

Photoluminescence of CdSe/ZnS quantum dots in a porous silicon microcavity

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ABSTRACT

It is known that manufacturing and applications of photonic crystals is currently an area of much interest. One of the focuses of special attention in this area is various microcavity (MC) devices. Porous silicon is one of the most promising materials for manufacturing such devices because it is simple to prepare, its optical parameters are precisely controllable, and it has an enormous surface area. This allows to inject different kinds of luminophores into porous silicon MC devices. Apparently, semiconductor quantum dots (QDs) are among the most interesting of them. QDs are characterized by a wide absorbance spectrum, large absorption cross-section, high quantum yield, and excellent photostability. To date, there have been few studies on QD injection into porous silicon photonic structures. In addition, many structures used lack the desired characteristics; the depth of QD penetration also remains a question. This is the first study to analyze the photoluminescence spectrum and kinetics of QDs in a high-quality porous silicon MC. A drastic narrowing of the luminescence spectrum has been observed after QD injection. We have found that the MC morphology considerably affects the penetration of QDs. The kinetics of photoluminescence has also been investigated. Measurements have shown a decrease in the QD characteristic photoluminescence decay time after QD injection into a porous silicon MC compared with the QD photoluminescence decay time in a toluene solution. However, we have not observed a significant difference between the photoluminescence decay times of QDs in an MC and in single-layer porous silicon.

Keywords: photoluminescence, quantum dots, porous silicon, photonic crystal, microcavity, CdSe/ZnS

1. INTRODUCTION

At the present time photonic crystals are one of the promising objects of research. Key feature of photonic crystals is changing of electromagnetic radiation spectrum by periodically varying refractive index. Consequently it's possible to fabricate high quality distributed Bragg reflectors (DBR), filters and microcavities (MC). In practice such devices are widely used in photonics, laser physics and biology^{1,2}. Particularly it's possible to create different optical sensors on their basis³. On the other side, photonic crystals could be used for effective control of luminophore optical properties, for instance, modulating luminescence spectrum and obtaining laser generation^{4,5}. Among many photonic crystals, one-dimensional DBR and MC on the base of porous silicon (pSi) can be distinguished. These types of photonic crystals have traditionally been produced by electrochemical etching of monocrystalline silicon. Nowadays this method allows to fabricate highly ordered one-dimensional photonic structures in which layer quantity reaches several tens layers. Refractive index of qualitative DBR exceeds 99%^{6,7} and mode width for the best pSi MC is less than 1 nm⁸. By varying layers thickness, porosity value and oxidation it's possible to obtain one-dimensional structures that modulate electromagnetic radiation spectrum in visible, IR and even UV range^{6,7}. Important feature of pSi is its very high surface area that opens up opportunities for embedding different luminophores inside it just from the solution and fabrication optical gas sensors based on luminescence quenching effect⁹. At present time there is a considerable success in that direction. It is shown that luminophore luminescence spectrum in pSi MC is significantly modifying. Its width decreases and becomes comparable to the width of the microcavity eigenmode⁹⁻¹¹. In some works^{10,12} it's reported about luminescence enhancement effect. In most of such studies organic dyes are used as luminophores. At the same time nowadays semiconducting quantum dots (QDs), CdSe/ZnS particularly, are becoming more common as an effective

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luminophores. Compared with organic dyes CdSe/ZnS QDs have a broad excitation band, narrow luminescence spectrum, one order of magnitude higher molar extinction coefficient value and extremely high photostability¹³. Besides that by changing the size of CdSe/ZnS QDs in the range of 2 to 10 nm it's possible to obtain luminescence almost in all visible range. Therefore the task of fabricating and studying the optical properties of photonic crystals based on pSi doped with CdSe / ZnS QDs is of great fundamental and applied scientific interest. However despite of the high relevance today there are only few works in that area^{14,15}. Wherein researches either use low quality photonic structures or apply difficult QDs embedding technology. For instance in study¹⁵ for creating high quality QDs doped pSi MC authors used technique of separate fabrication of two DBR which were merged in one device. Within this work for the first time high quality pSi MC doped by CdSe/ZnS QDs has been fabricated via simple technology of QDs embedding from the solution and its optical and luminescence properties have been investigated.

