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Quantum Dot–Incorporated Hybrid Light-Emitting Diodes

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Abstract

Quantum dots are very promising candidates to enhance the performance of hybrid devices. Their size-dependent wavelength tunability owing to quantum size effect, narrow full width at half maximum, high quantum yield, and several other optoelectronic properties enable their use as potential components in GaN-based light-emitting diodes. This chapter explains methods to fabricate color-converted and white light-emitting diodes with the incorporation of semiconductor quantum dots.

Keywords: quantum dots, light-emitting diodes, color conversion, white light

1. Introduction

Thanks to their physical, optical, and electronic properties, semiconductor nanocrystals attracted enormous interest as promising nanomaterials with potential applications in optoelectronics [1]. These nanocrystals can be chemically synthesized with different sizes and shapes including nanowires, nanodiscs, and quantum dots (QDs). Spherical QDs possess several advantages that make them more flexible nanomaterials to be utilized in wider range of applications. QDs can be synthesized as a core, core-shell, or core-multi shell as shown in Figure 1. The size of QDs determines their emission wavelength; emission energy of these nanocrystals is related to their quantum confinement property that changes with the radius of the nanocrystals. Thus, it is possible to synthesize nanocrystals emitting with wavelength range covering the whole visible spectrum. This property makes them powerful optoelectronic components. The full width at half maximum (FWHM) of semiconductor QDs is generally in the range of 30–40 nm. Recently, QDs with very high quantum efficiency (one of the main performance measures of QDs) values were reported.
Although, QDs exhibit high optical properties, their electrical properties are not at the desired level. Thus, the efficiency of the devices utilizing electrically injected QDs is very low [2]. One of the main reasons for this low performance of QD-incorporated devices is the existence of organic ligands on the surface of QDs that prevents an efficient current injection. On the other hand, ligands play an important role in the enhancement of the stability of QDs. Further research is needed to be done to improve the electrical injection properties of these semiconductor nanocrystals. However, their optical properties can be used to enhance the performance of the devices with lower optical outputs. In the following sections, the device structures incorporating QDs are introduced and their effectiveness is thoroughly discussed.

2. Color-converter QDs on GaN-based devices

Since the important inventions mainly by Nakamura, Akasaki, and Amano in the development of GaN-based light-emitting diodes (LEDs) (they received Nobel Prize in Physics for the invention of blue LED in 2014) [3–5], these devices were widely investigated to enhance the external quantum efficiency and optical power as well as to reduce the electrical injection issues [6, 7]. GaN-based LEDs are mostly grown with metalorganic chemical vapor deposition (MOCVD) on c-plane sapphire substrates. The main drawbacks of sapphire as a growth substrate are the lattice mismatch and thermal expansion coefficient mismatch. The former drawback significantly reduces the performance of devices due to the formation of strain in the epitaxial layers. However, the performance of LEDs grown on sapphire is still higher than those grown on other substrates [8]. The higher efficiency can be achieved in the LEDs incorporating InGaN quantum wells in between the p-type and n-type GaN epitaxial layers. Figure 2 depicts a schematic structure of a typical multiple quantum well InGaN/GaN LED. To achieve blue emission, the special care needs to be taken during the growth of InGaN quantum wells as the emission is mainly realized through the recombination of electrons and holes in these wells. The amount of In incorporated during the growth defines the emission wavelength of the device. Thus, it is possible to achieve high-quality blue emission with the incorporation of the correct amount of In (usually around 15%) [9]. Photoluminescence from an epitaxially grown blue LED is shown in Figure 3. In order to fabricate a GaN-based
device emitting light with longer wavelength, a larger amount of In should be introduced into the InGaN compound layer. However, the growth of InGaN layer with larger amounts of In results in the segregation of In [10]. Thus, InGaN/GaN LEDs utilizing more In exhibit significantly lower optical power and external quantum efficiency when compared with the blue LEDs using smaller amounts of In.

Figure 2. Schematic diagram of multiple quantum well InGaN/GaN LEDs.

