Light-emitting structures based on colloidal quantum dots of cadmium sulphide having a high color rendering index

E M Stepanov, P O Tadtaev, O S Vatalev, I I Mikhailov, S A Tarasov, A V Solomonov

Department of Microelectronics, Saint-Petersburg Electrotechnical University
"LETI", 5 Prof. Popov Str., St. Petersburg197376, RUSSIA

E-mail: stepanovem2015@mail.ru

Abstract. Quantum dots created by colloidal synthesis (CQD’s) were investigated. The paper shows how by changing the size and concentration of CQDs the emission spectrum of the structure with a color rendering index greater than 90 was achieved. Creation of the light-emitting structures involved spin-coating of CdS CQDs onto the glass substrate and consequent high-vacuum annealing. Methods allowing the increase of the emission intensity to achieve better approximation of the radiation spectra shape of white LEDs’ spectra.

1. Introduction

Creation and investigation of structures containing quantum dots (QDs) are some of the most important tasks of modern Photonics as soon as the QDs-based devices exert substantially enhanced performance. The widespread application of such structures is limited to relatively high cost of their creation. From this point of view, the methods of colloidal synthesis are very promising, allowing simplification of the production technology of such particles [1, 2]. Quantum dots created by colloidal synthesis (CQDs) are highly efficient and enable the emission wavelength’s adjustment by the synthesis parameters’ variation [3]. It is essential that CQDs absorb light in a wide range of wavelength (Figure 1) [4] which makes excitation of their photoluminescence possible by the same short-wave emitter.
A colloidal solution of QDs consists of a large number of nanocrystals with different sizes. Consequently, emission from the sample will occur in a wide range of wavelengths. Therefore, the peak of the photoluminescence (PL) spectrum will have a certain width. The greater the dispersion of particle size is, the greater the width of the peak will be. So far, the technology of the QDs’ colloidal synthesis allows to obtain samples with a high degree of monodispersity, which, in this case, results in the half-width of the PL peak of several tens of nanometers [5].

Another feature of colloidal synthesis is the presence of the second PL peak besides the primary one [6]. It is considered to happen due to the presence of the defects such as surface states and others. However, the character of such defects remains poorly studied which complicates the prediction of their influence on the formation of the structure’s spectrum.

The application of CQDs in the light-emitting structures’ and, consequently, thereon based devices’ creation offers some advantages [7]. First of all, it is a high spectral purity of the color, due to a narrow half-width of the emission line. Additional advantages can be obtained if CQDs are deposited on porous matrices [8-10] which increases the control over the shape of the spectra. Another important feature is that QDs are not an organic material which makes them more photostable than any organic structure, providing the possibility of increasing power of the exciting pump and structure’s durability.

Color rendering index is one of the main characteristics of emission sources in the visible range of the spectrum. The importance of obtaining the high color rendering index is due to the high sensitivity of live forms to this parameter. Therefore, light emitting devices that have a higher value of color rendering index are more commercially successful.

2. Sample preparation
The cadmium sulfide CQDs were used to create light-emitting structures, since the dots of this type have a high value of quantum yield in the visible range of spectrum [11-13]. The toluene was used as a solvent. To create the structures, CQDs of various sizes were spin-coated onto the glass substrate (15 seconds, 2000 rpm). These parameters define the film thickness on the surface. Further annealing was performed in a high vacuum in order to evaporate the solvent and to form an ordered layer from the amorphous structure. This procedure is necessary for creating structures with electrical pump, since it...
requires the transmission of charge carriers. Annealing time was 30 minutes at the temperature of 90 degrees Celsius. The resulting thickness of the active region was several nanometers. Wavelengths of the main luminescence peaks were in the range from 380 nm to 480 nm (Figure 2).

Fig. 2. The photoluminescence spectra of the CdS CQDs.

Fig. 3. The absorption spectra of the CdS CQDs.

Knowing the position of the first excitonic peak, we can estimate the mean size of the nanoparticles in ensemble. The estimation is based on empirical data (1) and (2), obtained from transmission electron
microscopy [13-15]. (1) and (2) stand for CdSe and CdS CQDs respectively. The results of calculations are summarized in the Table 1.

\[ a = 1.6122 \cdot 10^9 \lambda^4 - 2.6575 \cdot 10^6 \lambda^3 + 1.6242 \cdot 10^3 \lambda^2 - 0.4277 \lambda + 41.57 \]  

\[ a = -6.6521 \cdot 10^{-8} \lambda^3 + 1.9557 \cdot 10^{-4} \lambda^2 - 9.2352 \cdot 10^{-2} \lambda + 13.29 \]  

where \( a \) – particle size, \( \lambda \) – wavelength of first excitonic peak.