2. EXPERIMENTAL

2.1. Materials

Cadmium oxide (powder, 99.5%), zinc oxide (powder, 99.99% trace metals basis), 1-octadecene (ODE, technical grade, 90%), oleic acid (OA, technical grade, 90%) selenium (powder, 100 mesh, 99.5%), thiourea (ACS reagent, $\geq 99.0\%$) tri-*n*-octylphosphine (TOP, technical grade, 97%), tri-*n*-octylphosphine oxide (TOPO, reagent grade, 99%), triethylene glycol dimethyl ether (TEGDME, ReagentPlus, 99%), anhydrous solvents (chloroform, hexane, ethanol, methanol and 2-propanol) and hydrogen peroxide solution (30 wt. % in H₂O) were purchased from Sigma-Aldrich; *n*-hexadecylphosphonic acid (97%) was purchased from PlasmaChem GmbH.; hydro-fluoric acid (48 wt. % in H₂O) was purchased from Component-Reaktiv. All chemicals were used as received without any purification. Highly boron doped p-type <100> Si wafers were purchased from Telecom-STV.

2.2. Fabrication of pSi microcavities

For fabrication of pSi MC standard electro-chemical etching technology was used. Hydroalcoholic solution of hydrofluoric acid with ethanol in ratio of 3:7 was used. Current density was varied for different porosity layers in the range of 6-50 mA/cm². Before etching silicon wafers were sonicated in 2-propanol. After etching pSi samples were rinsed in methanol and hexane preventing surface destruction during drying. Layers quantity, thickness and cavity thickness also were chosen experimentally based on existing models for calculating of pSi photonic structure parameters. As a result front mirror of MC consisted of 5 pairs of high and low porosity layers; quantity of rear mirror layers equaled 20. The last step of pSi MC preparation was oxidation. For this purpose MC was kept within day in hydrogen peroxide solution with ethanol in ratio of 9:1. Oxidation of MC produced to prevent QD luminescence quenching. QD luminescence spectrum overlaps pSi absorbance spectrum, so effective nonradiative energy transfer from QDs to pSi becomes possible. Presence of the oxide layer on pSi surface should prevent this process.

2.2. Synthesis of core-shell CdSe/ZnS quantum dots

Core CdSe quantum dots were prepared using a modified procedure reported in¹⁶. Briefly, 1 mmol of cadmium oxide, 2.5 mmol of oleic acid, and 8 ml of ODE were placed into a 25 ml three-necked reaction flask. The flask was heated to 120°C and evacuated at 10 mbar for 10 minutes. Then, under argon atmosphere, the cadmium oxide was dissolved at 220°C. After complete dissolution of CdO, the reaction mixture was cooled down to 120°C and evacuated again to remove residual water. The selenium precursor was prepared by dissolution of 2 mmol of Se powder in 2 ml of TOP and 0.5 ml of ODE under an argon flow without external heating. Selenium solution was swiftly injected into the cadmium precursor solution at 270°C, kept in argon atmosphere under vigorous stirring. The reaction was monitored by UV-Vis spectroscopy and was stopped after 5 minutes by intensely cooling the reaction vessel down to 100 °C with an air flow. The core solution was kept at this temperature under argon flow until shell deposition was started in approx. 20 minutes. Precursor stock solutions for the coating of a ZnS shell were prepared prior to beginning of synthesis of CdSe cores according to the following procedures. Zinc stock solution was prepared by dissolving 25 mmol of ZnO in 52 mmol of 2-EHA diluted with 20 ml of TEGDME. Oxide dissolution was conducted at 220°C under vigorous stirring until clear solution was obtained. The sulfur stock solution was prepared by dissolving 34 mmol of thiourea in 40 ml of TEGDME under sonication. All solutions were leveled with TEGDME to obtain final precursor concentrations of 0.85 M. Shell coating was done without isolation of CdSe cores from growth solution. Under argon atmosphere, 1 mmol of TOP was injected into the flask, and the core solution was allowed to settle for 15 minutes prior to the beginning of shell growth. Then the mixture was heated to 170 °C, and the injection of shell precursors was started with a syringe pump at a

flow rate of 5 ml/h. The total amount of injected shell precursors was calculated to yield two ZnS monolayers over CdSe cores. The growth of the shell was monitored using UV-Vis spectrophotometry and PL measurements. After completion of shell growth, the resulting QDs were isolated from the crude solution by precipitation with 2-propanol, and then were purified in two successive dissolution/precipitation cycles using chloroform and methanol as the solvent and coagulant, respectively. Finally, the product was dissolved in chloroform, and 1 mmol of TOPO was added to this solution to change surface ligands from oleic acid to TOPO for storage and further processing.