Figure 3. Photoluminescence of an epitaxially grown blue multiple quantum well InGaN/GaN LED.
To enhance the output performance of InGaN/GaN LEDs emitting the longer wavelength range, QDs can be incorporated as color-converter components [11]. Thus, by utilizing the optical properties of QDs and electrical properties of InGaN/GaN LED structure, it is possible to fabricate a color-converted hybrid LED emitting at longer wavelength. To realize this kind of device, QDs are placed on top surface of InGaN/GaN LED structures. One of the critical points during the construction is to place the correct amount of QDs. As the emission wavelength of the LED and the QDs are different, the process of placing QDs on top can result in either full color conversion or mixed color emission. Thus, the optimized amount of QDs will help to achieve the conversion of blue emission to the emission wavelength of the QDs. The schematic diagram demonstrating the color conversion process described above is shown in Figure 4. As it can be clearly seen from the figure, the process starts with the electrical injection of electrons and holes to the quantum wells of InGaN/GaN LEDs. Following their radiative and nonradiative recombination in the wells, carrier relaxation occurs. The radiative recombination results in the generation of photons with the wavelength corresponding to the bandgap of the InGaN wells (In incorporation defines the bandgap of the wells as stated above). The process of photon generation with this kind of electrical injection is called electroluminescence. These photons are absorbed by QDs placed on top of the device. The energy of the photons generated in the InGaN quantum wells should be higher than the bandgap of QDs to result in a successful excitation of charge carriers in QDs. Following the excitation of carriers with the incoming photons, the excited carriers recombine either radiatively or non-radiatively. Radiative recombination leads to the emission of photons with the wavelength corresponding to the bandgap of QDs. This kind of excitation of QDs which is a result of interaction between the photons of InGaN quantum wells and the charge carriers of QDs is called photoluminescence. Figure 5 demonstrates the emission intensity of a color-converted InGaN/GaN LED incorporating QDs at 10, 20, 30, and 50 mA current levels.

The process of color conversion with the incorporation of semiconductor QDs is an equivalent method to the color conversion utilizing phosphors [12]. However, there are several drawbacks in using these phosphors for down-conversion. The bandwidth of emission in most...
phosphor compound materials is very large, almost spanning the whole visible spectrum. On the other hand, QDs emit with the FWHM of around 40 nm which is significantly smaller than that of the phosphors. Moreover, very large amount of phosphor material is required to achieve the full color conversion. In comparison, QDs can result in color conversion with significantly less amount of material. The optical absorption is another key parameter during the fabrication of a hybrid color-converted device. The color-converter materials should have decent absorption to exhibit high efficiency during the conversion process. QDs can absorb almost all the photons with the wavelength slightly shorter than the emission wavelength of these nanocrystals. On the other hand, phosphors can absorb only narrow range of wavelength. These superior properties of QDs over phosphors make them very promising candidates as efficient color-converter layers.

Although QDs are highly effective in color conversion, their localization in a suitable structure defines their efficiency. QDs generally exhibit significantly high quantum yield when dispersed in a medium-like toluene. However, making close-packed films out of these nanocrystals may result in a significant reduction of quantum yield. The main underlying reason for this behavior can be explained as follows. When QDs are dispersed in toluene, the separation distance between individual QDs is very large. This separation prevents any kind of close interaction between the nanocrystals. However, when they make close-packed solid films, the separation distance between the QDs is very short. This close construction gives rise to the interaction of QDs via nonradiative resonance energy transfer through dipole-dipole coupling process. When a close-packed film is excited with a source, the photogenerated electrons and

Figure 5. Emission intensity of a color-converted InGaN/GaN LED incorporating semiconductor nanocrystal QDs at 10, 20, 30, and 50 mA current levels.
holes in the QDs builds dipoles (this is called donor in the energy transfer process). These dipoles can create a mirror dipole in the QDs placed in sub-10 nm range (acceptor). The generation of the dipole in the adjacent QD is a nonradiative process owing to the absence of photon generation by the donor QD and absorption by the acceptor QD. Not all of the transferred dipole energies result in the radiative recombination in the acceptor QDs. Thus, a huge amount of energy is lost during the resonance energy transfer process. To prevent this energy transfer resulting from the close interaction of QDs, the QDs should be separated in their solid films. To realize this, QDs can be dispersed in a special matrix. This will help to reduce the quantum yield loss originating from the nonradiative energy transfer [13].

