Photoluminescence Properties of Porous Silicon with CdSe/ZnS Quantum Dots

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In this work we have produced visible light emitting quantum dots (QD) of CdSe/ZnS and precipitated them onto the surface of porous silicon structure. Combining basic materials, such as porous silicon, with nanoparticles enables producing of low-cost light emitting materials, what is economically useful and important nowadays. The porous silicon (PS) structures were prepared from 5 min to 60 min by chemical etching at room temperature in $HF : HNO_3$ solution and cleaned in the $H_2SO_4 : H_2O_2$ mixture. The structures of PS and PS-QD were investigated by SEM and UV-VIS spectroscopy. Absorption and photoluminescence of the samples, were measured in the near UV and visible spectral region. Two peaks of photoluminescence of PS-QD at 550 nm and 682 nm were found and different increase of photoluminescence intensity of these peaks depending on excitation wavelength was detected and discussed.
Keywords: chemical etching, porous silicon, photoluminescence, absorption, quantum dots.

INTRODUCTION

Semiconductor nanoparticles have attracted much attention during the last few years because of their unique optical and electronic properties, which might have a great potential in many applications, such as light emitting diodes, lasers, luminescent nanocomposites, diagnostic agents in medicine and solar cells [1 – 4]. In recent years, quantum-dot (QD) chalcogenide semiconductors such as CdS [4 – 6], PbS [7, 8], and CdSe [2, 9] have been employed as sensitizers due to two specific advantages. First and foremost, the size quantization effect allows one to tune the band energy and visible response by simply varying the QD size [10, 11]. Another advantage is that these QDs open new ways to utilize hot electrons or generate multiple electron-hole pairs with one single proton through the impact ionization effect [12].

Especially useful are core-shell type nanoparticles composed of two kinds of semiconductors, e.g. CdSe/ZnSe [13], CdSe/ZnS [14], CdSe/CdTe [15] and CdS/CdSe [16] where first semiconductor denotes the core, while second one is the shell, which has a wider band gap than the first one. Recently quantum dots attracted many authors attention, because the overcoating of a CdSe core with higher band gap compounds (e. g., ZnS) significantly enhances the quantum yield of luminescence and is therefore frequently applied in the synthesis of core/shell structured QD nanocrystals [17].

Porous silicon is well-known and useful material for many applications, such as for photodiodes [18, 19], solar cells [20], etc. Stain etching of silicon provides a spontaneous, self-limiting chemical method to produce nanocrystalline silicon films (porous Si), which exhibit photoluminescence (PL) properties [21]. PS has attracted attention due to the property of PL in visible light range. Over the past fifteen years many different models have been elaborated interpreting the visible light luminescence in PS, several overviews have been published to weigh arguments for/against to understand this phenomenon [22, 23]. From all the pool of models, including hydrogenated amorphous silicon model, surface hydrides model, defect model, siloxen model, surface states model and quantum confined model, the last two have got most of support from the PS research community. Complex models state the absorption occurring in quantum-confined structures (nanocrystallites core), but the radiative recombination passing via localized surface states. This explains rather well the size-dependent absorption blue shift and various emission bands of PS, respectively [24]. However, the exciton coupling with momentum-conserving phonons, the exchange splitting energy values, the polarization measurements point against the luminescence from localized states. Therefore, more sophisticated models were proposed, e. g., a conjugated three region model, including photoluminescent interfacial Si layer between silicon core and amorphous SiO_2 surface layer [25].

Combining basic materials, such as porous silicon, with semiconductor nanoparticles one can change optical properties of PS and it enables producing of low-cost light emitting materials, what is economically useful and important nowadays. However the mechanism of photoluminescence of QD on different surfaces is under discussions.

In this work we have produced porous silicon and QDs and after its precipitation on PS layers we investigated absorption and photoluminescence properties of PS, QD and PS-QD samples.

EXPERIMENTAL

For QD production cadmium oxide (CdO, Aldrich, 99.5 %), selenium powder (Se, Aldrich, 95 %), oleylamine (OA, Aldrich, 70 %) were used. Paraffin liquid (chemical grade), stearic acid (analytical grade), zinc acetate dihydrate ($Zn(OAc)_2 \cdot 2H_2O$, analytical grade), sulfur powder (S, analytical grade), n-hexane (analytical grade), methanol (analytical grade), and acetone (analytical grade)

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were obtained from Aldrich. All chemicals were used as received without further purification. The CdSe/ZnS QD were obtained using methods and techniques described in articles [26, 27].