2.4. Instruments and methods

To control the etching process programmable DC power supply Aktakom APS7151 was used. Morphology of structures was studied using scanning electron microscope (SEM) Raith 150 TWO. Reflectance and luminescence spectra were measured with Ocean Optics USB2000+ spectrometer. For excitation of QDs studying their spectral properties second harmonic radiation of the DPSS YAG:Nd³⁺ laser with $\lambda_{ex}=532$ nm was used. To study the QD luminescence kinetic radiation of the second harmonic of the Q-switch YAG:Nd³⁺ ($\lambda_{ex}=532$ nm) laser with pulse duration of ~ 100 ps was used. Automated monochromator M266 (Solar LS) equipped with PMT Hamamatsu (time resolution 1,5 ns) was used for registration luminescence kinetics signal.

3. RESULTS AND DISCUSSION

3.1. Structural and optical properties of the pSi microcavities and the quantum dots

For quality control of fabricating MC scanning electron microscopy and optical spectroscopy was used. Typical images of the surface and cross-section of MC obtained on SEM are presented on fig. 1. It could be seen that front and rear DBR of MC has strictly periodical structure and individual layers have high degree homogeneity at a characteristic thickness ~ 100 nm. The average pore size for layers of low and high porosity is about 10 and 30 nm, respectively. It's important for the front mirror to be thinner than the rear one. It should reduce the quality of MC theoretically. However as shown in studies too thick front mirror prevents effective embedding of QDs to the cavity layer. Therefore mirrors thickness ratio which allows keeping rather high Q-factor of MC along with effective QDs embedding into the cavity layer was chosen experimentally.

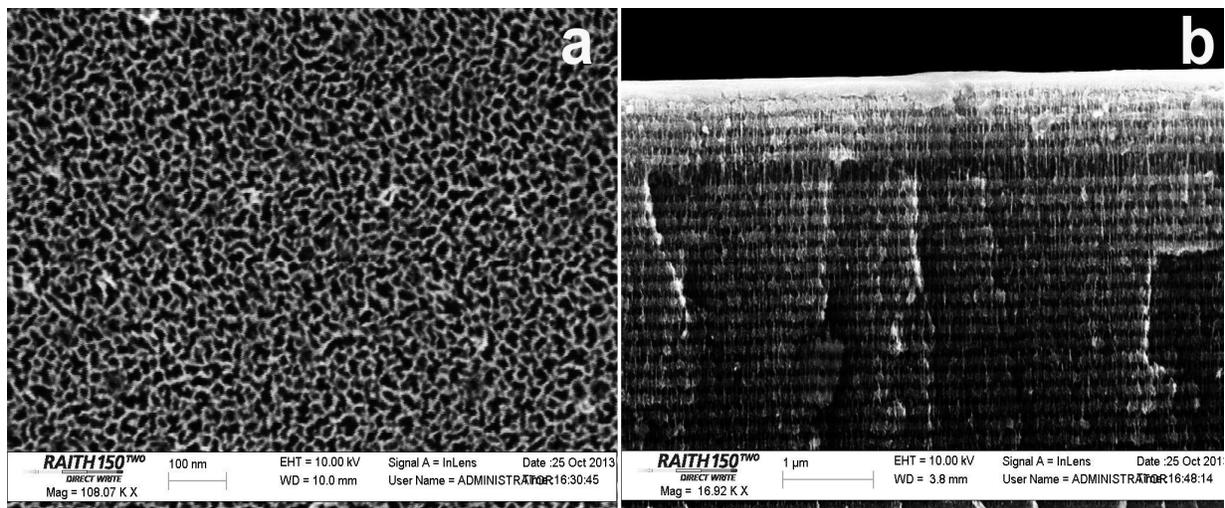


Figure 1. SEM surface (a) and cross-section (b) images of pSi microcavity. The white (dark) layers correspond to the low (high) porosity.