Another important change during the formation of solid films is the shift of emission wavelength. One of the main underlying reasons for this shift is the change in the medium. The refractive index strongly affects the emission wavelength. Moreover, the nonradiative resonance energy transfer between the nanocrystals also plays a significant role in the shift of the peak. The transfer mechanism is depicted in Figure 6. In very close proximity in their solid films, there is a high chance of energy transfer through nonradiative dipole-dipole coupling to occur. As it is well known, nanocrystals are not perfectly synthesized; there is a finite size distribution of the synthesized nanocrystals. Nanocrystals with smaller radius exhibit larger bandgap energy owing to the reverse proportionality of the bandgap energy with the nanocrystal radius in the calculation of quantum confinement. Thus, smaller nanocrystals (energy donor) tend to transfer their energy to larger nanocrystals (energy acceptor) close to them. Since the photoluminescence of the donor nanocrystals has a large spectral overlap with the absorbance of the acceptor nanocrystals as well (see Figure 7), the donors are able to transfer their excitons to the acceptors. These transferred excitons relax to the ground states and recombine for possible radiative emission. As a result of this transfer, collective emission intensity of the nanocrystals with smaller radius and higher energy (emitting with shorter wavelength) decreases. Moreover, emission intensity of the nanocrystals with larger radius

![Figure 6. Energy transfer mechanism between smaller (donor) and larger (acceptor) nanocrystals.](image-url)
and lower energy (emitting with longer wavelength) increases. This results in the red shift of the emission intensity when compared with their emission in toluene.

3. QD-incorporated hybrid white LEDs

As it is clearly discussed in the previous section, semiconductor QDs can effectively change emission color of a device by fully converting the incoming photons. On the other hand, it is possible to achieve a mixed color emission by utilizing the optimized amounts of the red, blue, yellow, and green QDs. In this context, Figure 8 shows the CIE chromaticity diagram with the emission wavelengths and chromaticity coordinates. As it can be clearly seen from the diagram, white light is in the center, and it can be observed only by mixing several colors.

As it is well known, the main properties defining a white light emission of a high quality are its correlated color temperature (CCT), color rendering index (CRI), and luminous efficacy of optical radiation (LER). CRI measures how efficiently a white light emitting device reflects the real color of an illuminated object. In order to have a high-quality white light source, CRI should be higher than 90. LER is a measure of how well the produced light is perceived by the human eye. The unit of LER is lumens per watt. It is calculated with the following equation.

\[
LER = 683 \int \frac{W_{op} \cdot s(\lambda)}{V(\lambda)} d\lambda
\]

(1)

\(s(\lambda)\) is the spectral distribution of the radiated optical power and \(V(\lambda)\) is the eye sensitivity function. Although mathematically the highest LER is 683 lm/W \(_{op}\), it is almost impossible to achieve this number experimentally. A high-quality white light source should exhibit LER of...
above 300 lm/W \textsuperscript{[14]}. Another important photometric figure-of-merit is CCT. Figure 9 demonstrates CCT chart on the chromaticity diagram to clearly understand the color quality difference between several CCT values. As it is seen from the figure, the amounts of individual colors define its chromaticity coordinates and consequently its CCT.

It indicates the temperature of a Planck black-body radiator whose perceived color most closely resembles that of the light-source. The optical output of a white light-emitting device can be either cool or warm white light. CCT of a warm white light source is below 3500 K. Warm white (right) and cool white light (left) emission are shown in Figure 10. Warm and cool white light sources differ in their areas of applications. For example, in the interior house...

Figure 8. CIE Chromaticity diagram with emission wavelengths and chromaticity coordinates.

