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Quantum dot-induced photoluminescence enhancement of InGaN nanowires

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Abstract. In this work, we propose a simple method to enhance the photoluminescence of InGaN nanowires using CdSe/ZnS colloidal quantum dots. It is found that decoration the surface of InGaN NWs with QDs leads to an increase in the integral and peak photoluminescence intensity by more than 3 times. The observed enhancement is attributed to the nonradiative energy transfer between quantum dots and nanowires.

Keywords: InGaN nanowires, CdSe/ZnS quantum dots, photoluminescence, hybrid nanostructures

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Усиление фотолюминесценции нитевидных нанокристаллов InGaN с помощью квантовых точек CdSe/ZnS

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Аннотация. В данной работе предлагается простой метод усиления фотолюминесценции нитевидных нанокристаллов InGaN с использованием коллоидных квантовых точек CdSe/ZnS. Установлено, что декорирование поверхности нитевидных нанокристаллов InGaN с помощью квантовых точек приводит к увеличению интегральной и пиковой интенсивностей фотолюминесценции более чем в 3 раза. Наблюдаемое усиление фотолюминесценции связывается с безызлучательным переносом энергии между квантовыми точками и нитевидными нанокристаллами.

Ключевые слова: нитевидные нанокристаллы InGaN, квантовые точки CdSe/ZnS, фотолюминесценция, гибридные наноструктуры

Финансирование: Синтез экспериментальных образцов и исследования их оптических свойств были выполнены при финансовой поддержке Российского научного фонда (проект № 00012-79-23). Исследования морфологических свойств синтезированных наноструктур были выполнены при финансовой поддержке Санкт-Петербургского государственного университета в рамках исследовательского гранта № 94031047.

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Introduction

Nowadays, the hybrid systems consisting of various dimension semiconductor nanostructures are actively studied [1, 2]. A special place is occupied by hybrid nanostructures based on nanowires (NWs) [3–5] since the latter exhibit high surface-to-volume ratio [6] and can be grown with high crystal quality on lattice-mismatched substrates, for example on cost-efficient Si [7–9]. In addition, NWs are suitable for growing ternary compounds,in particular, InGaN, which are of considerable interest for creating micro-RGB LEDs and nanolasers [10–12].

It was previously shown that hybrid nanostructures based on NWs and colloidal quantum dots (QDs) allows one to create efficient infrared sources, white light-emitting diodes (LED), solar cells, photocatalysts, photodetectors and gas sensors, etc. [3, 5, 13–16]. The interaction between the parts of the hybrid nanosystem can manifest itself in Förster Resonance Energy Transfer (FRET). Experimental and theoretical validity of FRET in semiconductor nanostructures with

different dimensions was described in the [3, 17]. We have recently shown that the deposition of a trioctylphosphine oxide (TOPO)-CdSe/ZnS QDs on the arrays of InP/InAsP/InP NWs leads to a significant increase in the duration and intensity of the photoluminescence (PL) of the InAsP nanoinsertion [3, 18].

In this work, we fabricate NW/QD hybrid nanostructures based on InGaN NWs and study their photoluminescent properties. The initial InGaN NWs exhibit a PL at room temperature (RT) in the red region of the spectrum. We show that the deposition of CdSe/ZnS QDs on InGaN NWs results in the significant PL enhancement. The results open the ways to increase the photoluminescence efficiency of the high In content InGaN NWs by colloidal QDs.

Materials and Methods

The InGaN NWs were grown on 1-inch *n*-type Si(111) substrate using Riber Compact 12 MBE system equipped with In and Ga effusion cells and a nitrogen plasma source. Prior to the growth, the substrate was thermally treated at 920 °C to remove silicon oxide from the growth surface. The substrate temperature was then decreased to 605 °C. At this moment, an atomically clean growth surface was detected by in-situ reflection high-energy electron diffraction showing (7×7) surface reconstruction. After stabilization of the substrate temperature, the nitrogen plasma source was ignited and the Ga and In shutters were simultaneously opened. The growth lasted 20h. The nitrogen flux and power of the nitrogen plasma source were set at 0.4 sccm and 450 W, respectively. Beam equivalent pressures of In and Ga measured by the Bayard-Alpert vacuum gauge were equal to each other and amounted to $1 \cdot 10^{-7}$ Torr.