Measuring of optical characteristics confirmed high quality of fabricated MC. Typical MC reflectance spectrum before and after oxidation presented on fig.2. It could be seen that MC has wide region with high reflection coefficient in range of 540-700 nm and narrow eigenmode with width at half-maximum of less than 10 nm. Notable reflection fluctuations to the right of eigenmode of MC were associated with asymmetry of front and rear mirror thickness. Position of MC eigenmode was chosen corresponding to the location of QD luminescence spectrum maximum. The characteristic value of produced MC Q-factor is in the range of 70-80. Oxidation and hence changing of refractive index caused a blue shift of MC reflectance spectrum by ~ 30 nm.

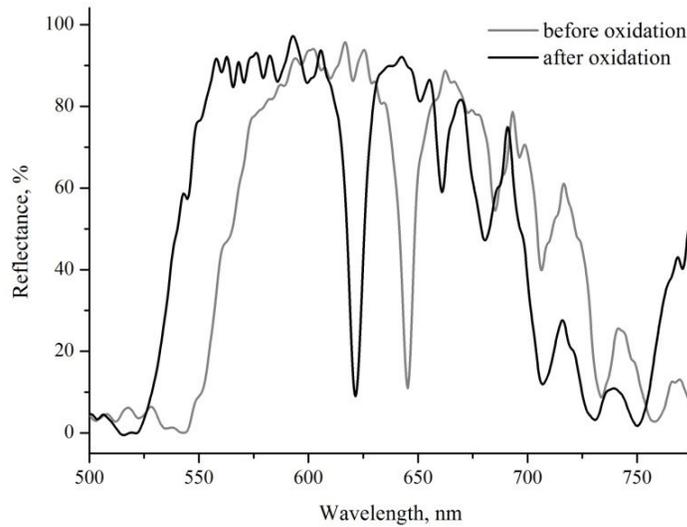


Figure 2. Porous silicon MC reflection spectrum before and after oxidation.

For characterization of synthesized QDs methods of optical absorbance and luminescence was used. Absorbance spectrum of QD solution in toluene (fig. 3) has a specific peak corresponding to the energy of the first exciton level. Position of this peak accurately correlates with average diameter of QDs which, according to the work of W. William Yu et al¹⁷ is $\sim 5,5$ nm. QD photoluminescence spectrum (fig. 3) is a symmetrical domed Gaussian curve. Photoluminescence spectrum width at half-maximum is 30 nm. QD photoluminescence quantum yield (QY) measured, relative to a standard Rhodamine 6G dye, was 70%. It is important to note that the QDs have a wide absorption spectrum which allows to effectively excite of QDs by different radiation wavelength. This fact is a big advantage in comparison with organic dyes which have narrow absorption band. With the embedding of dyes in MC there are additional requirements to the high reflectivity region. Too narrow high reflection region wouldn't inhibit the luminescence at the edges of spectrum. On the other side too wide high reflection region would overlap dye absorbance spectrum and limit excitation possibility. It's obvious that using QDs as luminophores such difficulties absent.

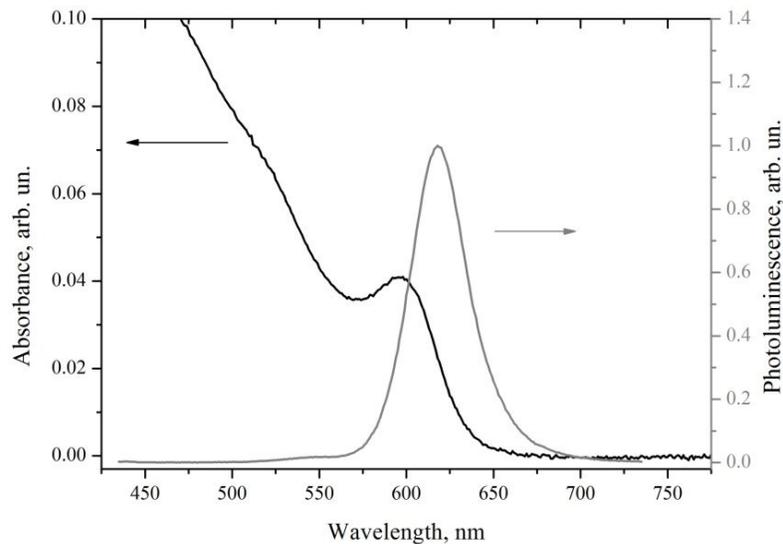


Figure 3. The absorbance and photoluminescence spectra of CdSe/ZnS QD solution in toluene.