Figure 9. CIE chromaticity diagram with CCT chart.
design, it is more suitable to use warm white light in the bedrooms, living rooms, and hallways, while cool white light is generally used in kitchen, study rooms, and bathrooms.

In general, to achieve a high-quality white LED with the incorporation of semiconductor QDs, the mixture of blue, green, yellow, and red emission is essential. If blue InGaN/GaN LED is used as an electrically injected device with nearly 450 nm emission, QDs with green, yellow, and red QDs are necessary to generate a white light with a high brightness. The schematics of the hybrid white LED utilizing blue InGaN/GaN LED is depicted in Figure 11.

As it is shown in Figure 11(a) and (b), hybrid white LEDs can be constructed by adding layered and blended QDs. In the layered architecture (Figure 11(a)), it is necessary for the QDs to be in the deposition order of red, yellow, and green that results in a device with highest efficiency.

Another architecture for generating white light is utilizing dual wavelength InGaN/GaN LEDs. In this design, only two kinds of semiconductor QDs are incorporated. Dual wavelength multiple quantum well InGaN/GaN LEDs are epitaxially grown on c-plane sapphire.
substrates [15]. Unintentionally doped thick GaN layer (4 μm) is grown following the deposition of a thin low temperature (550°C) nucleation layer (30 nm). Then a 3 μm thick n-doped GaN layer is grown at high temperature. Si with a doping concentration of $5 \times 10^{18}$ cm$^{-3}$ was utilized as a p-type dopant. Three blue quantum wells (2.5 nm) were grown with GaN quantum barrier (10 nm) separation layers. An In composition of 15% was used to achieve blue emission from these three quantum wells. Subsequently, three quantum wells with higher In composition were grown to achieve green emission. p-Type doped 30 nm thick AlGaN layer was grown on top of a 10 nm GaN cap layer to serve as an electron-blocking layer. Utilizing the electron-blocking layer helps to prevent the leakage of excess electrons to the quantum wells to result in carrier imbalance. Finally, a 200 nm thick p-doped GaN layer was deposited on electron-blocking layer. Devices were fabricated with patterning, mesa etching, and electrode deposition. The device can emit the mixture of blue and green colors. The intensity of emission can be modified with the operation current of the device. In our architecture whose construction is described above, green quantum wells are closer to p-contacts when compared with blue quantum wells. Thus, at low current levels, green emission dominates the device output. However, once the current level is increased to a certain value, radiative recombination starts to happen more frequently in blue quantum wells as well. This will increase the blue emission intensity of the dual wavelength device. Once the device is fabricated, quantum dots with yellow and red (or amber) emission are placed on top of fabricated devices either in a layer or in a blended architecture. Figure 12 shows the schematics of the dual wavelength multiple quantum well InGaN/GaN LED emitting blue and green colors covered with yellow and red semiconductor QDs.

Figure 12. Dual wavelength multiple quantum well InGaN/GaN LED-emitting blue and green colors covered with yellow and red quantum dots.
4. FRET-enhanced hybrid LEDs

Forster resonance energy transfer (FRET) can enhance the optical power and power conversion efficiency of the conventional color converted and white LEDs. In this context, the relative quantum efficiency of color converter of QDs is increased by nonradiatively transferring extra excitons from the defect states of the closely placed donor QDs. The relative quantum efficiency enhancement mechanism of QDs is explained as follows. The optically excited semiconductor QDs contain excitons that recombine either radiatively or nonradiatively. The so-called “non-radiative” excitons are able to transfer their excitonic energy to the neighboring acceptor QDs before they recombine in defects in the host QDs. This increased the quantum efficiency of the acceptor QDs with increased emission yield. The process of transferring these excitons through nonradiative FRET process with dipole-dipole coupling is called exciton recycling [16].

