrolyte dissolves the oxide layer, resulting in the lifting-off the porous silicon structure from the substrate. The lower HF concentration also makes it possible to reduce the current density necessary for the lift-off by 1-2 orders of magnitude. Thus, our electropolishing current density was 6 mA/cm^2 [15]. After all, freestanding porous silicon microcavities were placed in hexane to avoid adhesion to the silicon substrate and to minimize the possibility of shattering of the film due to the strong capillary forces and thermal stresses exerted when ethanol evaporates from the pores. The same monocrystalline silicon wafer can be etched multiple times. Finally, the reflection spectra of freestanding porous silicon microcavities were measured and compared with the reflection spectra of non-lifted-off samples.

3. Results and discussion

The comparison of the reflection spectra of porous silicon microcavities on the substrate with the freestanding is shown in Figure 1. It can be seen, that the spectra do not differ significantly: the form of the reflection spectra remains almost unchanged, its eigenmode and characteristic secondary peaks are preserved. There is also a 5-10 nm blue shift, which could be attributed to the partial oxidation and subsequent dissolution of the silicon on the surface of inner porous layers during the lift-off. The fact that the reflection spectra of microcavities, the eigenmode position and full width at half maximum in particular, remain almost the same allows us to state that the technique we used for lifting-off porous structures from the substrate does not lead to the collapse of multilayer structure and does not affect their morphology. Minor blue shift observed is due to the change of effective refractive indexes of porous layers.

In order to stabilize optical properties of freestanding microcavity samples we performed thermal oxidation. We used thermal oxidation in soft regimes to prevent freestanding porous films from crushing due to high mechanical stresses arising during the transition of silicon into silicon oxides. In details, after the lifting-off the photonic crystal samples have been oxidized in air atmosphere in tube furnace at 500°C during 3 hours and the reflection of the oxidized samples have been measured (Figure 2). One can see that the photonic bandgap was shifted by about 140 nm, while the shape of the spectrum did not change significantly (Figure 2). Narrowing of the photonic bandgap full-width-at-half-maximum was attributed to the decrease of the refractive index contrast between the layers with different porosity. Thus, we can conclude that the oxidation of the freestanding porous silicon microcavities does not lead to the destruction of multilayer structure and preserves the photonic properties of the microcavity.

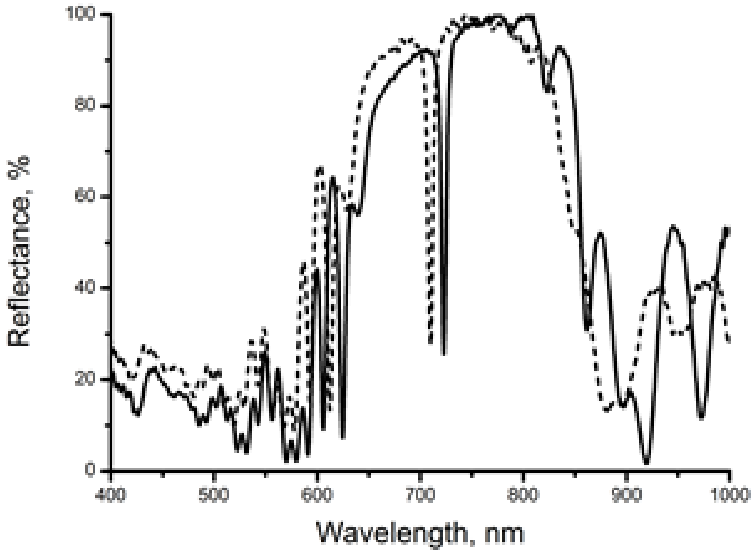

Figure 1: Reflection spectra of porous silicon microcavity on the substrate (solid line) and lifted-off from the substrate (dashed line).

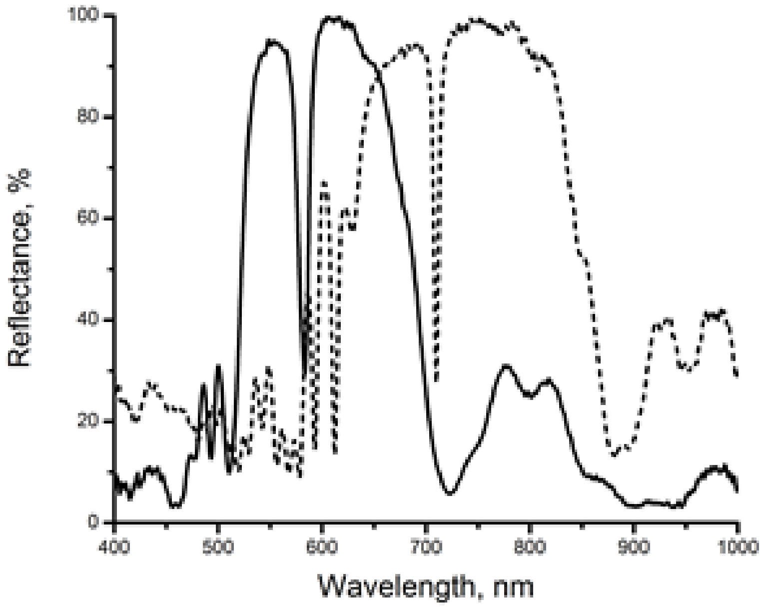

Figure 2: Reflection spectrum of porous silicon microcavity lifted-off from the substrate before (dashed line) and after (solid line) thermal oxidation.