3.2. Luminescent properties of QD in pSi microcavity.

For embedding QDs in MC 2 μ l of QD solution in toluene with concentration of 0.024 mg/ml were deposited on MC surface. QD luminescence spectrum significantly modulated after the evaporation of the solvent. Modification character depended on the order of the first MC DBR (fig. 4). In case when porosity of the front DBR first layer was higher than porosity of the second layer there was a gap in luminescence spectrum in position of cavity mode (fig. 4a). In the opposite situation luminescence spectrum significantly narrowed (fig. 4b). Herewith its width and position also corresponded cavity mode. This fact could be explained considering that in first case QDs hadn't embedded deep into MC and mostly stayed on the MC surface. So their radiation directed towards the MC surface was reflected front mirror. But on the wavelength of the MC eigenmode λ_{MC} structure had a gap in the reflection spectrum. Thus QD radiation on λ_{MC} wavelength went deep inside structure without reflecting. This effect would lead to the appearance of gap in PL spectrum and that is what was seen in the experiment. The second case corresponds to the situation where QDs embedded deeply into pSi and whole structure worked like usual cavity with the Q-factor around 70. Hereby it had been found that for effective embedding of QDs inside the pSi MC it was necessary for the first layer to have less porosity than the second. Such effect was earlier observed for organic dyes solution and could be explained by the capillary forces.

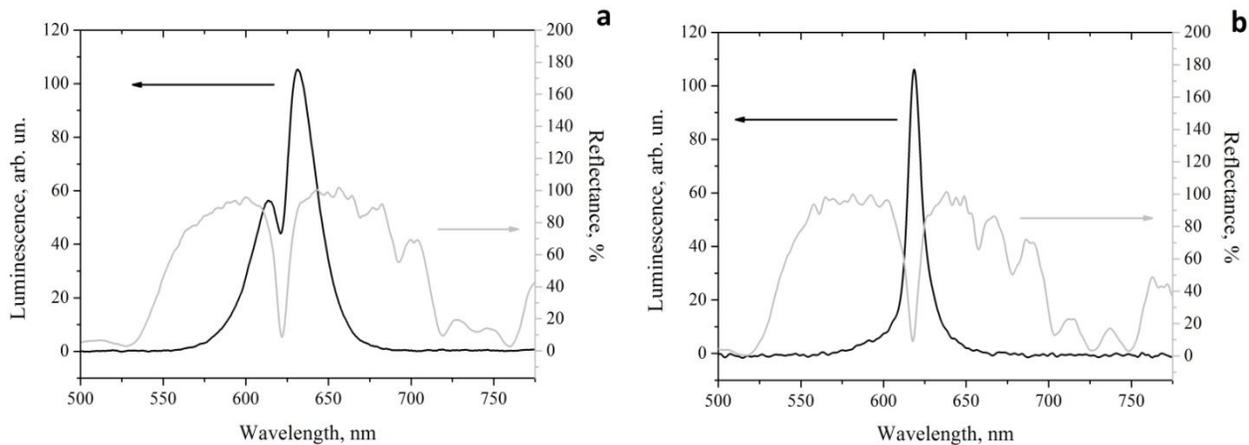


Figure 4. Luminescence (black) and reflectance (gray) spectra of MC doped with QDs in cases: (a) high porosity first layer of the front mirror (b) low porosity first layer of the front mirror.