Electronic band structure of FRET-converted LEDs is depicted in Figure 13. Excitons and/or charge carriers are transported to quantum wells following the electrical injection to blue LEDs. The radiative recombination in the InGaN (In composition of 15%) quantum wells leads to blue emission. This emission optically excites the donor semiconductor QDs. The excitons of these QDs are transferred to the acceptor QDs. The excited acceptor color-converter QDs emit with the emission wavelength corresponding to their bandgap energy. To support the existence of FRET process occurring between the donor and acceptor QDs, several types of experiments can be done. One of the most commonly known methods to examine FRET is measure the lifetimes of the acceptor and donor molecules with time-resolved fluorescence spectroscopy. If FRET occurs, donor’s lifetime should be shortened owing to the exciton migration from these host molecules. On the other hand, the acceptor molecules should exhibit longer lifetime in the presence of their donor counterparts thanks to the exciton feeding. Another method to check whether exciton migration in donor-acceptor pairs is present or not is to acquire the photoluminescence excitation spectral behavior of the acceptor QDs in the presence and in the absence of the donor QDs. Although this method can also provide a strong argument on the presence/absence of FRET, the former time-resolved spectroscopy method is more effective in evaluating the efficiency of the FRET process.

Figure 13. Electronic band structure of FRET-converted LEDs.
The FRET-based architecture above only demonstrates the enhancement process in the color-converted LED. However, it is possible to enhance the color quality of white LEDs with the utilization of FRET as well by individually increasing the quantum efficiency of less efficient QD components in the hybrid white emitting devices. Using this way, the intensity of the individual (green, yellow, or red) can be modified. This modification leads to the changes in the chromaticity coordinates of the white light and CCT.

5. Plasmon-enhanced hybrid LEDs

As it was stated above, FRET is a powerful concept to enhance the efficiency of the color-converter QDs incorporated in hybrid LEDs. Another method to increase the relative quantum yield of these semiconductor QDs is to make use of plasmon-exciton coupling mechanism [17]. Plasmon coupling can be realized by either forming localized surface plasmons or surface plasmon polaritons in the close vicinity of the emitter. Localized surface plasmons result in more pronounced absorption peaks. Moreover, their use within the device structures is more convenient owing to its simple configuration when compared with surface plasmon polaritons. The plasmonic absorption peaks of localized surface plasmons can be easily modified by changing the size of these particles. Figure 14 shows the absorption spectra of Ag nanoparticles with different deposition thicknesses and same annealing condition. 10, 15, and 20 nm thick electron beam deposited and annealed Ag (films become nanoparticles following the deposition of such thin layers and high temperature annealing) exhibit 450, 504, and 666 nm absorption peaks, respectively.

Figure 14. Absorption spectra of electron beam-deposited Ag layers with deposition thickness of 10, 15 and 20 nm.
To achieve a successful enhancement in the emission yield, the absorption spectrum of plasmonic metal structure should have a decent overlap with the luminescence spectrum of the emitter (semiconductor QD in this particular case). In this context, it is important to choose the correct metal material to achieve a good spectral overlap. Ag is a more convenient material for the emission in near UV and blue. On the other hand, Au can be utilized to get a plasmonic enhancement in the emitters with emission wavelength of more than 500 nm. Moreover, the position of plasmonic structure is also an important feature which needs extra care. The QD and the plasmonic metal should be in close proximity to realize an efficient coupling between them. On the other hand, if these two structures are placed very closely to each other, the emission of QDs will be strongly quenched thanks to nonradiative energy transfer from QDs to the adjacent metal structure. Thus, it is essential to optimize the relative locations of the QDs and the plasmonic metal structure to prevent the nonradiative energy transfer-induced emission loss and to achieve strong exciton-plasmon coupling simultaneously.