4. Conclusions

In this study, we have investigated the technique of lift-off of the porous silicon photonic crystals from monocrystalline silicon substrates using electropolishing method. It has been demonstrated that there is no significant changes in the reflection spectra of freestanding porous structures. Photonic bandgap width and position, reflectance and eigenmode position and full-width-at-half-maximum remained the same, and only the small blue shift has been observed. Further, the thermal oxidation of the freestanding microcavities can be performed without any subsequent disruptions of the multilayer structure and morphology. The obtained results show that the lifting-off technique developed we used in our study is not destructive for the multilayer structure of the samples and morphology of the photonic crystal and could be used to increase the performance of many devices in photonics and sensing.

Acknowledgement

This study was supported by supported by the Ministry of Education and Science of the Russian Federation under the grant no. 14.Y26.31.0011.

References

[1] G. E. Kotkovskiy, Y. A. Kuzishchin, I. L. Martynov, A. A. Chistyakov, and I. Nabiev, "The photophysics of porous silicon: technological and biomedical implications," Phys. Chem. Chem. Phys., vol. 14, pp. 13890–13902, 2012.

[2] G. Gaur, D. Koktysh, and S. M. Weiss, "Integrating Colloidal Quantum Dots with Porous Silicon for High Sensitivity Biosensing," MRS Proc., vol. 1301, no. 9, pp. 241–246, Jan. 2011.

[3] V. S. Lin, "A Porous Silicon-Based Optical Interferometric Biosensor," Science (80-.)., vol. 278, no. 5339, pp. 840–843, Oct. 1997.

[4] M. B. de la Mora, M. Ocampo, R. Doti, J. E. Lugo, and J. Faubert, "Porous Silicon Biosensors," in State of the Art in Biosensors - General Aspects, InTech, 2013, pp. 141–161.

[5] U. Resch-Genger, M. Grabolle, S. Cavaliere-Jaricot, R. Nitschke, and T. Nann, "Quantum dots versus organic dyes as fluorescent labels," Nat. Methods, vol. 5, no. 9, pp. 763–775, Sep. 2008.

[6] I. Levitsky, "Porous Silicon Structures as Optical Gas Sensors," Sensors, vol. 15, no. 8, pp. 19968–19991, Aug. 2015.

[7] C. S. Solanki, R. R. Bilyalov, J. Poortmans, G. Beaucarne, K. Van Nieuwenhuysen, J. Nijs, and R. Mertens, "Characterization of free-standing thin crystalline films on porous silicon for solar cells," Thin Solid Films, vol. 451–452, pp. 649–654, Mar. 2004.

[8] S. Setzu, P. Ferrand, and R. Romestain, "Optical properties of multilayered porous silicon," Mater. Sci. Eng. B, vol. 69–70, pp. 34–42, Jan. 2000.

[9] V. Kochergin and H. Foell, "Commercial applications of porous Si: optical filters and components," Phys. status solidi, vol. 4, no. 6, pp. 1933–1940, May 2007.

[10] E. V Osipov, I. L. Martynov, D. S. Dovzhenko, P. S. Ananev, G. E. Kotkovskii, and A. A. Chistyakov, "Silicon Photonic Structures with Embedded Polymers for Novel Sensing Methods," Opt. Spectrosc., vol. 122, no. 1, pp. 74–78, 2017.

[11] D. S. Dovzhenko, I. L. Martynov, P. S. Samokhvalov, I. S. Eremin, G. E. Kotkovskii, I. P. Sipailo, and A. A. Chistyakov, "Photoluminescence of CdSe/ZnS quantum dots in a porous silicon microcavity," in Proceedings of SPIE - The International Society for Optical Engineering, 2014, vol. 9126, no. April, p. 91263O.

[12] R. L. Smith and S. D. Collins, "Porous silicon formation mechanisms," J. Appl. Phys., vol. 71, no. 8, pp. R1–R22, Apr. 1992.

[13] Y. H. Xie, M. S. Hybertsen, and William L. Wilson, "Absorption and luminescence studies of free-standing porous silicon films," Phys. Rev. B, vol. 49, no. 8, pp. 5386–5397, 1994.

[14] J. von Behren, L. Tsybeskov, and P. M. Fauchet, "Preparation and characterization of ultrathin porous silicon films," Appl. Phys. Lett., vol. 66, no. 13, pp. 1662–1664, Mar. 1995.

[15] M. J. Sailor, "Freestanding Porous Silicon Films and Particles," in Porous Silicon in Practice, Weinheim, Germany: Wiley-VCH Verlag GmbH & Co. KGaA, 2012, pp. 119–131.