**Table 1.** The sizes of the CdS and CdSe CQDs.

| The emission wavelength, nm | CdS | CdSe |
|-----------------------------|-----|------|
| 380                         | 2.3 |      |
| 400                         | 2.6 |      |
| 420                         | 3.1 |      |
| 440                         | 4.1 |      |
| 460                         | 4.8 |      |
| 480                         | 5.7 |      |
| 500                         | 2.3 |      |

The presence of the second peaks on the PL spectra (Fig. 2), as mentioned, is due to the defects such as surface states. These peaks’ presence appears to be random in the solutions of CQDs consisting only of cores. In the solutions of “core/shell” CQDs density of these defects seem to decrease. The CQDs with significant intensity of the second peak were selected from a set in order to provide better correlation between the spectra’s shape of our structures and the spectra’s shape of white LEDs.

### 3. Results and discussion

The CQDs mixture with increased color rendering index containing a certain composition of different sized QDs was designed. Shortwave part of such structures’ visible luminescence spectrum consists of major CQDs luminescence peaks; the long-wave part of the spectrum is caused by the surface states emission. A spectrum of a black body at 6504 K was chosen as an ideal one because of its similarity to an object CRI equal to 100. The modeling aim is to create a mixture of different sized CQDs which spectrum is identical to ideal (black body) one so the intensity of CQDs’ peaks fit the black body’s spectrum at the corresponding wavelengths. The resulting CQDs spectrum is shown on Figure 4 and in this case the mixture’s CRI is 99.9.

Above described CdS CQDs samples allowed us to obtain an emission spectrum with a color rendering index of 90.6 (Figure 5). Each QDs ensemble’s contribution could be controlled by mass concentration and quantum yield accounting. The concentration of CdS nanoparticles in the original solution was 5 mg/mL (100 mg/mL for CdSe). Nanoparticles’ quantum yield in the CdS samples was about 10% (40% for CdSe sample). The original concentration (5 mg/mL) was used to prepare a mixture of CdS CQDs. CdSe CQDs were diluted by toluene solvent to 1.25 mg/mL concentration with the aim of intensity decrease.
Fig. 4. The Black Body’s (6504 K) spectrum and the modeled CQDs spectra

Fig. 5. The modeled CdS CQDs mixture spectrum
CdS CQDs with 440, 460, 480 nm emission wavelengths and CdSe CQDs with 500 nm emission wavelength were used for CRI calculation (Fig. 5) although actual wavelengths are slightly different. The measured spectrum of designed light emitting structure containing CQDs is shown on Figure 6 where the red curve is a black body’s spectrum. The summary spectrum covers almost the whole visible range and has three typical peaks. The work principle of this structure is based on photoluminescence mechanism, i.e. it is an optical pump structure. An optical pump is provided by UV gallium-aluminum nitride LED with the maximum of emission at 209 nm [16].

![Graph showing photoluminescence spectra of CdS and CdSe CQDs deposited on glass substrate](image)

The density of QDs film deposited on the glass substrate was especially high after the evaporation of the solvent. Theoretically, this could cause an energy transfer from smaller dots to larger ones. This mechanism of energy transfer is called Förster mechanism and the main required condition for this transfer is a small distance between the dots (5-10 nm). Förster mechanism affects PL spectra by decreasing the intensity of short-wave peaks and increasing the intensity of long-wave ones. In our case, the intensities of all peaks were proportional to calculated ones. It might be concluded that the Förster energy transfer impact on the structure’s spectra is extremely small. Perhaps, it is due to the dots ligand shell which is about 5 nm thick.

Details of the electrical pump structures creation are also determining factors of the final result. It is important to use inorganic layers in the structure because of organic materials’ rapid degradation. For the purpose of creating high color rendering index LEDs a structure with optical pumping should be used because of its high efficiency and characteristics’ stability.

4. Conclusion
The modeling of luminescence spectral characteristics of various sized CdS CQDs mixture was carried out and the possibility of obtaining CRI greater than 95 was shown. The structure with a CRI greater than 90 was successfully created. A simple and inexpensive method of creating light-emitting nanostructures was used. It was shown how the selection of the different sized CQDs’ concentration can be used to effectively control the light emitting structure’s spectral characteristics. The creation of a structure with color rendering index exceeding 95 by presented method is a work in progress.
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