A thin metallic layer can be chemically grown on top of QDs to achieve plasmon-induced enhancement (Figure 15-left). However, placing a metal layer directly on the surface of QD would result in nonradiative resonance energy transfer-induced quenching of QD emission. Thus, it is important to insert a spacer shell layer in between the semiconductor QD and metallic shell. Moreover, the thickness of these shells (spacer and metal) cannot be too large; thick shells would block a significant amount of light coming out of QDs. Another useful mechanism to achieve strong coupling between the plasmons generated in metals and excitons in QDs is to make use of blended structure (Figure 15-right). In this configuration, chemically synthesized small metallic nanoparticles are mixed with QDs in solution. Later, they will make a solid blended film on a flat surface. However, direct contact of core QDs with metallic nanoparticle would again give rise to a strong quenching of emission owing to nonradiative energy transfer. To prevent nonradiative quenching, QDs can be synthesized in a core-shell configuration such as CdSe/ZnS with optimized shell thickness. In both of the configurations explained above, surface plasmons provide additional radiative channels for the excitons of QDs. This leads to the enhanced emission yield of QDs. The two powerful methods to examine the existence of plasmon-exciton coupling are photoluminescence measurement of QD films and time-resolved photoluminescence decay experiments. The former method shows the photoluminescence peak enhancement of QDs owing to the existence of plasmonic nanostructures in close vicinity. In most cases, there is a peak shift in the plasmon-incorporated films owing to the difference in the absorbance peak of metal and photoluminescence of the emitter; the spectral region of

![Figure 15. QD-plasmon coupling mechanisms with core-shell (left) and blended (right) configurations.](http://dx.doi.org/10.5772/intechopen.68356)
QDs corresponding to the absorbance peak location of metallic nanostructures gain maximum photoluminescence enhancement. This leads to the shift of photoluminescence peak toward the absorbance peak. The second useful method to examine the existence of plasmon-exciton coupling is to draw the photoluminescence decay curves of QD films in the presence and in the absence of the plasmonic nanostructures. Due to the presence of additional radiative channels in the QD-metal structure, the photoluminescence of this structure should decay faster; the reduction in the lifetime of QD film in the presence of plasmonic metal nanostructures is attributed to the strong plasmon-exciton coupling induced by the increased radiative recombination rate.

The optimized blended and core-shell configurations (Figure 15) can be incorporated as efficient color-converter materials on top of blue InGaN/GaN LEDs. These novel architectures would exhibit enhanced power conversion efficiency and optical power when compared with conventional color-converted hybrid LEDs utilizing pure QD film owing to the plasmon-induced quantum efficiency enhancement of QDs.

6. FRET-converted LEDs

Color conversion process in hybrid LED designs utilizing InGaN/GaN LED structures and QDs can be photonic or excitonic. In photonic color conversion, photons are generated in the quantum wells of InGaN/GaN LEDs following an efficient electrical injection, and they excite the color converter semiconductor QDs placed on top of the structure. In this design, there is a significant separation between QDs and the quantum wells of LEDs. On the other hand, excitonic color conversion process does not involve the generation of photons to excite the semiconductor QDs. In this configuration, excitonic energy of the InGaN quantum wells is directly transferred to the QDs through FRET (nonradiative dipole-dipole coupling). It is possible to achieve white light emission (or any other mixed color emission) by carefully controlling the emission intensity of InGaN quantum wells and the QD film.

The interaction of QDs and the quantum wells of InGaN/GaN LEDs can be realized through constructing several hybrid systems [18, 19]. One of the methods to achieve excitonic color conversion is to place QDs directly on top of the quantum wells (Figure 16-right). However, there should be a thin GaN cap layer with optimized thickness to control the amount of transferred nonradiative energy. Very small separation between the donor (InGaN quantum well) and the acceptor (QD) would result in higher emission intensity of QDs and lower intensity of InGaN wells. Thus, by modifying the thickness of cap layer, it is possible to optimize the quality of white light; CCT can be effective shifted. Moreover, QDs can be placed in between the nanopillars of InGaN/GaN LED structure to realize the interaction of QDs and sidewalls of InGaN quantum wells (Figure 16-left). Nanopillars can be fabricated either by etching the epitaxially grown bulk LED structure or by selectively growing LED structures in the holes of SiO2 layer on top of a sapphire substrate. Furthermore, LEDs with microholes can be fabricated and QDs can be inserted into these holes to observe the possible coupling between QDs and quantum wells. Energy transfer between the abovementioned donor and acceptor components are examined with photoluminescence, optical power measurements, and time-resolved photoluminescence spectroscopy studies.
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