Particuology 15 (2014) 90–93

Contents lists available at ScienceDirect

Particuology

journal homepage: www.elsevier.com/locate/partic

White-light-emitting diodes using GaN-excited CdSe/CdS/ZnS quantum dots

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ARTICLE INFO

Article history:
Received 31 October 2012
Received in revised form 13 January 2013
Accepted 25 January 2013

Keywords:
GaN
Quantum dots
White-light-emitting diode
Stability

ABSTRACT

Fluorescence-based white-light-emitting diodes (WLEDs) were fabricated using blue GaN chips and green- and red-emitting CdSe/CdS/ZnS quantum dots (QDs). The coordinate and color temperature of the WLEDs could be varied because of the size-tunable emission of CdSe QDs from 510 to 620 nm. Warm and cold white emissions were confirmed with the color temperature ranging from 4000 to 9000 K. Color coordinates were analyzed at different bias. The fast enhancement of blue emission resulted in the shift of color coordinates to the cold side. The stability of white emission during operation was analyzed; stable spectra were achieved within 90 min.

1. Introduction

White-light-emitting diodes (WLEDs) have attracted increasing attention recently because of their major advantages of low power consumption and long lifetime. These advantages mean WLEDs have great potential for lighting and display applications. Two kinds of WLEDs have been investigated: electroluminescence-based WLEDs (Anikeeva, Halpert, Bawendi, & Bulovic, 2007; Zhang, Xie, et al., 2011) and fluorescence-based WLEDs (Lim et al., 2007). Normally, white emission *via* electroluminescence is constructed of three emission bands including red, green, and blue electroluminescence. Good color rendering is achieved by control of the bias and device components. However, the complicated structure of such devices makes them expensive and each chip degrades at different rates (Yam & Hassan, 2005). Although organic molecules and inorganic quantum dots (QDs) have been used to fabricate the film-based WLEDs, they have lower emission efficiency and a shorter lifetime than current commercial WLEDs (Zhang, Xie, et al., 2011).

WLEDs based on a single chip and phosphors have been used for general lighting because of their low cost and high luminescence efficiency (Tanabe, Fujita, Yoshihara, Sakamoto, & Yamamoto, 2005). This kind of WLED consists of a blue-emitting GaN chip and a yellow-emitting yttrium aluminum garnet (YAG) phosphor (Lu, Hong, & Jaganathan, 2002). White light is produced by mixing GaN light-emitting diode (LED)-excited yellow emission from YAG and the blue emission from GaN LEDs. YAG doped with cerium is widely used as a fluorescent powder; however, the lack of a red component results in poor color rendering (Sheu et al., 2003). Consequently, some novel fluorescent powders, including organic phosphors with tunable emission color and high efficiency, have been reported (Xiang, Yu, Che, & Lai, 2003). The poor stability of organic materials means devices containing lack long-term reliability.

The photoluminescence of colloidal QDs of cadmium compounds, such as CdE (E = S, Se, Te), exhibits size-tunable spectral emission (450–760 nm) and narrow bandwidth (full width at half-maximum of ~30–40 nm), allow color-saturated red, green, and blue QD-based LEDs with simple device configurations to be designed and fabricated. The high luminescence efficiency and size-tunable bandgap of colloidal CdSe QDs make them a good candidate for fluorescent powders, so they have attracted considerable interest (Chen, Hsu, & Hong, 2006). The shell growth of high-bandgap

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http://dx.doi.org/10.1016/j.partic.2013.01.009

CdS and ZnS can passivate surface states and further enhance the photoluminescence intensity of CdSe QDs. Core/shell-structured CdSe/CdS/ZnS QDs exhibit high emission efficiency (quantum yield 60% or higher) in the visible range from 500 to 700 nm. The emission maxima of CdSe can be tuned from red to green by reducing the particle size (Talapin et al., 2004).

In this letter, WLEDs based on blue GaN chips with an emission peak at 460 nm and CdSe/CdS/ZnS QDs are investigated. The bilayer structure was proposed to remove the self-absorption of QDs with different band gaps compared with the current QDs fluorescence-based WLED. Tunable coordinate and color temperature are achieved using the controllable visible emission of QDs. White emission is obtained in the whole working bias range of the GaN LED. The stability of white emission at the same bias over time is investigated. It is the first investigation on the tunable spectra properties and stability of QDs-based phosphor WLEDs. The observed stable white spectra indicate that CdSe/CdS/ZnS QDs are a promising phosphor in white lighting applications.

2. Experimental

2.1. Materials

Cadmium oxide (99.99%), selenium (99.99%, 100 mesh), sulfur (99.98%, powder), trioctylphosphine oxide (TOPO, 90%), trioctylphosphine (TOP, 97%), 1-octadecene (ODE, 90%), oleic acid (OA, 90%), and octadecylamine (ODA, 97%), hexadecylamine (HDA, 90%), zinc oxide (99.99%) were purchased from Sigma–Aldrich. All organic solvents were purchased from Sigma–Aldrich. All chemicals were used directly without any further purification.