The porous silicon (PS) structures were prepared by chemical etching of n-type (100) oriented silicon (resistivity 1.0 Ωcm – 1.5 Ωcm) in HF:HNO_3 solution (volume ratio 4 : 1) at room temperature, varying the etching time from 5 to 60 minutes. Afterwards, the etched samples were cleaned in the $H_2SO_4 : H_2O_2$ mixture (volume ratio 1 : 4) at room temperature for 30 min. The visible light emitting CdSe/ZnS quantum dots (QD) were precipitated onto the surface of porous silicon from CdSe/ZnS colloidal solution.

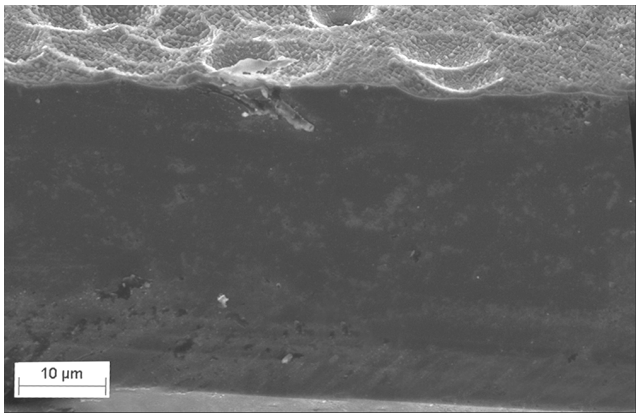
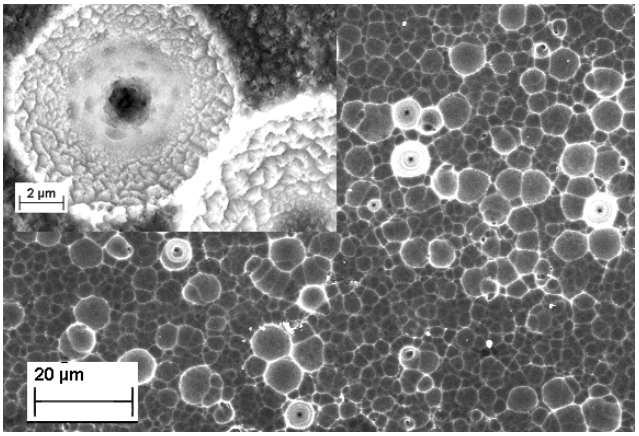


Fig. 1. Cross-section of silicon wafer after etching for 30 min



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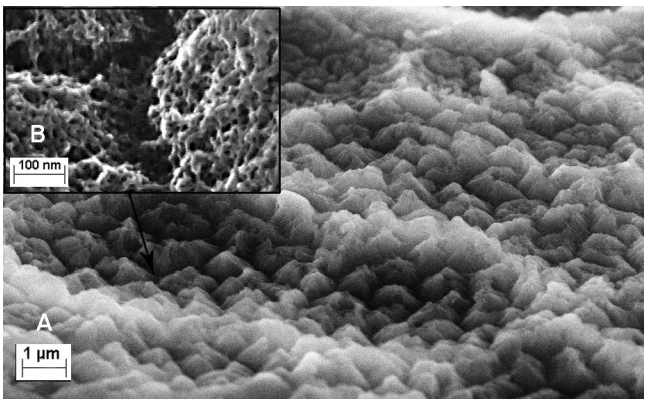

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Fig. 2. SEM image of silicon after chemical etching (etching time 30 minutes)

The surface of silicon after etching process and porous silicon with doped quantum dots (PS-QD) was investigated by scanning electron microscope (SEM) Quanta 200.

The absorption of samples in the near-UV and visible region of spectrum was measured with Shimadzu UV 3100 Spectrometer (the range from 200 nm to 1000 nm).

The luminescence of QD, PS and PS-QD samples were investigated with FS900 Spectrofluorimeter System (Edinburgh Analytical Instruments) in the near UV and visible spectral regions. The excitation source was a 450 W xenon lamp, the excitation wavelengths were 300, 350, 400, 450 nm.

RESULTS AND DISCUSSIONS

The surface of silicon after chemical etching and precipitation of QDs was investigated by SEM. Depth of porous silicon layer was found from 14 µm to 42 µm, when etching time was from 5 to 60 minutes. Cross-section of silicon wafer after etching for 30 min is presented in Fig. 1. The thickness of porous layer is about 35 µm.