Also investigations of QD luminescence decay time τ_{PL} were performed (fig. 5). Measurements carried out for QD solution in toluene, QDs embedded in MC and QDs embedded in pSi monolayer. It's well known QD τ_{PL} depends on luminescence wavelength. Thus for unification of received data all measurements were carried out at wavelengths near λ_{MC} . Characteristic luminescence lifetime of QD solution in toluene at a wavelength of 619 nm was 17 ns. When embedded in pSi QD luminescence lifetime decreased to 8.5 ns in MC and 8.8 ns in pSi monolayer indicating approximately 2-fold decrease of QD photoluminescence quantum yield (QY). The reason of this falling was nonradiative excitation transfer from the QD to the pSi. For its inhibition pSi surface was oxidized. But it's obvious that presence of oxide layer on the pSi surface couldn't fully prevent QD luminescence quenching. At the same time it should be noted that QY value for QDs in pSi stays rather high $\sim 30\%$ when in QD films on glass QY decreased more than an order and equaled few percent¹⁸. Along with the absolute τ_{PL} value at a specific wavelength comparison of $\tau_{PL}(\lambda)$ dependence for QD in solution and in MC was of interest. On fig. 5b it could be seen that $\tau_{PL}(\lambda)$ dependence for QD solution at investigated wavelength range is linear. When embedding QDs in pSi MC character of dependence remains unchanged. Together with the fact that τ_{PL} for QD in MC and in pSi monolayer is equal this means that nonradiative recombination process of QD in MC is spontaneous. If there were spontaneous emission enhancement effect, $\tau_{PL}(\lambda)$ dependence for QD in MC would differ from the one for QD solution because first (A) and second (B) Einstein coefficients related as $B \sim \lambda^3 \cdot A$. Lack of QD luminescence enhancement effect in this work apparently due to the low concentration of QDs in MC and low intensity of optical excitation.

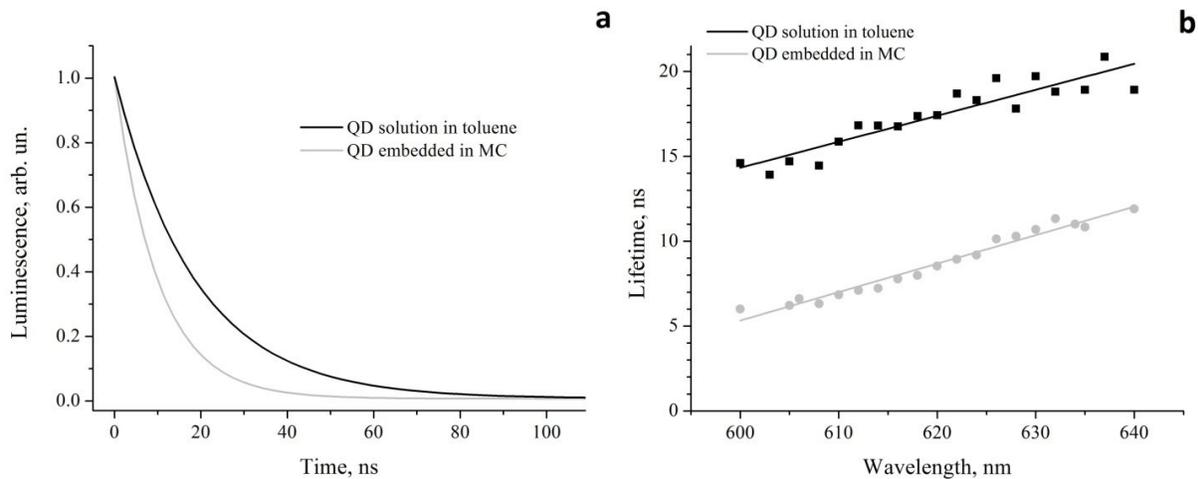


Figure 5. Comparison of QD's luminescence kinetics in toluene and MC; (a) – kinetic lifetime at PL spectrum peak, (b) – kinetic lifetime dependence on wavelength.

3.3. Conclusion

In this work for the first time high quality pSi MC doped by CdSe/ZnS QDs had been created via simple method of deposition of QDs from solution. It's shown that QD embedding efficiency depends on the order of layers with low and high porosity in the front DBR of MC. When embedded inside MC QD photoluminescence spectrum demonstrated severe narrowing. QD luminescence kinetics in MC had been investigated. Based on the obtained data it was concluded that quantum yield of QD in MC remains on rather high level of ~30%.

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