2.2. Synthesis of CdSe/CdS/ZnS

CdSe QDs were prepared *via* a synthetic route using inorganic precursors and noncoordinating solvents (Yu & Peng, 2002; Yu, Wang, & Peng, 2003). CdS/ZnS double shells were grown by successive ionic layer adsorption reactions (Li et al., 2003; Zhang et al., 2010; Zhang, Dai, et al., 2011). For a typical core synthesis, 77.04 mg CdO, 677.9 mg OA, and 8.1 g ODE were loaded in a 25 mL three-neck flask and heated to about 230 °C to obtain a colorless clear solution. After the solution was cooled to room temperature, 1.5 g HDA and 1.5 g TOPO were added in the flask. The mixture was heated to 280 °C. After Se solution (0.285 g Se in 0.472 g of TOP and further diluting with 1.106 g of ODE) was quickly injected, the temperature was then reduced to 250 °C. The injection temperature and reaction time can be tuned to obtain the particle with different emission peaks. The reaction mixture was allowed to cool to room temperature and purified to remove unreacted precursors. The purified particle was dispersed in hexanes for the shell growth. The cadmium injection solution (0.04 M) was prepared by dissolving CdO (0.0448 g) in oleic acid (0.5935 g) and ODE (8 mL) at 250 °C. The zinc injection solution (0.04 M) was prepared by dissolving ZnO (0.0228 g) in oleic acid (0.3162 g) and ODE (6.64 mL) at 250 °C. The sulfur injection solution (0.04 M) was prepared by dissolving sulfur in ODE at 200 °C. After clear solutions were obtained under N_2 flow, the Cd and Zn injection solution was allowed to cool to about 60 °C and the sulfur injection solution was allowed to cool to room temperature. For a shell formation, CdSe QDs dispersed in 5 mL of hexanes were loaded into a 25 mL three-neck flask and mixed with 1500 g ODA and 5000 g of ODE. A mechanical pump was employed at room temperature for 30 min to remove hexanes from the flask. Subsequently, the reaction mixture was heated to 180 °C under N_2 flow. Then, the predetermined amounts of the cadmium, zinc and sulfur solutions were alternatively injected into the three-neck flask drop by drop with syringes using standard air-free procedures. The reaction time for each anion and cation layer was ten minutes. The reaction was stopped by the injection of toluene. The core/multi-shell QDs were dispersed in chloroform after purification.

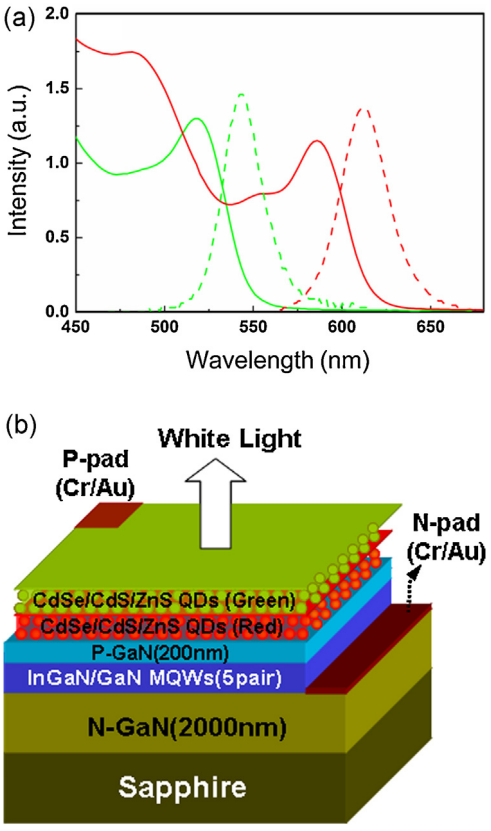

Fig. 1. (a) Absorption (Abs, solid line) and photoluminescence (PL, dash line) spectra of green (green line) and red (red line) QDs. (b) Device structure. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

2.3. Device fabrication

QD solution (typically contain 100 mg QDs) was added to silicon resin B (0.8 g, OE6630B, Dow Corning Inc, PO Box 994, Midland, MI, United States) by vortex mixing and ultrasonic treatment for 20 min until the mixture became transparent. The mixture was combined with silicon resin A (0.2 g, OE6630A, Dow Corning Inc.) to give a weight ratio of 1:4 (OE6630A:OE6630B). The mixture was stirred until it became homogeneous. The mixture was added dropwise onto the surface of GaN chips and heated in a vacuum oven at 100 °C for 20 min. A bilayer structure was employed in this paper to avoid the self-absorption between green and red QDs.