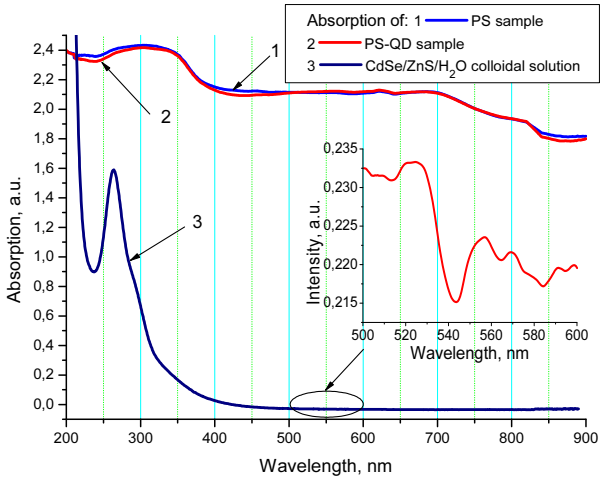
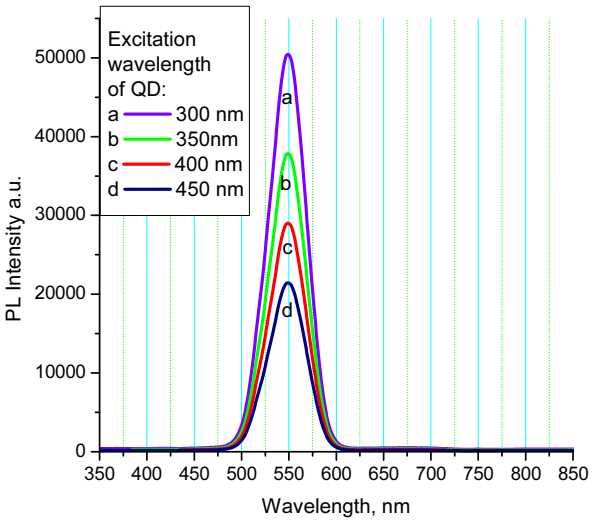


Fig. 3. Absorption spectra of PS, PS-QD samples and CdSe/ZnS colloidal solution

The absorption spectra of PS, PS-QD samples and CdSe/ZnS colloidal solution are shown in Fig. 3. Measured absorption of both PS and PS-QD samples was very similar, and it was the same at 550 nm, where PL peak in PS-QD sample was detected. The absorption maxima of PS and PS-QD samples were found at 310 nm. Detected absorption of PS is very similar to absorption, which was found by other authors, who called this material a “black” silicon [28]. The colloidal solution of CdSe/ZnS exhibits maximum at 266 nm and absorption intensity is very low in the VIS-IR region comparing with porous silicon samples. After absorption investigation of QDs in the range from 500 nm to 600 nm, where the PL of QDs was observed and the peak at 527 nm was found. This maximum was found near the PL peak (Fig. 4, a). These results correlate with the other authors results [26, 29, 30].

The photoluminescence (PL) of QD, PS and PS-QD samples were measured in the region of light wavelength from 350 nm to 850 nm (Fig. 4, a). Depending on excitation wavelength, the PL intensity of CdSe/ZnS colloidal solution decreases from 50337 a.u. to 21109 a.u. and stable peak at 550 nm was detected. The photoluminescence



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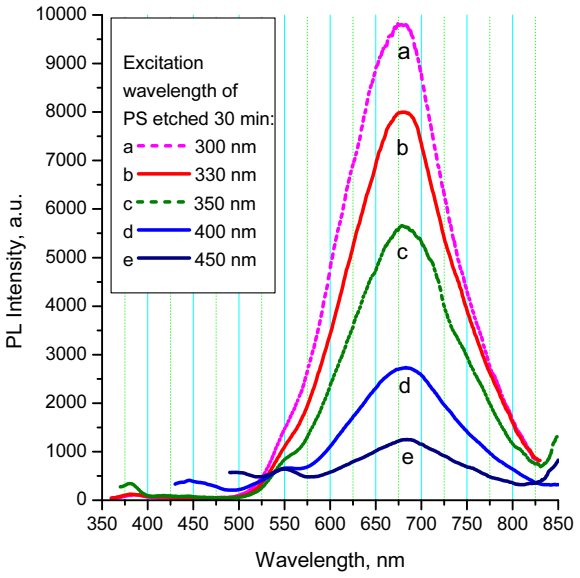