The synthesized NWs have a core/shell structure [8]. To achieve FRET between the TOPO-CdSe/ZnS QDs and the InGaN core, we subjected the initial NW arrays to chemical treatment. Wet chemical etching was carried out in the solution KOH:H_2O (1:5) at a temperature of 75 °C for 2 minutes to remove the GaN shell. 12 μl of the QDs solution in toluene ($C \approx 10^{-6}$ M) were deposited on a substrate with InGaN NWs using a micropipette to create hybrid nanostructures. Deposed QDs had a structure with a CdSe core (about 3 nm in diameter) covered with a ZnS shell and TOPO ligand layer.

The initial NW array was placed in isopropyl alcohol and subjected to ultrasonic treatment for estimating the absorption properties of InGaN NWs. The absorption properties of the resulting suspension were detected by measuring optical density spectra with a spectrophotometer Thermo Scientific Multiskan GO. The PL measurements of QDs were performed at room temperature (RT) using a He-Cd laser with a wavelength of 325 nm at 15.5 mW. The laser spot diameter was approximately 100 μm. The PL signal was detected using a MS5204i Sol instruments monochromator and a single-channel Si detector.

The optical properties of InGaN NWs and hybrid nanostructures were studied using an Integra Spectra (NT-MDT) confocal microscope at room temperature. The Nd:YLF laser operating in continuous mode (527 nm wavelength) was used for excitation. The excitation laser beam was focused using a 100x objective (Mitutoyo, M Plan APO NIR) with a numerical aperture NA = 0.5. The same objective was used to collect the photoluminescence of nanostructures. The radiation was directed to the entrance slits of the monochromator (Sol Instruments MS5204i) using mirrors. Detection was performed using a cooled InGaAs CCD array (iDus). Morphological properties of the samples were examined using a SUPRA 25 C. Zeiss scanning electron microscope (SEM).

Results and Discussion

Several conditions should be performed simultaneously for FRET between a donor and an acceptor. The PL spectrum of the donor should overlap with the absorption spectrum of the acceptor (condition 1), and the distance between the donor and acceptor should be approximately 1−10 nm (condition 2) [5]. In our case, donors are CdSe/ZnS QDs, and acceptors are InGaN NWs. Fig. 1,*a* shows the fulfillment of the condition 1. The QD PL band (wavelength of PL maxima 530 nm) completely falls within the absorption region of InGaN NWs.

As it was mentioned above, the synthesized NWs have a core/shell structure with a shell thickness of about 20 nm [8]. Therefore, to carry out condition 2, the shell was removed. The initial diameter of the NW core/shell is 110−120 nm, and the diameter of the InGaN NWs is 65−75 nm (see Fig. 1, *b*, *c*).

Fig. 1,*d* shows a typical SEM image after deposition QDs to an array of InGaN NWs. It can be seen that QDs predominantly fill the space between NWs, thus being deposited on their lateral surface.

