Conference Paper

Porous Silicon Photonic Crystal as a Substrate for High Efficiency Biosensing

Dovzhenko D.S.[1], Chistyakov A.A.[1], and Nabiev I.R.[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

Abstract

Photonic crystals offer great possibilities for the improvement of performance of different kinds of devices. Due to the ability to control the light propagation and to change optical properties via interaction with the media photonic crystals have been widely used to increase the sensitivity of biosensing in many experimental setups. Among them some of the most interesting for practical applications are one-dimensional porous silicon photonic crystals. They could be easily fabricated, have big surface area, high sorption abilities, and have been shown to be able to change the emission of embedded luminophores. In this study we have fabricated and performed the comprehensive investigation of the properties of hybrid system consisting of the porous silicon one-dimensional photonic crystals embedded with semiconductor quantum dots as the luminophores. We have demonstrated the ability of these systems to enhance the photoluminescence of luminophores and serve as the substrate for the high efficient biosensing.

Keywords: Porous silicon, microcavity, quantum dots, luminescence enhancement

Corresponding Author:
Dovzhenko D.S.
dovzhenkods@gmail.com

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1. Introduction

Improvement of detection efficiency in biosensing is of great interest due to the potential ability to reveal diseases at the early stages. One of the most widely used sensing methods is the measurement of luminescence signal obtained from the fluorescent markers which could selectively bind to the antigen in the analyte [1]. Detection efficiency could be significantly improved with the use of highly luminescent markers such as semiconductor quantum dots (QDs), or by the use of more sensitive detection setups [1]–[3]. Photonic crystals allow one to influence on the luminescent properties of luminophores embedded into their structure and provide the possibility to improve the efficiency of collection of luminescence signal [4]–[6]. On the other hand the activated

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surface of the photonic crystal should be able to interact with the analyte in order to use it for sensing. Photonic crystals made of porous structures thus could be effectively applied in biosensor field [3], [7], [8].

One of the most interesting materials for fabrication of porous photonic crystals is porous silicon [8] (pSi). Ability to precisely control the fabrication process allows one to obtain highly ordered multi-layer structures and to construct one-dimensional photonic crystals such as distributed Bragg reflectors, Rugate-filters and microcavities [9]–[11]. Due to the oriented cross-cutting pores liquid samples could easily infiltrate the whole porous structure and hence the entire surface could be activated and used for detection. Furthermore, after the embedding of the luminescent particles their luminescence could be enhanced with the Purcell effect at the certain wavelength [12].

In our study we have performed deep investigation of porous silicon as the material for sensor substrates. We have fabricated different types of porous silicon photonic crystals using electro-chemical etching, characterized them and measured their optical characteristics. In order to estimate the influence on the photoluminescence (PL) of the embedded luminophores, QD solutions have been embedded into the structures and spectra and spatial distribution measurements of the luminescence have been made. Finally, we have shown the possibility to improve the detection efficiency of biosensors with the use of porous silicon photonic crystals as the substrates.

2. Materials and methods

Porous silicon photonic crystals have been fabricated using conventional electrochemical etching method in water-alcoholic solutions of hydrofluoric acid [13]. We have used home build PTFE etching cell with etching surface area around 1 cm^2. Highly doped p-type monocrystalline silicon wafers with (100) orientation have been used as a substrate. Fabricated samples of pSi photonic crystals have been oxidized in order to stabilize their properties and prevent embedded luminophores from quenching.

CdSe/CdS/ZnS QDs have been synthesized using hot injection method described in [14] in details. QD surface have been covered with hexadecylamine. QD photoluminescence has symmetrical Gaussian shaped spectrum with the maximum at 620 nm and a full width at half maximum (FWHM) around 45 nm. QDs have been embedded into the porous structures using drop-casting of small amounts (1-10 μl) of hexane solutions with concentrations around 0,01-0,05 mg/ml.

Scanning electron microscopy (SEM) of the surface and cross-section of porous photonic structures has been made after the fabrication. Results are shown on Figure 1. It could be seen that pSi surface has relatively big pore sizes (10-30 nm), which makes it possible to fill the structure with solutions containing analytes as well as luminescent markers.

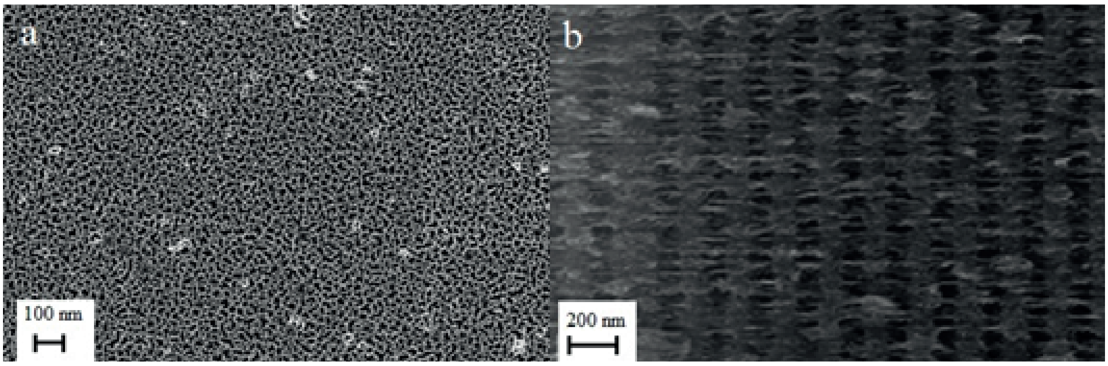

Figure 1: Scanning electron microscopy images of (a) the surface and (b) cross-section of the one-dimensional porous silicon photonic crystal.