2.4. Characterizations

Absorption spectra were measured on a Perkin-Elmer Lambda 950 UV-vis spectrophotometer. Luminescence spectra were measured on a Perkin-Elmer luminescence LS50B spectrophotometer.

3. Results and discussion

Fig. 1a shows the photoluminescence (PL) spectra of the CdSe/CdS/ZnS QDs, which exhibited a quantum yield of 70%. The wavelength maxima of green and red CdSe/CdS/ZnS QDs were 545

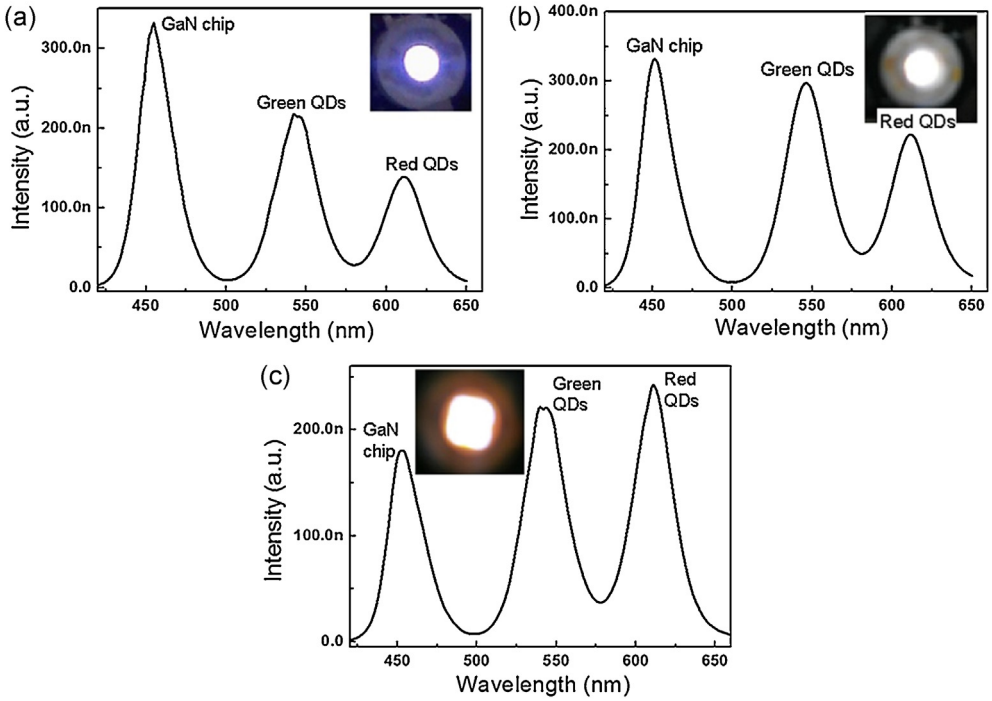

Fig. 2. Luminescence and white light photographs of three white LEDs with different CIE coordinates and color temperatures. (a) CIE coordinate (0.283, 0.289), color temperature 9630 K; (b) CIE coordinate (0.324, 0.329), color temperature 5920 K; (c) CIE coordinate (0.367, 0.367), color temperature 4320 K.

and 615 nm, respectively. Bilayer structure was employed as shown in Fig. 1b. Two layers were deposited separately. Red QDs was deposited on GaN LED first before the deposition of Green QDs because the red QDs will absorb the green emission.

Luminescence spectra and photographs of the WLEDs are presented in Fig. 2. The WLEDs exhibit three emission peaks. A blue GaN LED (Lextar Inc., Product No. HXGD-DZ-3w-40) was used as an excitation source with an emission peak of 460 nm, and green- and red-emitting CdSe/CdS/ZnS QDs were used as a fluorescent powder. The overlaps of the absorption band with the PL bands of the QDs are shown in Fig. 1. Larger QDs (red) absorb light emitted by the smaller ones (green) in the resin, reducing the color rendering and efficiency of the WLED. Therefore, red QDs were coated on the surface of WLEDs first. The different ratios of green and red