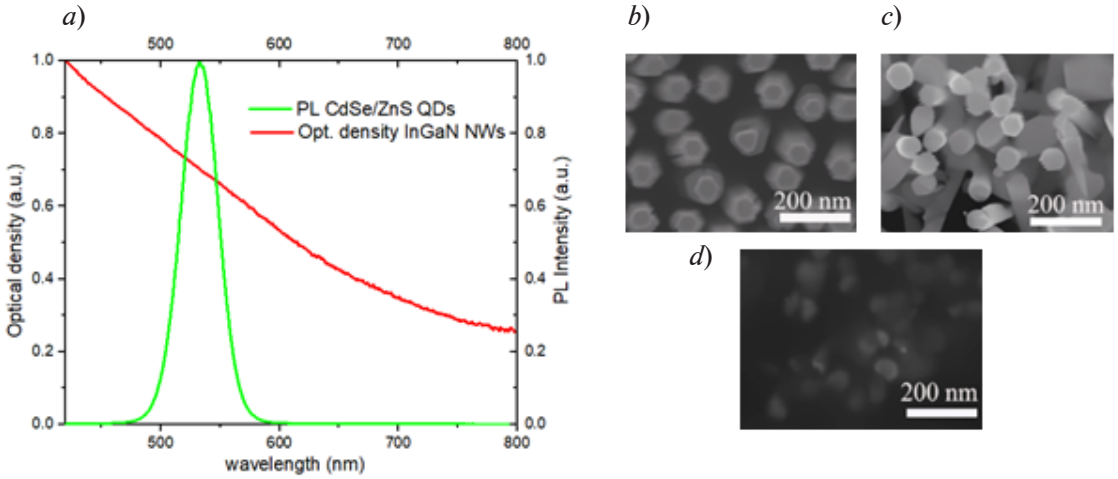

Fig. 1. Implementation of conditions for effective FRET; overlap between the optical density spectrum of InGaN NWs and the PL spectrum of CdSe/ZnS QDs (*a*), plan-view SEM images: core/shell InGaN/GaN NWs (*b*), InGaN NWs (*c*), InGaN NWs with QDs (*d*)

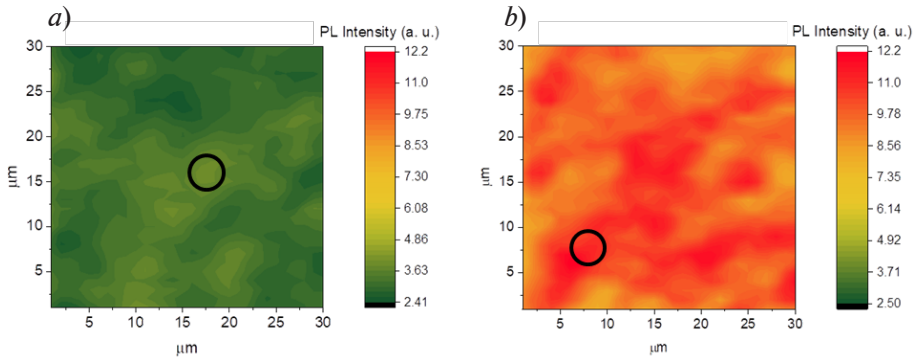

Fig. 2. Micro-PL maps; InGaN NW array before deposition of QDs (*a*), InGaN NW array after deposition of QDs (*b*)

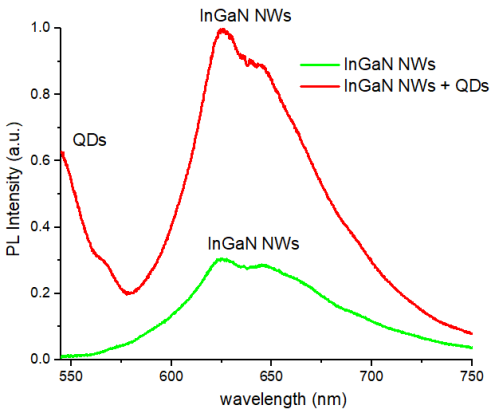

Fig. 3. PL spectra before and after deposition QDs

In general case, nonradiative energy transfer manifests itself in a decrease in the PL intensity of the donor and an increase in the PL of the acceptor [3]. Fig. 2 shows the PL distribution of InGaN NWs before and after QD deposition. The relative inhomogeneity of the NW PL distribution before QD deposition does not exceed 2. The surface decoration of the NW array leads to an increase in the PL signal over the entire area of the sample.

Fig. 3 shows the PL spectra at the maximum points of the micro-PL maps (black circles in Fig. 2). The InGaN NWs exhibit a PL at RT in the range of 600–700 nm. The PL spectrum contains short-wavelength (625 nm) and long-wavelength (645 nm) maxima. The two pronounced maxima and relatively broad PL can be explained by the different composition of indium in InGaN NWs.

After decoration the NW surface with QDs, the following is observed. The full width at half maximum of PL decreases by 10 nm, and the ratio between the short- and long-wavelength peaks decreases slightly. The peak and integrated PL intensity increases by more than 3 times. Thus, the reason for the PL enhancement is apparently the FRET mechanism. Moreover, another reason for this may be the passivation of surface states by the TOPO-QDs layer [18]. A detailed study of the nature of PL enhancement will be carried out in further works.

Conclusion

To conclude, we have synthesized InGaN NWs on the Si substrate by plasma-assisted MBE. The obtained sample has RT PL peaks in the red region of the visible spectrum. The deposition of colloidal TOPO-CdSe/ZnS on the surface of InGaN NWs allowed to enhance the PL of the initial nanostructures. The results obtained are of interest for the development of optically efficient devices based on InGaN NWs.

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