In order to characterize the optical properties of fabricated photonic crystals reflectance spectra have been measured. Maximum reflection reached 100% in the photonic bandgap region comparing to the aluminum mirror in the visible spectral range. High reflection band was typically around 150-200 nm wide. Microcavities have an eigenmode inside the photonic bandgap with quality factor (Q-factor) in a range of 100-150.

3. Results and discussion

Photoluminescence of the QDs changed significantly after the embedding into the structure of the photonic crystal depending on the distribution of the QDs inside the structure [15]. Morphology of the porous structures determined the embedding depth [16]. In case of the lower porosity of the front porous layer QD solution effectively penetrated into the structure due to the capillary effect. As the result QDs have been uniformly distributed through the whole porous structure with depth around 6 μm. Hereupon PL spectra narrowed and the maximum shifted to the wavelength of the microcavity eigenmode, Figure 2. PL FWHM decreased to 6 nm corresponding to the microcavity Q-factor. In the opposite case of high porosity the front layer QDs mostly formed the film on the surface of photonic crystal leading to the modulation of their photoluminescence by the reflectance of the microcavity. The dip in the photoluminescence spectra appeared at the microcavity eigenmode position.

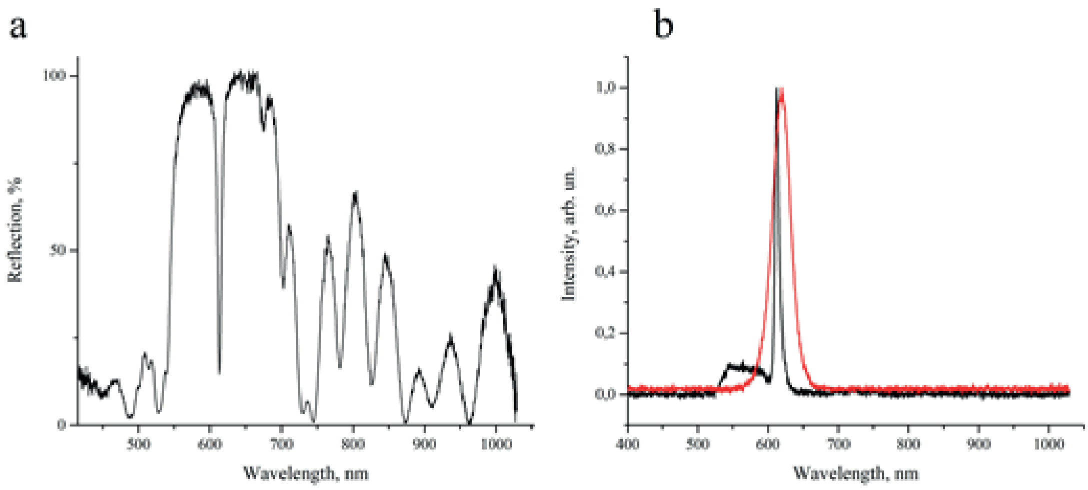

Figure 2: (a) Microcavity reflection spectrum and (b) photoluminescence spectra of QDs inside the microcavity (black) compared to the luminescence of the QD film on the silicon wafer (red).

Angle resolved measurements were made to control the spatial distribution of the photoluminescence of fabricated structures [17]. Results were compared to the QD PL distribution from the QD film on silicon wafer. Photoluminescence of the QDs embedded inside the pSi microcavity became unidirectional perpendicular to the photonic crystal surface. Such modification makes it very suitable for the improvement of the performance of the biosensors measuring the photoluminescence signals: detector placed just above the substrate surface will collect luminescent signal much more effectively.

Finally we have made time-resolved measurements of the photoluminescence decay rates. QD PL lifetime in hexane solution was around 20 ns. After the embedding it decreased to the 9 ns which is mostly due to the quenching caused by the interaction with the silicon surface. Proper treatment of the silicon surface together with the covering of QDs to stabilize their properties could eliminate the quenching effect and would make it possible to estimate the influence of Purcell enhancement on the change of the PL decay lifetime. Enhancement of the photoluminescence in such structures could significantly improve the sensitivity of biosensing methods based on the measurements of the PL signal values by the lowering of the detection limit.

4. Conclusions

In our study we have fabricated hybrid systems based on the porous silicon photonic crystals with embedded QDs and performed the investigation of their properties. Also we have analyzed the perspectives of the use for the improvement of biosensors sensitivity. We have shown spectral narrowing of the QD photoluminescence after embedding into the pSi microcavities as well as the unidirectional distribution of the PL in the perpendicular direction to the photonic crystal surface. Porous silicon photonic crystals have shown to be the promising material for improving of the biosensors efficiency.

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