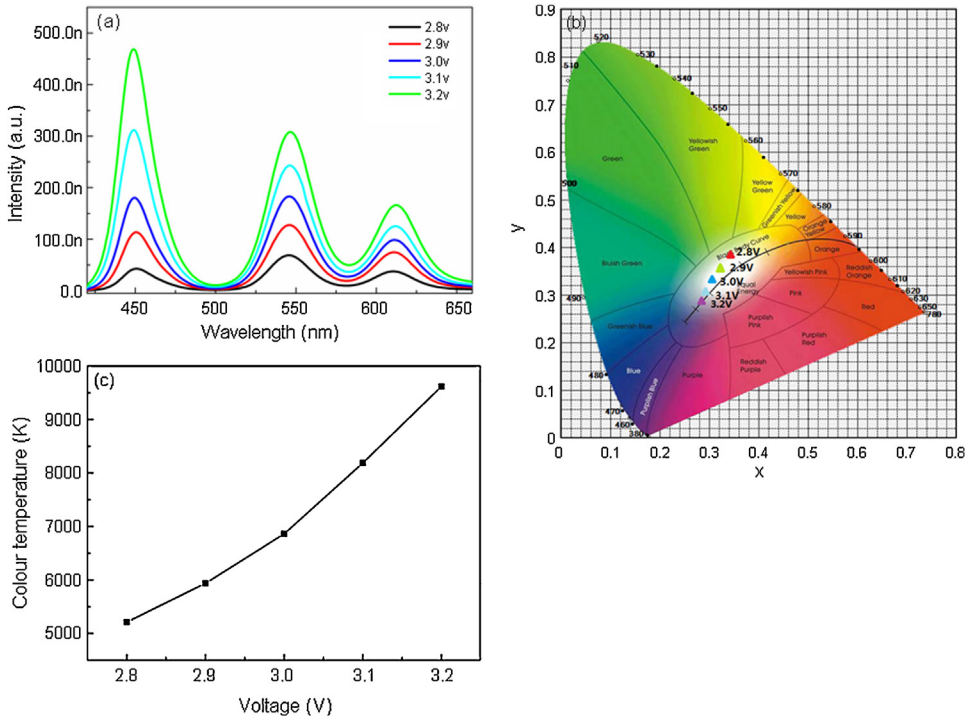

Fig. 3. (a) Luminescence, (b) CIE coordinates, (c) and color temperature of QD-based phosphor WLEDs at different working bias.

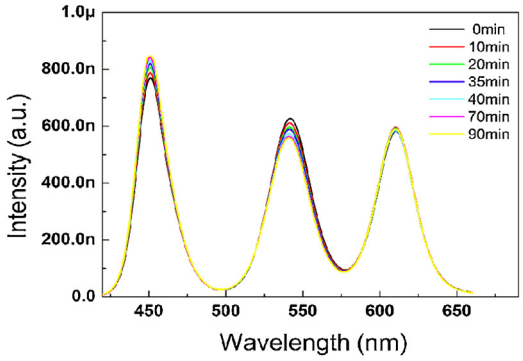

Fig. 4. Stability of luminescence spectra of WLEDs.

QDs caused the color coordinate and temperature of the WLEDs to shift. Fig. 2 shows the luminescence spectra of three devices with different Commission Internationale de l'Eclairage (CIE) chromaticity coordinates of (0.283, 0.289), (0.324, 0.329), and (0.367, 0.367). As the intensity of red emission increases, the color temperature decreases from 9630 to 4320 K. The color temperature of the QD-based fluorescence WLEDs was tunable between cold and warm white.

Luminescence spectra of a WLED under different forward bias are shown in Fig. 3(a), in which the emission peaks of the blue LED chip, and the green- and red-emitting QDs were located at 460, 545, and 615 nm, respectively. As the forward bias increased from 2.8 to 3.2 V, the CIE coordinates varied from (0.341, 0.384) to (0.285, 0.285), as shown in Fig. 3(b). The intensity of blue emission from the bottom blue LED chip increased slightly faster than those of the red and green emissions from the QDs. The red and green peaks exhibited red shifts because the high voltage caused the device temperature to increase. However, the device still operated in the white area. The color temperature increased because the intensity of blue emission increased, as illustrated in Fig. 3(c).

Fig. 4 shows the stability of the luminescence spectra of a WLED. The device was operated under a bias of 2.8 V. After 90 min, the intensity of blue emission increased slightly, indicating that the emission from the GaN LED became stable. The QDs exhibited a good PL stability except a red shift of a few nanometers induced by the increase in temperature under bias.

4. Conclusions

CdSe/CdS/ZnS QD-based WLED were successfully fabricated. Warm and cold white emissions with color temperatures ranging from 4000 to 9000 K were achieved by tuning the proportions of the three emission signals. Enhancement of red emission causes the color coordinate to shift from (0.283, 0.289) to (0.367, 0.367) and the color temperature to shift to the warm side from 9630 to 4320 K. The color coordinate varies from (0.341, 0.384) to (0.285, 0.285) as the working bias of GaN chip increases because of the fast enhancement of GaN chip-induced blue emission. Although the color coordinate depended on the working bias, white emission was observed for the whole working bias of the GaN chips. A stability experiment confirmed that stable performance from the QD-based WLED was achieved within 90 min.

Acknowledgements

This work was financially supported by the National High Technology Research and Development Program 863 of China (2011AA050509), National Natural Science Foundation of China (61106039), National Postdoctoral Foundation (2011049015) and Jilin Province Youth Foundation (201101025).

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