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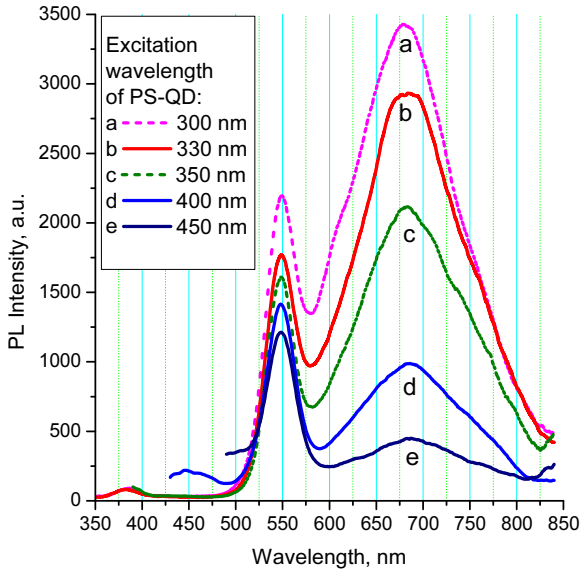

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Fig. 4. Photoluminescence of CdSe/ZnS colloidal solution (a), PS (b) and PS-QD (c) at different excitation wavelength

peaks of CdSe/ZnS QD reported by other authors were found at 565 nm [31] and at 539 nm – 562 nm of CdSe/ZnS QD deposited on Si with various concentrations of QD [32]. PL of QDs was detected green (565 nm), when QDs size was found 3.6 nm ±0.3 nm [31]. Zhu Ch. Q. and others emphasize, that position of QD PL peak can depend on the thickness of ZnS shell onto the CdSe core [26].

The maximum of PL peak for PS was detected at 682 nm ±2 nm and PL was strong and its intensity decreased from 9930 a.u. to 1180 a.u., when excitation wavelength increased from 300 nm to 450 nm (Fig. 4, b).

After deposition of QDs on PS the PL was investigated and two peaks were detected: one at 682 nm ±2 nm (belongs to PS) and second (belongs to QDs) at 550 nm ±2 nm (Fig. 4, c). PL intensity of PS decreased from 9824 a.u. to 1233 a.u. and the PL intensity of QDs peak decreased from 2201 a.u. to 1182 a.u., when excitation wavelength was increased from 300 nm to 450 nm. QDs screen irradiative centres of PS layer and quenching PL in the range from 580 nm to 850 nm, but they increase the PL of PS in the range from 525 nm to 580 nm. Different velocity of decreasing of two PL intensities maximums denotes that QDs have longer lifetime of particles than PS and can change the photoluminescence properties of porous silicon samples and samples can have different colors of emitted light, depending on excitation wavelength. The color of the emission depends on the energy difference between excited and ground states.

Comparison of photoluminescence of PS (Fig. 4, b) and PS-QD (Fig. 4, c) samples shows that intensity of PL of PS decreases about three times. It is a result of blocking of irradiation centres on PS surface by QD which create the new irradiation centres with light emitting at 550 nm ±2 nm.

CONCLUSIONS

1. Porous silicon (PS) layer was produced by chemical etching from 5 to 60 minutes and after investigation by SEM the thickness of porous silicon from about 14 μm to 42 μm was found.

2. The surface of porous silicon is formed from small pyramids with porous structure, where the width of pores is from 10 nm to 15 nm. Porous silicon layer formed on the silicon substrates by chemical etching contains also the macro pores with diameter about 1 μm – 2 μm.

3. Investigated absorption of porous silicon and porous silicon with precipitated quantum dots was very similar and after comparing with other authors results we can state that these thin layers show absorption as “black” silicon.

4. After precipitation of CdSe/ZnS quantum dots on the porous silicon surface, the decrease of photoluminescence intensity was detected and two peaks for PS-QD samples at 550 nm ±2 nm and 682 nm ±2 nm were found. The photoluminescence intensity decreased about three times and it was the result of blocking of irradiation centres on PS surface by QDs. CdSe/ZnS quantum dots have longer lifetime of particles than PS and it can change the photoluminescence properties of porous silicon samples and samples can have different colors of emitted light, depending on excitation wavelength.

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